Multiphase Catalysis and Microfluidic Reaction Mechanism Over Paper-Structured Catalysts

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Over Paper-Structured Catalysts

Taichi Homma

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Contents

Chapter 1: Introduction	
1-1 Green Sustainable Chemistry	2
1-1-1 Background	2
1-1-2 Green Chemistry	3
1-1-3 Renewable resources	4
1-2 Catalysts	6
1-2-1 Background	6
1-2-2 Use of catalysts in industry	7
1-2-3 Micro-structured reactors and catalysts	9
1-2-4 Prediction and control of fluidic chemical reaction	10
1-3 Fibrous materials and catalysts	15
1-3-1 Background	15
1-3-2 Wet-laid structure designed by papermaking	15
1-3-3 Fibrous catalysts	16
1-4 Alcohol oxidation	20
1-4-1 Background	20
1-4-2 Selective alcohol oxidation by metal catalysts	21
1-4-3 Mechanism of alcohol oxidation	22
1-4-4 Alcohol oxidation by fixed bed catalysts	24
1-5 Objectives	26
References	28

Chapter 2: Preparation of porous paper composites with ruthenium hydroxide and catalytic alcohol oxidation in a multiphase gas-liquid-solid reaction

41
42
45
45
46
47
48
50
50
53
57
61
62

Chapter 3: Multiphase catalytic oxidation of alcohols over paper-structured catalysts with micrometer-size pores

Abstract	66
3-1 Introduction	
3-2 Experimental	70
3-2-1 Materials	70
3-2-2 Preparation of paper-structured catalysts	71
3-2-3 Catalysts characterization	72
3-2-4 Alcohol oxidation reactions	72
3-2-5 Residence time distribution measurement in the cold flow model	74

3-3 Results and discussion	76
3-3-1 Characterization of paper and bead catalysts	76
3-3-2 Catalytic behavior of paper-structured catalysts	81
3-3-3 Residence time distribution analysis	83
3-3-4 Alcohol oxidation behavior	86
3-4 Conclusions	91
References	93

Chapter 4: Solvent-free alcohol oxidation via paper-structured catalysts:

Abstract	99
4-1 Introduction	100
4-2 Experimental	103
4-2-1 Materials	103
4-2-2 Catalysts preparation	104
4-2-3 Catalysts characterization	105
4-2-4 Alcohol oxidation	106
4-3 Results and discussion	108
4-3-1 Characterization of Pd/Al ₂ O ₃ paper-structured catalysts	108
4-3-2 Solvent free aerobic oxidation of benzyl alcohol	112
4-3-3 Kinetics study with microfluidic reaction	117
4-4 Conclusions	127
References	128
Chapter 5: General conclusions	133

137

Chapter 1

Introduction

1-1 Green Sustainable Chemistry

1-1-1 Background

The chemical industry plays important roles in mass production, the global economy and future technologies because it is closely involved in many other sectors in the value chain, such as construction, transportation, and production of chemicals, commodities, medicines and healthcare materials. However, these industries are currently facing many environmental issues, such as resource depletion and the potential to pollute air, water and land [1]. Accordingly, many approaches have been made at various levels to enable sustainable operation of the chemical industry. For example, the Kyoto Protocol was developed reduce greenhouse gas emissions based on the theory that global warming exists and has been caused by anthropogenic carbon dioxide emissions [2]. Additionally, the 'Responsible Care' program has been developed by the global chemical industry to ensure safety of the environment, health and overall security to drive continuous improvements in performance [3].

There is increasing demand for environmentally acceptable chemicals and industrial processes and practices. However, environmental issues should be assessed in a holistic fashion that considers financial, technical and other criteria, not simply short-term business benefits. Life Cycle Assessment (LCA) is a management tool that enables quantification of environmental burdens and their potential impacts over the entire life cycle of a product, including associated processes and activities. It has been used for over 30 years in several industrial fields [4].

1-1-2 Green Chemistry

In Green Chemistry, chemical products and processes are developed using methods that reduce or eliminate the use and generation of hazardous substances. Twelve Green Chemistry principles to establish an environmentally friendly chemical industry were proposed in 1998 by P. Anastas and J. Warner. These principles, which are summarized in Table 1, have since become key elements in establishment of sustainable chemistry [5, 6].

Table 1 The twelve principles of Green Chemistry.

1	Waste prevention instead of remediation
2	Atom efficiency
3	Less hazardous/toxic chemicals
4	Safer products by design
5	Innocuous solvent and auxiliaries
6	Energy efficient by design
7	Preferably renewable raw materials
8	Shorter syntheses
9	Catalytic rather than stoichiometric regents
10	Design products for degradation
11	Analytical methodologies for pollution prevention
12	Inherently safer processes

The three main goals of the Green Chemistry framework can be summarized as follows:

- (I) Green Chemistry designs consider all stages of the life cycle.
- (II) Green Chemistry seeks to design chemical products and processes in a fashion that
- inherently reduces their intrinsic hazard.
- (III) Green Chemistry works as a cohesive system of principles or design criteria [7].

Improved industrial sustainability is not only required at the product levels, but also in all processes and systems used in production. A Green Chemistry framework based on engineering known as Green Engineering focuses on how to achieve these goals through technology. When designing new materials, products or processes using Green Engineering, scientists and engineers should be provided with frameworks beyond standard engineering quality and safety specifications based on twelve principles that consider environmental, economic and social factors [8].

1-1-3 Renewable resources

Social awareness regarding limitations of available fossil resources and the environmental impacts of their use is driving efforts to identify alternative renewable resources and sustainable processes. These efforts have boosted interest in use of biomass as a resource for chemicals production. The sustainability of industrial applications of feedstocks originating from biomass requires development of new processes in agreement with Green Chemistry principles. Such new processes could be useful for minimizing wastes from forestry, agriculture and the paper industry and enabling their use as raw materials.

Nature produces 170 to 200 billion metric tons of biomass annually by photosynthesis, 75% of which consists of carbohydrates. However, only 3 to 4% of these compounds are used by humans. Biomass carbohydrates, which are the most abundant renewable resources available, are considered feedstocks that will be useful for the Green Chemistry in the near future [9].

Use of biomass is expected to play an important role in the promotion of sustainable development and handling global warming issues in two major areas:

(I) Direct or indirect energy uses

(II) As a base resource for chemicals, materials and products

For example, fossil fuels feedstocks used in the chemical industry can be replaced with renewable raw materials. Indeed, use of biomass instead of fossil fuels is the most important aspect of technologies employing their use with respect to reduction of CO_2 emissions, particularly development of liquid biofuels for transport, such as biodiesel and bioethanol.

Major chemical families of natural plant origins used widely in daily commodities include fatty alcohols, polysaccharides, oligosaccharides, lipids, polyols and amino acids [10]. Fatty alcohols are higher alcohols, such as monohydric aliphatic alcohols with six or more carbon atoms and long carbon chains. Aliphatic long carbon chain aldehydes, acids and esters are widely used in daily commodities, pharmaceuticals, fragrances and cosmetics. Wax esters, which are esters of long chain fatty acids with long chain fatty alcohols, are widely used as high pressure lubricants and hydraulic oils in many industries, including printing and leather manufacture. These valuable products can be produced by selective oxidation of their corresponding fatty alcohols [11]. However, advances in catalysts and reaction processes are needed to establish technologies for the efficient production of high quality products.

1-2 Catalysts

1-2-1 Background

Substances that increase the rate of a chemical reaction without changing the overall standard Gibbs energy are catalysts [12]. Catalysts can be classified as homogeneous or heterogeneous, with homogeneous catalysts involving only one phase and heterogeneous catalysts inducing reactions at or near an interface between phases.

Homogeneous catalysts, which are typically soluble metal complexes, are present in the same phase as reactants. Although these catalysts have the advantage of all catalytic sites being accessible to all the reagents, their use in industrial applications is limited by difficulties in separation of the catalysts from the final products. To overcome this problem, heterogeneous catalysts have been developed. Almost all heterogeneous catalysts are supported on metal oxides such as silica, alumina and titania owing to their chemical and thermal stability, porosity and good accessibility. However, some issues remain unsolved; specifically, the accessibility of regents to active sites is less efficient than that of homogeneous catalysts, and leaching of metal catalysts from solid supports sometimes occurs. As a result, metal nanoparticles are emerging as alternatives to conventional solid supported heterogeneous catalysts because they increase the exposed surface area of the active catalytic sites, resulting in enhanced contact between the reagents and the catalytic centers [13–16].

1-2-2 Use of catalysts in industry

Multiphase catalytic reaction plays a great role in industry and generally proceeds on a solid catalyst at an interface of gas and liquid phases. Two types of reactor systems are used depending on the size of the catalyst particles, slurry reactors, in which the reactions are carried out among moving catalyst particles, gas and liquid phases, and fixed bed reactors, in which the reaction proceeds between gaseous and liquid components on the fixed catalyst bed. When slurry reactors are used in small batch production, it is easy to organize effective temperature control and intensive mass transfer between all phases. However, slurry reactors have some drawbacks, including:

(I) Difficulties in separation of the catalyst from the product

(II) Abrasion of the equipment by moving hard particles

(III) Low specific productivity per the entire reactor unit volume

(IV) Complicated continuous processes that are difficult to control

Nevertheless, these slurry reactors are currently widely used in industry owing to their reliability and applicability in multi-product plants.

Fixed bed multiphase reactors are an alternative to the processes for suspended catalysts that have widely been applied in industry. The main advantage of these reactors is absence of the catalysts from the separation process. However, when compared to slurry reactors, fixed bed reactors have disadvantages associated with the large catalyst particles, such as:

(I) A far higher reaction pressure dictated by lack of catalyst utilization because of low intraparticle diffusion and low efficient mass transfer at the gas-liquid-solid phase

(II) Complex temperature control in exothermic reactions owing to "hot spots"

(III) The necessity for liquid and gas distributors inside the reactor [17, 18]

Industrial chemical plants can be designed as small batch plants of a few meters or as integral plants of hundreds of meters. The corresponding process times range from a few hours to continuous operation with only periodic shut downs for maintenance. The reactor residence time ranges from hours for a slow organic reaction to milliseconds for a partial oxidation reaction in a monolith reactor. [19].

Trickle-bed reactors (TBR) are the most widely used three phase gas-liquid-solid reactors commonly employed in industry. TBRs consist of a fixed bed of catalyst particles that is contacted by a co-current downward gas-liquid flow that carries both reactants and products (Fig. 1) [20]. Large catalyst loading per unit volume of the TBR and low energy dissipation rate are advantageous when compared to slurry reactors. However, TBR have poor applicability for reactions with rapidly deactivating catalysts, high pressure drop and a risk of liquid maldistribution, which may lead to hot spots and reactor runaway [21].



Fig. 1 Schematic of trickle bed reactor ^[20]

1-2-3 Micro-structured reactors and catalysts

Research pertaining to microscale devices has accelerated during the past 10 years. The smaller dimensions at the micrometer level lead to an extremely high surface to volume ratio, which provides several advantages over conventional equipment, such as reactors, mixers and heat exchangers, including [22]:

- (I) Higher transport of heat and mass
- (II) Less risk of hazardous or toxic chemicals
- (III) Simple process control and short response time
- (IV) On-demand or on-site synthesis of critical and unstable chemicals

These advantages are useful in a variety of chemical reactions, such as those involved in polymer nanoparticle synthesis [23], emulsion and microcapsules fabrication [24], the food industry [25], pharmaceutical production [26], cosmetics and dairy products products production [27] and analytical science [28]. Typical images of micro-structured reactors (MSRs) are shown in Fig. 2 [29, 30].

The surface to volume ratio of MSR ranges from 10,000–50,000 m²/m³, which is much higher than those of conventional reactors. The specific surface in conventional laboratory and production vessels is 10–100 m²/m³. In general, MSRs are operated under laminar flow conditions. Accordingly, the heat transfer coefficient is inversely proportional to the channel diameter, and their values for liquids are about one order of magnitude higher than those in conventional heat exchangers. The high heat transfer allows utilization of the full potential of catalysts during highly endothermic or exothermic reactions while avoiding formation of

hot-spots. The small diameters of the reactor channels ensure a short radial diffusion time, leading to a narrow residence time distribution (RTD). This is advantageous for consecutive processes because high selectivity for the desired intermediates would be expected. Isothermal conditions combined with short residence times and a narrow RTD are the main parameters of MSRs [31].



Fig. 2 Images of micro-structured-reactor, (I) five port silicon microreactor for glycosylation ^[29], (II) micro-block and microreactor for CO oxidation ^[30]

1-2-4 Prediction and control of fluidic chemical reaction

Fluidic dynamics in multiphase reactors are extremely complicated because of their convoluted interactions. Accordingly, it is very important to correctly predict their flow behaviors, such as pressure drops, liquid holdups, gas–liquid interface areas and mass transfer coefficients, to enable reactions to occur under suitable conditions during operation [20].

The gas and liquid flow regime, which describes the distribution of the two-phase flow in a reactor, is important because it strongly influences the overall performance of the reactor, particularly in terms of pressure drop, heat and mass transfer. A number of flow regimes can occur depending on several factors, including the gas and liquid feed flow rates, fluid properties, surface tension, viscosity and density, wettability of the catalysts and geometry of catalysts and reactors. Fig. 3 shows examples of flow regimes in MSRs at different superficial gas and liquid velocities [32]. The preferred flow regime in a microfluidic reactor is slug flow (Taylor flow), which is characterized by gas bubbles and liquid slugs flowing consecutively through the small channels. The rate of mass transfer during slug flow is relatively high because the liquid layer between the gas and catalyst is so thin that it forms an easily surmounted barrier to mass transfer, and convective mixing is enhanced by recirculating velocity components [33, 34].



Fig. 3 Flow regime maps for gas-liquid flow in microchannels ^[32]

The gas/liquid interface, a_v [m²/m³], possesses a scale effect in heterogeneous catalytic reactions. According to the concentration gradient shown in Fig. 4, the efficient reaction rate related to the volume of the liquid, $R_{eff,V}$, is as follows:

$$R_{eff,V} = k_L a_v S_A P_A \tag{1}$$

where k_L is the mass transfer coefficient related to the volume of the liquid, S_A represents the solubility of species A [mol/bar/m³], P_A represents partial pressure of species A [bar] and C_A represents the concentration of A. In this case, $R_{eff,V}$ is proportional to a_V . Gaseous reactant A diffuses through a liquid film and reacts on the surface of a solid catalyst. To reach the surface of the solid, the reactant penetrates the liquid film, then passes through the film surrounding the catalyst. In MSRs, the gas/liquid interface, a_V , is up to three orders of magnitude higher than in traditional stirred tank reactors. Therefore, the process efficiency can be enhanced considerably using microfluidic reactors [35].



Fig. 4 Schematic of concentration gradient of gas/liquid/solid reaction

As mentioned above, RTD is one of the key factors involved in fixed bed reactors. In batch reactors, the reaction time is determined by how long a vessel is held at a particular temperature to reach the target conversion. In contrast, when the reaction is operated under flow conditions, the reaction time is determined by both the volume of the reactor and the flow rate. Since the flow rate is correlated with the residence time, these factors determine the amount of product formed in a given time. It is desirable to reach complete conversion in the reactor with the highest possible flow rate. Typical examples of RTD function E(t) are shown in Fig. 5 [36]. Good flow corresponds to uniform distribution centered on the mean residence time t_m (Fig. 5 (A)), while stagnant backwaters or short-circuits are indicated by an early peak followed by a long tail (Fig. 5 (B)). Furthermore, control of the flow rate and therefore the residence time is critical to handling the reaction appropriately in terms of Green and Sustainable Chemistry [37-39].



Fig. 5 Residence time distribution curves ^[36]

The concept of "Flash chemistry" defined by Yoshida et al. involves extremely fast reactions in organic synthesis through the use of microreactors. Chemical reactions are extremely fast at the single molecule level, with only several hundred femtoseconds required for the conversion of a single starting molecule to a single product molecule. Therefore, if all reactant molecules in a reactor react at once, the reaction time should be several hundred femtoseconds. A concept image of the time/space relationship is shown in Fig. 6 [40]. Reaction times for chemical synthesis usually range from minutes to hours when batch reactors such as flasks at the laboratory level or stirred tank reactors at the industrial production level are used. However, the aforementioned microreactors are expected to act as new tools that enable much faster reactions to be conducted in a controlled way [41].



Fig. 6 Time-scale relationship between chemical reactions ^[40]

1-3 Fibrous materials and catalysts

1-3-1 Background

Paper is a versatile thin material with a three dimensional fiber network structure that was developed as early as the 2nd century AD in China. Paper is made by pressing together moist fibers, typically wood cellulose pulp, and drying them into flexible sheets. While it is most commonly used for writing and printing, it is also widely used as money, packaging, for cleaning, as well as other uses in the industrial, construction and agricultural fields [42].

1-3-2 Wet laid structure designed by papermaking

The general procedure of papermaking is summarized as follows. Wood is broken down to cellulose pulp by mechanical, thermomechanical or chemical treatment. Pulp fibers suspended in water are then dewatered through a papermaking wire mesh, resulting in formation of a randomly oriented fiber mat on the mesh. Water is then removed by pressing and drying to make the paper. Papermaking is a high-speed, low-cost and well established green process.

The addition of fillers is common during paper production. Usually, fillers provide benefits such as cost and energy savings, as well as improved optical properties, smooth sheet formation, dimensional stability, printability and writeability of cellulosic paper. In addition, fillers can increase the drainage rate, machine speed and productivity. The use of inorganic fillers and fibers instead of traditional fillers can deliver impart unique characteristics such as magnetic, flame retardant, antibacterial, frictional, thermal buffering and catalytic properties. Filler addition involves direct dosing at a wet end, lumen loading, *in situ* synthesis of filler particles, formation of fiber/filler composites and surface filling [43].

1-3-3 Fibrous catalysts

The size of catalyst pellets in a fixed bed is determined by a compromise between the requirement for high catalytic effectiveness and a low pressure drop. Fibrous catalysts are structured catalysts made from fiber materials that satisfy these requirements when they are small, but avoid technical problems associated with powders. Gauze woven wires of fine precious metals such as Pt, Ru and Ag have long been used in industrial production of nitric acid, hydrocyanic acid and aldehydes [44]. However, these homogeneous metal wires are exceedingly expensive, which has limited their practical application. Fibrous catalysts made of inexpensive materials such as carbons, glasses or ceramics have become available in the last few decades. Fibrous materials offer flexibility that cannot be obtained using powder or pellet materials. Cloth or sheets made of fibers can be designed to fit almost any geometric shape and applied for various catalytic applications. This property enables their use in multifunctional reactors, which combine reactions and separation, such as the catalytic fabric filters used to treat exhaust gases [45]. Another advantage of fibrous catalysts is their low resistance to the flow of liquids and gases relative to powders or pellets. Therefore, they can be used as an alternative in complicated three-phase operation for fixed bed reactors. Other advantages of these architectures include short diffusion length, high geometrical surface area, easy scale-up and absence of maldistribution. These properties make fibrous catalysts

especially attractive for liquid phase catalytic reactions [46]. However, there have been few investigations of the application of fibrous catalysts for liquid/solid or gas/liquid/solid reactions. In addition, fibrous structured catalysts have been reported to have advantages with respect to pressure drop and mass transfer; however, most studies of fiber-based catalysts have not focused on mass transfer, hydrodynamics and transport properties [47].

Fibrous catalysts are categorized by their component materials, which consist of metal, glass and ceramic fibers. Metal fiber-based catalysts have attractive properties, but the application of noble metal fibers is limited by their cost and relatively low active surface. Glass and ceramic fibers are commonly applied to various catalytic applications due to their chemical resistivity, flexibility and low cost. Fibrous catalysts are also classified as string reactors, robocasted lattice structures and wet laid structures based on their structure [47]. String reactors are composed of filaments placed in parallel inside a tube, resulting in a unique microstructure comparable to that of multichannel microreactors (Fig. 7). These reactors have the advantages of a narrow RTD and good axial temperature distribution due to laminar flow [48, 49]. Robocasting is a moldless fabrication technique that has recently been widely applied in 3D printers. This method can produce desired structures of three-dimensional lattices to control mass transfer and pressure drop properties through on-demand design (Fig. 8) [50, 51].



Fig. 7 Schematic of filament reactor ^[(a); 41, (b); 42]



Fig. 8 Schematic of robocasted three-dimensional lattice [44]

Papermaking techniques have been applied to create porous structures of fiber networks. For example, catalyst particles can be added to a suspension of fibers to form a group of catalysts known as microfibrous entrapped catalysts (MFEC). These structures typically consist of fibers with diameters smaller than 20 µm and catalyst particles entrapped in a sinter-locked network of fibers (Fig. 9). Advantages of MFECs include the adjustability of voids over a wide range, which leads to smaller pressure drops, higher radial heat and mass transfer, decreasing hot spot formation and higher volumetric processing rates relative to particle beds [47]. Most investigations of MEFCs have dealt with gas phase reactions, such as hydrogen supply via methanol reforming [52, 53], autothermal reforming [54-56], ammonia decomposition [57], and NOx reductions [58].



Fig. 9 Images of fibrous catalysts formed by the papermaking technique

(A) Optical and SEM images of SiC containing catalyst paper ^[52], (B) Optical and SEM images of CuNPs@ZnO whisker-containing paper catalyst ^[56]

1-4 Alcohol oxidation

1-4-1 Background

Selective oxidation plays an important role in the current chemical industry. Oxidation is the second largest process applied by the industry after polymerization, contributing to up to 30% of total production in the chemical industry [59]. Oxidation reactions have traditionally been conducted in non-catalytic procedures with stoichiometric oxidants such as chromium and manganese compounds in the presence of mineral acids that produce large amounts of toxic metal salts as wastes.

In the past few decades, many oxidation processes have been developed to upgrade hydrocarbons that originate from crude oil *via* petrochemical pathways. In parallel, different approaches aimed at determining the suitability of renewable resources as chemical feedstocks are being investigated. At first glance, the use of bio-derived substances for chemical syntheses appears to be beneficial. Indeed, the use of biomass as a chemical substrate introduces a new level of complexity because it is socially, ethically and economically unacceptable to allow feedstock to compete with global food demands [60].

From an environmental viewpoint, it is important to develop methods that use cleaner oxidants and minimize the amount/toxicity of waste. Moreover, the use of catalysts that allow processes to occur under mild conditions to reduce overall energy use is strongly desired [61]. Oxygen is less expensive and has fewer adverse environmental effects than other stoichiometric oxidants because it produces no waste except water as a by-product [62]. As a result, the use of metal catalysts in combination with molecular oxygen via aerobic oxidation represents an emerging alternative to traditional oxidation procedures.

1-4-2 Selective alcohol oxidation by metal catalysts

Selective aerobic alcohol oxidation represents efficient molecular transformations for chemical valorization, which proceeds under mild conditions in the presence of noble metals. Platinum-group metals, such as platinum [63–65], palladium [66–68] and ruthenium [69–72], are the most versatile heterogeneous catalysts employed in organic synthesis. In addition, a range of transition metals including Ag [73–75], Cu [76, 77] and Au [78–81] have been shown to be effective for selective aerobic oxidation. TEM images of these metal catalysts are shown in Fig. 10. These metals are effective catalysts when used alone. Moreover, significant stability and improved selectivity have been reported upon incorporation of another metal promoter. Such catalysts are known as bimetallic catalysts [82, 83].

Most investigations of liquid phase oxidation reactions by platinum group metal catalysts have considered those supported on activated carbon or alumina. In such studies, catalysts were prepared by impregnation methods, such as solvent evaporation or dry impregnation, or by anionic adsorption and by cationic exchange methods [84, 85].



Fig. 10 TEM images of metal nano catalysts

(A) Pd/Al_2O_3 ^[67], (B) Ru/carbon nanotubes ^[72], (C) Au/ZrO₂ ^[81]

1-4-3 Mechanism of alcohol oxidation

Traditionally, stoichiometric metal oxides or metal salts are used for oxidation reactions. These procedures are summarized as follows:

$$R^{1}R^{2}CHOH + [OM^{n}] \rightarrow R^{1}R^{2}C = O + [M^{n-2}] + H_{2}O$$
⁽²⁾

$$R^{1}R^{2}CHOH + [M^{n}X_{2}] \rightarrow R^{1}R^{2}C = O + [M^{n-2}] + 2HX$$
(3)

where, R represents hydrogen, alkyl groups or aryl groups, and M and X represent metal species and halogen, respectively. These procedures are not compatible with environmental regulations owing to the copious amounts of heavy metal wastes produced at the same time [86].

A number of methods, which are often referred to as oxidative dehydrogenation, have been described as interesting alternatives to metal-catalyzed aerobic oxidation of alcohols. In this process, the oxidation of primary alcohol proceeds to a corresponding aldehyde and then to a carboxylic acid (Fig. 11). The oxidation of alcohol to aldehyde over heterogeneous catalysts occurs in three steps as illustrated in Fig. 12. First, the alcohol absorbs to the metal surface, producing an absorbed metal alkoxide. β -hydride elimination then occurs to produce a carbonyl species and a metal hydride. Finally, the metal hydride is oxidized by dioxygen to regenerate the metal surface [87-91].

$$\begin{array}{cccc} OH & O & O \\ R - C - H & \xrightarrow{1/2 O_2} & R - C - H & \xrightarrow{1/2 O_2} & R - C - OH \\ \vdots & & catalyst & catalyst & catalyst & C - OH \end{array}$$

Fig. 11 General oxidation scheme for primary alcohol oxidation to acid



Fig. 12 Alcohol oxidation mechanism by metal surface

1-4-4 Alcohol oxidation by fixed bed catalysts

Catalytic selective alcohol oxidation in the liquid phase is a developing research area owing to industrial interest in these types of environmentally friendly reactions. As mentioned above, there have been significant advances in the development of catalysts for these reactions using clean oxidants, such as O₂ and H₂O₂. However, use of these catalysts is still challenging from an industrial process point of view due to the risk of explosion of flammable substrate, solvent and oxygen mixtures, as well as the need to carefully control the oxygen concentration to avoid over oxidation, and the introduction of an additional mass transfer step of the dissolution of gaseous reactants. Slurry stirred-tank reactors or traditional TBRs are used in industrial fields of alcohol oxidation, but both suffer from significant drawbacks, such as poor mixing, mass and heat transfer, low catalytic efficiency and low selectivity. The potential solution is to use a micro-structured reactor that offers control of three phase flow hydrodynamics, intensifying gas-liquid and liquid-liquid mass transfer, and integrated heat transfer functionality [92].

There have been studies of fibrous catalysts, such as ethanol and methanol oxidation with silver catalysts [93, 94], benzylalcohol oxidation with nickel on silver fiber catalysts [95, 96], gold nanoparticles on nickel fiber catalysts [97, 98], gold and palladium bimetal catalysts on stainless steel fiber matrix [99], and silver nanoparticles on mesoporous silica [100]. However, all of the above-mentioned studies have been conducted in the gas phase under high temperature conditions.

Only a few studies have investigated selective aerobic oxidation in the liquid phase by

fixed bed catalysts. Benzylalcohol oxidation was performed by a microchannel reactor a few mm in length, loaded with Ru/Al₂O₃ powder catalysts [92, 101], or with iron oxide nanocatalysts supported by mesoporous silica [102]. Aromatic and aliphatic alcohols were oxidized in capillary columns with immobilized gold nanoparticles [103]. Monolith catalyst containing a 0.7 mm square cell loaded with platinum was tested during continuous benzylalcohol oxidation [104]. These reports have shown the effectiveness of catalysts and suggested that there is good selectivity in oxidation; however, the mechanism of liquid and gas distribution remains insufficient.

1-5 Objectives

Chemical industries are demanding that more environmentally acceptable processes, products and practices employ the concept of Green Sustainable Chemistry. Use of renewable natural resources can play important roles in sustainable development that must be achieved by efficient catalytic conversion processes. Multiphase catalytic reactions carrying out reactions between gas and liquid phases on a solid catalyst have attracted a great deal of attention in both industrial and academic circles. Catalytic selective oxidation of alcohol in the liquid phase is also important as an environmentally friendly reaction, and there have been significant advances in the catalysts applied for these reactions using clean oxidants such as oxygen. However, catalytic selective oxidation is challenging from an industrial point of view due to difficulties in process control with complex multiphase mixtures of gas and liquid flow over solid catalysts.

Recently, reactors with micrometer-sized dimensions known as microreactors have received a great deal of attention. The advantages of these reactors include a high surface to volume ratio, high mass and heat transfer rate, and narrow RTD. The narrow RTD is advantageous for consecutive industrial processes because selective reaction control of the desired products would be achieved. Fibrous catalysts, which are structured catalysts made of fiber materials, can be fitted to various reactor geometries and processes. In addition, they are easier to fabricate at lower cost than common microreactors. Fibrous catalysts have advantages with respect to pressure drop and mass transfer characteristics; however, the hydrodynamics of these catalysts remain unclear.

In this study, a new type of paper-structured catalyst, a type of fibrous catalyst, was prepared using a high-speed, low-cost papermaking technique. First, a paper-structured composite catalyst composed of ruthenium hydroxide $(Ru(OH)_x)$ and alumina/silica (Al₂O₃/SiO₂) fibers was prepared by an on-paper *in situ* synthesis method. Paper composites with a porous microstructure were then applied to multiphase catalysis for alcohol oxidation using a fixed bed external recycling loop reactor. Benzyl alcohol was chosen as a model substrate. The catalytic conversion of benzyl alcohol to benzaldehyde was subsequently compared using pellet and beads catalysts without any microstructures. Second, the hydrodynamic behavior of fibrous paper-structured catalysts was investigated in detail. Specifically, residence time distribution (RTD) studies were carried out by tracer monitoring in a cold flow model. To elucidate the unique kinetics of the heterogeneous catalyst, the relationship between the flow rate of liquid/gas and catalytic reactivity was examined by comparing paper and bead catalysts. Finally, reaction kinetics and mechanism studies were performed based on the solvent free selective oxidation of benzylalcohol.

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Chapter 2

Preparation of porous paper composites with ruthenium hydroxide and catalytic alcohol oxidation in a multiphase gas-liquid-solid reaction

Abstract

In situ synthesis of ruthenium hydroxide catalysts on a microporous fiber-network structure of ceramic paper composites was achieved. The efficient catalytic oxidation of alcohol was investigated in a heterogeneous, multiphase gas-liquid-solid reaction. A simple papermaking technique and subsequent immersion in a ruthenium chloride solution allowed us to fabricate novel-concept microstructured catalysts. The paper-structured catalysts possess micropores ca. 30 µm in diameter with high porosity of ca. 90%. They exhibited much higher catalytic efficiency in the O2-mediated oxidation in toluene of benzyl alcohol to benzaldehyde in a fixed bed external loop reactor, as compared with conventional pellet- and bead-type solid catalysts. This excellent catalytic effect is possibly attributed to the porous paper composite microstructure like microreactors.



2-1 Introduction

Catalysts play an indispensable role in the efficient mass manufacture of energy and products, resulting in catalyst research and development being promoted with great interest [1]. In particular, the catalytic oxidation of alcohols to provide the corresponding carbonyl compounds is one of the most important reactions in chemical industries, because of the extremely broad application of these oxidized products as major intermediates for medicines, fertilizers and various chemicals [2, 3]. Traditional synthesis has been performed using toxic inorganic oxidants such as chromium (IV) and manganese (VII); however, from both economic and environmental viewpoints, there have been demands to achieve greener processes that operate at lower temperatures using cleaner oxidants such as O₂ and H₂O₂[3, 4]. A variety of homogeneous and heterogeneous catalysts have been developed for the O₂-mediated alcohol oxidation processes [5, 6]. Homogeneous catalysts have several advantages of efficiency, selectivity and yields; however, their use in industrial applications is strictly limited because of difficulties in the separation of used catalysts from final products. Therefore, in practical applications, heterogeneous catalysts in solid form are sought after to effectively perform in complex multiphase mixtures of gas (air/O₂), liquid (substrates/media) and solid (fixed catalyst).

The most popular use of heterogeneous catalysts in industry for liquid and multiphase applications is in slurry-type reactors. Small catalyst particles are stirred in a vessel to a quasi-homogeneous state, minimizing temperature and concentration gradients [7]. However, the slurry reactors have several disadvantages: (I) difficult separation of products from the

finer catalysts because of catalyst attrition, (II) inevitable abrasion of the process equipment by moving hard particles, and (III) low productivity and complicated operation in continuous processes. Therefore, fixed bed reactors are required as an alternative to slurry reactors, and have been applied widely in current industries [8]. Particle packed bed reactors are typical items of equipment, and there are no issues for the separation of products from catalysts, because all catalysts are fixed strongly on the beds. Although the simple structure and low operating cost are beneficial [7], the particle packed bed reactors display critical disadvantages because of (I) large particle sizes, (II) high pressure drops and low mass transfer efficiencies in the gas-liquid-solid phases, (III) complicated temperature control and the uncontrollable generation of hot spots (exothermic reactions), and (IV) additional demand on liquid and gas distributors [8]. Catalyst particle sizes larger than those in slurry reactors are undesirable for efficient heterogeneous catalysis, and eventually cause lower reactivity and selectivity because of intraparticle diffusion limitations and low specific surface area. Thus, balanced properties to reconcile the large interfacial reactivity and practical utility that slurry and packed bed reactors possess, respectively, are a major target to improve catalytic reaction engineering [9].

Recently, fixed bed reactors having micrometer-sized pore structures, termed microreactors, have attracted much attention in industrial circles because of improvements in mass and heat transfer inside the flow path at a micrometer scale [10]. Various types of microreactors such as honeycomb [11], foam [12] and string assembly [13] reactors have been investigated, and fibrous catalysts especially are expected to satisfy the requirements of high catalytic efficiency and low pressure drop. Fine catalyst particles fixed on the boundary

surfaces forming microflows would enable high geometrical surface area, short diffusion distance and smooth flow in the gas-liquid-solid phases. Further advances in the structural and functional design of microreactors using carbon, glass and ceramic fibers instead of expensive metal fibers would provide a new insight and approach to realize the practical applications of fibrous microreactors [14]. In previous studies, paper-like catalysts composed of inexpensive ceramic fibers were developed by a high-speed and low-cost papermaking technique. As-prepared paper composites, termed paper-structured catalysts, are easy to fabricate and handle and possess porous microstructures derived from layered fiber networks such as paper [15–18]. Cu/ZnO catalyst powders were loaded into a paper matrix and demonstrated efficient catalytic hydrogen production from methanol in the gas phase [15]. Direct in situ synthesis of Au nanoparticles on a microstructured paper matrix composed of ceramic fibers and ZnO whiskers was achieved, and showed excellent performances for low temperature gas phase CO oxidation [16] and for liquid phase 4-nitrophenol reduction [17]. Pt nanocatalysts were synthesized on surface-activated carbon fibers, and exhibited a high removal efficiency of NO_x and CH₄ from exhaust gases [18]. These results suggested that the unique porous microstructures of the paper-structured catalysts must play significant roles in two phase reactions such as gas-solid [15, 16, 18] and liquid-solid reactions [17].

In this study, a new type of paper-structured catalyst was prepared using ruthenium hydroxide ($Ru(OH)_x$) and alumina/silica (Al_2O_3/SiO_4) fibers by established papermaking technique, and first applied to multiphase catalysis for efficient alcohol oxidation. Much attention has focused on $Ru(OH)_x$ as a promising alcohol oxidation catalyst, and the aerobic

oxidation of alcohols has been reported using Ru(OH)_x on hydroxyapatite [19], Ru(OH)_x on TiO₂ [20, 21], Al₂O₃ [22], silica [23], and Fe₃O₄ [24]. However, few studies have been devoted to develop the structured catalysts toward practical applications [25–27]. Herein, inexpensive commercial Al₂O₃-rich ceramic fibers were fabricated into a paper matrix, followed by the impregnation of Ru(OH)_x *via* the on-paper synthesis approaches [16–18]. As-prepared Ru(OH)_x/Al₂O₃ paper composites with a porous microstructure were characterized by scanning electron microscopy (SEM), atomic absorption spectrophotometry (AAS) and other instrumental analysis. The catalytic conversion of benzyl alcohol to benzaldehyde in multiphase aerobic oxidation (O₂ fed into toluene) was investigated using a fixed bed external recycling loop reactor, as compared with pellet and bead catalysts without any microstructures.

2-2 Experimental

2-2-1 Materials

Ceramic fibers (DENKA ALCEN B80L, Al₂O₃: 80% and SiO₂: 20% by weight, Denki Kagaku Kogyo Kabushiki Kaisha, Tokyo, Japan) were cut into an average length of *ca*. 0.5 mm using a four-flute end mill. An alumina sol (520, Nissan Chemical Industries Ltd, Tokyo, Japan) was used as an inorganic sol binder to improve the physical strength of the catalyst papers, and also as a catalyst carrier. Two types of flocculants were used as retention aids; polydiallyldimethylammonium chloride (PDADMAC; molecular weight: *ca*. 3×10^5 ; charge density: 5.5 meq g⁻¹; Sigma-Aldrich Co. LLC, St. Louis, MO, USA) and anionic

polyacrylamide (A-PAM, A125S; molecular weight; *ca.* 1×10^7 ; charge density: 3.2 meq g⁻¹; MT Aquapolymer, Inc., Tokyo, Japan). Pulp fibers, as a tentative supporting matrix in the papermaking process, were obtained by beating commercial bleached hardwood kraft pulp to 300 ml of Canadian Standard Freeness with a Technical Association of Pulp and Paper Industry (TAPPI) standard beater, according to established preparation method [15–18]. Gamma-alumina powder and beads as catalysts supports were purchased from Sumitomo Chemical Co. Ltd, Tokyo, Japan (powder: A-11, beads: KHS-24). The Ru(OH)_x catalysts in powder and bead form were prepared and tested according to literature procedures [22]. Catalyst pellets 3 mm in diameter × 5 mm in height were molded using a tablet machine (AUTOTAB-500, ICHIHASHI-SEIKI Co. Ltd, Kyoto, Japan). Other chemicals were reagent grade and were used without further purification.

2-2-2 Preparation of paper-structured catalysts

A water suspension of ceramic fibers was mixed with PDADMAC (0.5 wt% of total solid), alumina sol and A-PAM (0.5 wt% of total solid), in that order, with each step being performed at an interval of 3 min. The mixture was added to the pulp fiber suspension, and paper composite sheets were prepared according to previous reports [15–18]. The wet state sheets were pressed at 350 kPa for 3 min, and then oven dried at 105°C for 1 h. The resulting paper composites (2×10^4 mm²) consisted of ceramic fibers (5.0 g), alumina sol (0.54 g) and pulp fibers (0.25 g). The paper composites obtained were calcined at 600°C for 5 h to remove organic pulp fibers and to improve the physical strength by alumina binder sintering.

On-paper synthesis of Ru(OH)_x on an as-prepared paper matrix was carried out in the following sequence. First, paper composites were cut into disc-shaped pieces (diameter: 23 mm) and immersed in an aqueous solution of ruthenium chloride (RuCl₃; 8.3 mM, 50 mL) for 5 h. The discs were then removed from the solution using tweezers, and oven dried at 105°C for 1 h. In the second step, the discs were immersed in an aqueous solution of RuCl₃ (8.3 mM, 50 mL) for 24 h, and the solution pH was adjusted to 13 by the addition of an aqueous solution of NaOH (1.0 M). The discs were removed from the solution, washed with deionized water, and dried at 105°C for 1 h.

2-2-3 Characterization

Specific surface areas were obtained from nitrogen absorption-desorption isotherms (BELSORP-mini, BEL JAPAN INC.). The specific surface areas were calculated by the Brunauer-Emmet-Teller (BET) method. Surface observation of the paper-structured catalysts was performed by SEM (S-4300SE/N, HITACHI Corp.), and elemental mapping was also obtained by energy dispersive X-ray spectrometry (EDS, EMAX-500, HORIBA Ltd). Mercury intrusion analysis was carried out using an AUTOPORE IV 9500 (Micromeritics Instrument Corp.). Pore size distribution was obtained from a pressure-cumulative mercury intrusion volume curve normalized by each catalyst weight. The Ru content was determined by AAS (AA-6600F, Shimadzu, Co. Ltd). The concentration of Ru ions eluted from the samples with hydrochloric acid was measured. X-ray diffractometry (XRD) was performed using a Cu K α radiation (λ =1.541 Å; MX-2000, MAC Science Co., Ltd).

2-2-4 Alcohol oxidation test

A schematic diagram of the fixed bed alcohol oxidation reactor used in this study is illustrated in Fig. 1, i.e. a typical external recycling loop reactor. Ten disc-shaped paper catalysts were stacked vertically (6.2 mm³) and placed on a perforated support base inside a stainless steel cylindrical reactor vessel. The catalysts discs were packed against the inner wall of the reactor, to make good contact with the inner surface of the reactor. In a similar way, catalyst pellets and beads were used to fill the reactor and adjusted the occupied volume to 6.2 mm³. A mixture of substrate alcohol (5.6 mmol) and toluene as solvent (0.76 mol) was supplied by plunger pump (Hi-Cera Pump V, IWAKI Co., Ltd). Molecular O₂ gas was fed by a mass flow controller (3200, KOFLOC). Inlet gas and liquid phase mixtures were heated by a flexible ribbon heater. Temperatures at the reactor inlet and center were maintained at 85°C by ribbon and mantle heaters. The supplied reactants passing through the catalyst layers returned to a gas/liquid separator. Oxidant gas (O₂) was discharged from the reaction system, and liquid mixtures were subjected to recycling for continuous reaction. Feed flow rates of liquid and gas were set at a space velocity of 96 (Liquid hourly space velocity; LHSV) and 960 h⁻¹ (Gas hourly space velocity; GHSV), respectively. The alcohol conversion and product yield were determined periodically by gas chromatography (GC) after withdrawing small aliquots from the outlet of the reactor. GC analysis was carried out using a dimethylpolysiloxane column (DB-1, 30 m \times 0.25 mm \times 0.5 μ m, J&W) and flame ionization detector (GC-8A, Shimadzu, Co. Ltd). The reaction rates were determined as turnover frequency (TOF) values, which are defined as the number of moles of product per number of moles of catalyst per hour [22-24]. The TOF values were calculated on the basis of the molar amount of catalysts loaded into a reactor vessel and the time course of change in the molar concentration of alcohols in the reactor outlet, at an equivalent aldehyde conversion around 10 %.



Fig. 1 Schematic illustration of external recycling loop reactor system: whole system overview (left), reactor (right).

The catalyst durability was evaluated by the variations of the TOF values during the alcohol oxidation tests repeated five times. The reaction was first performed with new catalysts for 2 h, and then the catalysts were washed with the NaOH solution for recycling, based on reference literature [20, 22]. In particular, after the reaction, the liquid mixtures of substrate and solvent were discharged from the sampling valve. At the same time, 0.76 mol of fresh solvent was charged, and the catalysts were washed with the fresh solvent at reaction

temperatures. Subsequently, the reactor was cooled down to room temperature, the catalysts were washed with 50 ml of acetone, 50 ml of 1 M NaOH, and 100 mL of deionized water in this order, and finally dried at 105°C for 2 h. These washing processes were conducted in the reactor vessel.

2-3 Results and discussion

2-3-1 Fundamental characteristics of paper composites

Ceramic fibers and alumina sol were fabricated successfully into paper composites by a previously reported high-speed, low-cost papermaking technique. The retention of these inorganic materials reached ca. 100 % in a dual polymer retention system [15-18]. The paper-structured composites were strengthened by calcination at 600°C for 5 h, and then the alumina sol underwent a clear change in crystalline form. Fig. 2 shows XRD spectra for the alumina sol powder dried at 120°C (2a), calcined at 600°C (2b), ceramic fiber (2c), paper composites containing alumina sol after drying at 120°C (2d), and 600°C (2e), Ru(OH)_x-containing paper catalysts (2f). These results indicate a significant crystalline variation before and after calcination. At first, the crystalline structure of the as-dried alumina sol was boehmite (AlO(OH), ICDD no. 21-1307), but changed completely to gamma-alumina (ICDD no. 10-0425) after calcination at 600°C. The ceramic fiber possessed a theta-phase alumina (ICDD no. 11-0517). For the paper composite dried at 120 °C, boehmite was formed on the ceramic fiber surface by alumina sol deposition and cellulose peaks (ICDD no. 50-2241) were observed. The cellulose pulp fibers were used as a supporting matrix in the wet papermaking process. After calcination of the paper composites at 600°C, the boehmite and cellulose peaks disappeared, respectively, to possibly form gamma-alumina and to be burned up. A typical gamma-alumina peaks from 35 to 50 degrees of 2 theta were not observed because ceramic fiber showed a high XRD intensity, but the absence of boehmite peaks and higher intensity of peak around 67 degrees of 2 theta possibly indicated that gamma-alumina would be formed by calcination treatment like alumina sol powders. The BET surface area of ceramic fiber and paper composites after calcination at 600°C were 14.2 and 29.0 m² g⁻¹, respectively. Gamma-alumina of relatively high specific surface area was readily synthesized onto ceramic fiber surfaces in the paper composites.



Fig. 2 XRD spectra of (a) alumina sol powder dried at 120°C, (b) alumina sol powder calcined at 600°C, (c) ceramic fiber, (d) paper composite dried at 120°C, (e) paper composite calcined at 600°C, (f) Ru(OH)x-containing paper catalysts. \blacklozenge : boehmite (ICDD no. 21-1307), \triangle : gamma-alumina (ICDD no. 10-0425), \Box : theta-alumina (ICDD no. 11-0517), \circ : cellulose (ICDD no. 50-2241).

The direct synthesis of Ru(OH)_x on-paper composites was performed using as-formed gamma-alumina as a preferential scaffold for $Ru(OH)_x$. As-prepared paper composites were immersed in an aqueous solution of RuCl₃, to form the Ru precursor adsorbed on the fiber. Then, the composites were dried once, and immersed again in an aqueous solution of RuCl₃ at pH 13, followed by drying. In this sequence, Ru(OH)_x crystals grew from the Ru precursors on the fiber matrix before Ru(OH)_x-containing paper catalysts were obtained. Without alumina sol addition, efficient Ru retention was not achieved. Optical images of the original paper composites, paper composites with Ru precursors, Ru(OH)_x paper catalysts, pellet catalysts and bead catalysts are shown in Fig. 3. These paper composites with the appearance of flexible cardboard were lightweight and easy to handle. Each paper piece was ca. 23 mm in diameter and ca. 1.5 mm thick. Paper composites with Ru precursors changed in color from white to gray, and the Ru(OH)_x paper catalysts became darker in color. Atomic absorption analysis indicated that the Ru content of the paper composites with Ru precursor and Ru(OH)_x catalyst were 0.70 and 0.91 wt%, respectively. Solid pellet catalysts were made from powder catalysts by a molding method using a tablet machine, and circular cylindrical shape 3 mm in diameter and 5 mm in length. Bead catalysts were prepared by the impregnation method, in a similar way to the powder catalyst manufacture; $Ru(OH)_x$ covers the outer surface layer of the alumina beads in a 3 mm diameter. The Ru contents of the pellet and bead catalysts were 1.1 and 0.24 wt%, respectively. The XRD pattern of the Ru(OH)_x-containing paper catalyst (Fig. 2-f) was almost the same as that of paper composites (Fig. 2-e), and no diffractions originating from ruthenium metal or oxides were detected. This result possibly suggested that ruthenium hydroxide was highly dispersed on the gamma-alumina as reported [22].



Fig. 3 Optical images of (a) paper composite without catalyst, (b) paper composite with Ru precursor, (c) Ru(OH)x paper catalyst, (d) pellet-type catalyst, and (e) bead-type catalyst.

2-3-2 Microstructures of Ru(OH)_x-containing paper composites

SEM images of the paper composite surfaces with fiber-network microstructures composed of ceramic fibers (Fig. 4) show that there are significant differences in the fiber surface morphology. The ceramic fiber surface was very smooth. The paper composite fiber surfaces appeared to be covered with alumina sol. The surface morphology of the paper composites with or without Ru precursors resembled one other; however, the significant existence of Ru elements on the fiber matrix was confirmed by EDX elemental mapping as shown in Fig. 5. For the $Ru(OH)_x$ paper catalysts, small crystal-like particles were observed on the ceramic fiber surface (Fig. 4d), and EDX mapping obviously displayed a uniform distribution of Ru species on the ceramic fiber networks (Fig. 5b).



 $20\,\mu m$

Fig. 4 SEM images of (a) ceramic fiber, (b) paper composite without catalyst, (c) paper composite with Ru precursor and (d) $Ru(OH)_x$ paper catalyst.



Fig. 5 SEM and EDX mapping images of (a) paper composite with Ru precursor and (b) Ru(OH)_x paper catalyst.

Figs 6 and 7 profile the pore size distribution determined by a mercury intrusion method. For the paper composites, a clear peak around 30 μ m was observed, and the porosity reached *ca.* 90%. The characteristic microstructure of the paper composites remained almost unchanged before and after the on-paper synthesis of Ru(OH)_x. On the contrary, for pellet and bead catalysts, there were no significant peaks over 1 μ m, and the porosity was lower than 20%. The bead catalysts had sharp peaks around 10 nm, being derived from original matrix beads. The pellet catalysts had two peaks, around 800 and 5 nm, possibly resulting from powder particles and powder surfaces, respectively. These two control catalysts had no characteristic porous microstructures promoting microflow.



Fig. 6 Pore size distribution curves of paper composite without catalyst (closed triangles) and Ru(OH)_x paper catalyst (open diamonds).



Fig. 7 Pore size distribution curves of pellet-type catalyst (open triangles) and bead-type catalyst (closed squares).

2-3-3 Alcohol oxidation in a fixed bed reactor

The catalytic behavior of paper-structured catalysts was estimated in an alcohol oxidation reaction. The alcohol oxidation procedure was carried out in the fixed bed reactor as illustrated in Fig. 1, and benzyl alcohol was used as a model substrate. Fig. 8 shows the time-course conversion profiles of benzyl alcohol and as-formed benzaldehyde concentrations during the oxidation reaction with Ru(OH)_x-containing paper catalysts. These results indicate that benzyl alcohol was converted immediately to benzaldehyde, and an increase in benzaldehyde concentration corresponded stoichiometrically to a decrease in benzyl alcohol concentration. Nearly no intermediates were detected by GC analysis, and therefore Ru(OH)_x paper catalysts oxidized benzyl alcohol to benzaldehyde with as high a selectivity as reported for the powder catalysts [19]. The reaction rates were determined as turnover frequency (TOF) values, which are defined as the number of moles of product per number of moles of catalyst per hour. For the case of $Ru(OH)_x$ paper catalysts, the TOF representing a 12.8% yield of benzaldehyde (equivalent to 12.8% benzyl alcohol conversion with regard to the original feed amount of 5.6 mmol) on the 0.105 mmol Ru species for 0.03 h was estimated to be ca. 224 h⁻¹. TOF values were also calculated at the instant of 12.2% yield, 0.28 mmol Ru species and 0.3 h for the pellet-shaped catalysts and 11.0%, 0.105 mmol and 0.16 h for the beads-type catalysts, respectively (Fig. 9). This value was almost the same as that obtained in a batch reaction of Ru(OH)_x powder catalysts at 207 h⁻¹, 9.51% yield, 0.102 mmol of Ru and 0.05 h of a reaction time. Therefore, a high TOF value, *i.e.* efficient reactivity, was achieved in a fixed bed reaction by Ru(OH)_x-containing paper catalysts, under the same solvent and temperature as powder

catalysts.



Fig. 8 Catalytic conversion behavior of benzyl alcohol to benzaldehyde; benzyl alcohol (open triangles) and benzaldehyde (closed squares).



Fig. 9 Turnover frequency values of Ru catalysts with various forms.

Fig. 9 compares the catalytic oxidation behavior of paper-structured, pellet-shaped and bead-type catalysts. Reactions were conducted under the same catalyst volume. The Ru content of paper-structured, pellet and bead catalysts were 0.1, 0.3 and 0.1 mmol, respectively.

Compared with pellets and beads, paper-structured catalysts exhibited much higher TOF values, and could overcome the limiting applicability of a fixed bead reactor. When using pellet catalysts, internal diffusion was limited because of the large particle size (3 mm in diameter and 5 mm in length) and low porosity of less than 20%, resulting in poor reactivity. There were few micropores inside the pellet catalysts, and $Ru(OH)_x$ species existing inside the pellet could not function efficiently. Paper catalysts possessed a micrometer-sized pore structure, and the filling fraction was regarded as being ca. 100 % in a reactor. In the case of pellet and bead catalysts, the filling fractions in the reactor were smaller than those of the paper catalysts, possibly leading to submillimeter size gaps. Such large gaps for pellet and bead particles cause short-cut diffusion of liquid and gas in a multiphase heterogeneous reaction, and eventually the reaction efficiency decreases. A high TOF value, *i.e.* efficient reactivity, was achieved even in a fixed bed reaction using Ru(OH)_x-containing paper composites with microporous structures, and further applications of designed paper-structured catalysts are expected, aiming at practical, heterogeneous gas-liquid-solid multiphase reactions.

Catalyst durability is one of the essential properties for practical catalyst applications to ensure their industrial use. Fig. 10 shows the durability performance of $Ru(OH)_x$ paper catalysts with respect to the variation of TOF value in the alcohol oxidation test. The $Ru(OH)_x$ paper catalysts exhibited high durability performance: the decrease in TOF value was only 5% after 5-cycles alcohol oxidation tests. Atomic absorption analysis indicated that the Ru contents of paper catalysts remained unchanged during the reaction, that is, no Ru leaching occurred. This high durability and the easy recycling feature of paper catalysts are expected to have advantages for practical applications.



Fig. 10 Catalyst durability for alcohol oxidation

2-4 Conclusions

In situ synthesis of $Ru(OH)_x$ catalysts on the microporous fiber-network structure of paper composites and efficient catalytic heterogeneous gas-liquid-solid multiphase oxidation were achieved. A ceramic paper matrix was prepared successfully using a simple papermaking technique, and subsequent immersion in a $RuCl_3$ solution allowed us to fabricate novel-type microstructured catalysts. As-prepared $Ru(OH)_x$ -containing paper composites possessed a paper-like flexibility and porous microstructure because of layered fiber networks. The paper catalysts demonstrated high catalytic efficiency of aerobic alcohol oxidation from benzyl alcohol to benzaldehyde with high selectivity at a triple O₂-toluene/substrate-catalyst phase in a fixed bed external loop reactor. The $Ru(OH)_x$ paper catalysts showed significantly higher reactivity, as compared with conventional pellet- and bead-type solid catalysts, especially for the initial conversion rates and the durability for repeated uses, due to highly dispersed ruthenium hydroxide species on the porous paper composite microstructure like microreactors.

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[27] M. Deng, G. Zhao, Q. Xue, L. Chen, Y. Lu, Microfibrous-structured silver catalyst for low-temperature gas-phase selective oxidation of benzyl alcohol, Appl. Catal. B Environ. 99 (2010) 222–228. Chapter 3

Multiphase catalytic oxidation of alcohols

over paper-structured catalysts with micrometer-size pores

Abstract

Paper-structured catalysts were prepared using ceramic fibers by a wet papermaking technique, followed by the deposition of ruthenium hydroxide on the fiber-network microstructures. As-prepared flexible paper catalysts possessed large geometric surface areas with micrometer-size pores. The paper-structured catalysts exhibited high catalytic efficiency for selective aerobic oxidation of aromatic and aliphatic alcohols to their corresponding aldehydes and ketones, in a fixed bed multiphase reactor. Hydrodynamic behavior in the reactor filled with either paper or bead catalysts was evaluated by measuring the residence time distribution in a cold flow model. It was revealed that the paper composites exhibited good wettability and internal diffusion of liquid substances compared with ceramic beads, showing heterogeneous liquid flow. Efficient catalytic oxidation of various alcohols was achieved using the paper-structured catalysts because uniform fluid dynamic behavior formed a thin liquid layer on the catalyst surfaces, possibly resulting in favourable gas-liquid-solid interfaces.


3-1 Introduction

Selective oxidation reactions of alcohols to aldehydes, ketones and carboxylates play a critical role in the chemical industry and various applications because these compounds are important intermediates and/or precursors in pharmaceutical and chemical materials engineering. In particular, oxidation catalysts are key materials in realizing green and sustainable chemical processes. Traditional oxidation has been performed with stoichiometric oxidants, such as chromium (IV) and manganese (VII) reagents. However, from the viewpoint of atom economy and environmental efficiency, aerobic oxidations using O2 as a cleaner oxidant are becoming increasingly attractive as an alternative to using harmful oxidants [1, 2]. In comparison with other chemical reactions, biphasic oxidation at the interface between gas and liquid remains challenging because of the difficulty in preventing undesirable overreactions caused by exothermal behavior in oxidation reactions. Liquid-phase oxidation is often applied to selective oxidations of targeted functional groups under mild conditions because the solvents (or liquid substrates) can act as a heat sink, and promote mass transfer [3]. In recent years, extensive research on heterogeneous catalysts containing active noble metals has been carried out, for example on Pt, Pd and Ru [4-6]. However, the practical applications of bulk and supported catalysts require chemical engineering-based reactor design, such as fixed-bed and structured catalysts, with control of mass and heat transfer. Little work on immobilized catalyst systems for the aerobic oxidation of alcohols in continuous flow can be found in the literature [7].

Established technologies using pellets, honeycombs and fixed-bed reactors with

micrometer-sized pore structures, named microreactors or microstructured reactors (MSRs), have become popular in industrial use. MSRs have an equivalent hydraulic diameter of up to a few hundreds of micrometers and therefore provide high mass and heat transfer efficiency, which drastically improves reactor performance compared with conventional fixed-bed systems [8]. Amongst these MSRs, fibrous catalysts have received extensive attention with respect to theoretical and experimental issues in chemical processing. The size of catalyst pellets in packed bed reactors is decided by a compromise because of the conflicting requirements for high reaction effectiveness and low pressure drop. Fibrous catalysts are structured catalysts that offer high surface to volume ratios and the high void fractions, which can overcome such trade-off requirements [9]. Flexible fibrous materials can be fitted to various reactor geometries and processes. In addition, they are easier to fabricate at lower cost than common microchannel reactors. Many types of fibrous catalysts, prepared with various fibers and manufacturing methods, have been reported with regard to their advantages and disadvantages [10]. Woven wires of fine precious metals such as Pt, Ru and Ag have long been used in production of nitric acid and hydrocyanic acid [11]. Foam-type Ag, Cu and complex Ag-Cu catalysts, and sheet-type Ag/Ni fiber catalysts were reported for the selective oxidation of alcohols in the gas phase [12, 13]. Although such catalyst types possess high mechanical strength and thermal conductivity, the application of bulk noble metal fibers is of limited use because of high costs. However, ceramic fibers are commonly applied as support materials for catalytic combustion applications. Additionally, ceramic fibers are applied to prepare fiber-based structures as a catalyst support [10].

In previous studies, fibrous catalysts composed of inexpensive ceramic fibers were developed by a high-speed and low-cost papermaking technique. As-prepared wet laid structures of fibrous ceramic composites, termed paper-structured catalysts, are easy to fabricate, handle and possess porous microstructures [14-18]. Microfibrous entrapped catalysts (MFEC) loaded with Cu/ZnO catalysts powders demonstrated efficient catalytic hydrogen production from methanol in the gas phase [14]. Direct in situ synthesis of gold nanoparticles on a wet laid microstructured matrix composed of ceramic fibers and ZnO whiskers was achieved, and showed excellent performance in both low temperature gas-phase oxidation of CO [15] and liquid-phase reduction of 4-nitrophenol [16]. Platinum nanocatalysts were synthesized on activated carbon fibers and exhibited a high efficiency for removal of NO_x and CH₄ from exhaust gases [17]. Ruthenium hydroxide catalysts were synthesized on a ceramic fiber surface with gamma-alumina and superior reactivity was achieved in a fixed bed for selective oxidation of benzyl alcohol [18]. These catalysts showed high reactivity in multi-phase reactions such as gas-solid [14-17], liquid-solid [16] and gas-liquid-solid reactions [18]; however the relationships between fibrous microstructure and catalytic reactivity have not yet been elucidated. Fiber-based structured materials are often attributed with good mass transfer and pressure drop characteristics. In contrast with the large number of publications on fibrous materials, few papers have been reported that refer to mass transfer and pressure drop [10].

The current study focused on the liquid flow behavior inside paper-structured catalysts to enable highly efficient aerobic oxidation. Ruthenium hydroxide $(Ru(OH)_x)$ was synthesized on

alumina/silica (Al₂O₃/SiO₄) paper composites, and a fixed-bed external loop reactor was designed [18] to evaluate the selective oxidation of various alcohols to their corresponding aldehydes. To clarify the hydrodynamic behavior of fibrous paper-structured catalysts, residence time distribution (RTD) studies were carried out by tracer measurement in a cold flow model. The relationship between the flow rates of liquid/gas and catalytic reactivity was investigated by comparing paper and bead catalysts.

3-2 Experimental

3-2-1 Materials

Ceramic fibers (DENKA ALCEN B80L, Al₂O₃: 80% and SiO₂: 20%, Denki Kagaku Kogyo Kabushiki Kaisha, Tokyo, Japan) were cut into an average length of *ca.* 0.5 mm. An alumina sol (520, Nissan Chemical Industries Ltd., Tokyo, Japan) was used as an inorganic binder to improve the physical strength of the paper-structured catalysts. Anionic and cationic polymers were used as retention aids; polydiallyldimethylammonium chloride (PDADMAC; molecular weight: *ca.* 3×10^5 ; charge density: 5.5 meq g⁻¹; Sigma-Aldrich Co. Ltd, St Louis, MO, USA) and anionic polyacrylamide (A-PAM, A125S; molecular weight; *ca.* 1×10^7 ; charge density: 3.2 meq g⁻¹; MT Aquapolymer, Inc., Tokyo, Japan). Pulp fibers were obtained by beating commercial bleached hardwood kraft pulp to 300 ml of Canadian Standard Freeness with a Technical Association of Pulp and Paper Industry (TAPPI) standard beater (2505, KUMAGAI RIKI KOGYO Co., Ltd., Tokyo, Japan). Commercial ceramic beads (KHS-24, Sumitomo Chemical Co. Ltd, Tokyo, Japan) were used as catalyst supports.

Ru(OH)_x catalysts in beaded form were prepared following procedures described in the literature [19]. Other chemicals were reagent grade, purchased from commercial suppliers (Wako Pure Chemical Industries, Ltd., Osaka, Japan and Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and used without further purification.

3-2-2 Preparation of paper-structured catalysts

Paper-structured catalysts were fabricated by a wet papermaking process described previously in detail [18]. An outline of the papermaking procedure can be summarized as follows. A water suspension of ceramic fibers was mixed with PDADMAC (0.5 wt% of total solid), alumina sol, A-PAM (0.5 wt% of total solid) and pulp fibers (0.25 g of total solid) in that order, with 3-min intervals between each step. The mixture was then solidified by dewatering using a 200-mesh wire. The wet-state sheet was pressed at 350 kPa and dried at 105°C. The obtained sheet (2×10^4 mm²) consisted of ceramic fibers (5.0 g), alumina sol (0.54 g) and pulp fibers (0.25 g). The sheet were cut into disc shaped pieces and calcined at 600°C for 5 h to remove organic compounds and to improve their physical strength by binder sintering.

Synthesis of Ru(OH)_x on an as-prepared paper-structured matrix was carried out as follows. First, paper composite discs (23 and 47 mm diameter for flow and non-flow systems, respectively) were immersed in an aqueous solution of ruthenium chloride (RuCl₃; 8.3 mM) for 5 h. The discs were then removed from the solution and dried at 105°C for 1 h. Next, the discs were immersed in an aqueous solution of RuCl₃ (8.3 mM, solution pH was adjusted to 13

by adding an aqueous solution of NaOH) for 24 h. The discs were removed from the solution, washed with deionized water, and dried at 105°C for 1 h.

3-2-3 Catalysts characterization

Surface observation was carried out by scanning electron microscope (SEM; S-4300SE/N, HITACHI High-Technologies Corp., Tokyo, Japan). Pore size distribution and geometrical surface area were obtained from mercury intrusion analysis (AUTOPORE IV, Micromeritics Instrument Corp., GA, USA). Specific surface areas were obtained from nitrogen absorption-desorption isotherms (BELSORP-mini, BEL JAPAN Inc., Osaka, Japan), and calculated by the Brunauer–Emmet–Teller (BET) method. The Ru contents of catalysts were determined by atomic absorption spectrophotometry (AAS; AA-6600F, Shimadzu Corp., Kyoto, Japan). X-Ray diffraction (XRD) measurement was performed using Cu K α radiation (λ =1.541 Å; MX-2000, MAC Science Co., Ltd., Kanagawa, Japan).

3-2-4 Alcohol oxidation reactions

Catalytic behavior of paper-structured catalysts and beaded catalysts was estimated using the non-flow batch-type and the fixed-bed external recycling loop reactors. The non-flow reaction was carried out in a 200-ml round bottom separable flask (55 mm inner diameter) with a reflux condenser. Either one disc-shaped paper-structured catalyst (47 mm diameter) or beaded catalysts were placed on a perforated support in the flask with gentle stirring of reaction media at 358 K, purged by O_2 gas at a 100 ml/min flow using a mass flow controller (3200, KOJIMA INSTRUMENTS INC., Kyoto, Japan). A schematic of the fixed-bed reactor is shown in Fig. 1. Ten disc-shaped paper-structured catalysts were stacked vertically (6.2 mm³) and placed on a perforated support in a stainless steel reactor vessel (23 mm inner diameter and 75 mm height). The catalyst beads were packed into the vessel and adjusted to a consistent total volume of 6.2 mm³. A liquid phase mixture of each substrate alcohol (5.6 mmol) and toluene as solvent (0.76 mol) was supplied by pump (Hi-Cera Pump V, IWAKI Co., Ltd.). Oxygen gas was fed by a mass flow controller (3200, KOJIMA INSTRUMENTS INC., Kyoto, Japan). Reactor and supply piping were heated to 85°C. The supplied reactants passing through the catalyst layers were returned to a gas/liquid separator, oxidant gas was discharged from the system, and liquid mixtures were recycled. Feed flow rates of liquid and gas were set at 10 ml/min (liquid hourly space velocity, LHSV = 96), and 10 to 100 ml/min (gas hourly space velocity, GHSV = 96 to 960), respectively. The catalytic alcohol conversion and product yield were analyzed periodically by gas chromatography (GC) after sampling small aliquots from the outlet of the reactor. GC analysis was performed using a dimethylpolysiloxane column (DB-17, 30 m \times 0.25 mm \times 0.5 μ m, J&W) and flame ionization detector (GC6850, Agilent Technologies, Inc.). The reaction rates were determined as turnover frequency (TOF), which is defined as the number of moles of product per number of moles of catalyst per hour [20, 21]. The TOF values were calculated based on the amount of catalyst loaded into the reactor and alcohol concentration in the outlet, at an equivalent alcohol conversion of around 15%.



Fig. 1 Schematic of the external loop recycling reactor system.

3-2-5 Residence time distribution measurement in the cold flow model

RTD measurement was carried out by cold flow model tests. A schematic of the experimental apparatus is shown in Fig. 2. The main vessel was made from poly(methyl methacrylate), measuring 130 mm length and 26 mm in diameter, and equipped with a perforated support. 2-propanol and nitrogen were used as liquid and gas models, respectively, at room temperature and atmosphere pressure. The liquid phase was fed by tubing pump (Masterflex, Cole-Parmer, IL, USA). The flow rate was calibrated before experiments and monitored by a flow meter. The gas phase was fed by a mass flow controller (3200, KOJIMA INSTRUMENTS INC., Kyoto, Japan). Disc shaped paper composite (diameter, 26 mm) and ceramic beads were used as packing materials.





Fig. 2 Schematic of the cold flow model. Paper-structured (A) and beaded (B) catalysts.

The RTD functions were obtained *via* absorbance tracer response. A 0.2 ml methylene blue solution (0.02 wt%) was injected into the liquid feed line by a syringe connection port. The tracer response was measured at the reactor outlet using an absorption spectrophotometer equipped with flow cell (U-2910, Flow cell: 290-2173, Hitachi, Ltd., Tokyo, Japan). The spectrum was recorded every 10 seconds at 653 nm, which is the maximum absorption wavelength of methylene blue solution.

3-3 Results and discussion

3-3-1 Characterization of paper and bead catalysts

Ceramic fibers and alumina sol were fabricated into paper-shaped composites by established papermaking technique. The retention value of ceramic fibers and alumina sol reached ca. 100% in a dual polymer flocculation system [14-18]. By calcining at 600°C for 5 h, the paper composites were strengthened by sintering of the alumina sol binder onto the ceramic fiber surfaces. Optical images of the paper-structured composites and catalysts are shown in Fig. 3. These paper-structured composites and catalysts were lightweight and easy to handle, in the form of flexible cardboard with 1.5 mm thickness. XRD measurements indicated that the crystalline structure of the alumina sol binder was gamma-alumina, as shown in Fig. 4, which was the same as alumina bead; therefore the catalyst supports were regarded as being identical for paper-structured and beaded catalysts. The BET surface area of the original ceramic fiber and paper composites after calcination were 14.2 and 29.0 m² g⁻¹, respectively, as listed in Table 1. Gamma-alumina of relatively high surface area (150 m² g⁻¹) was thus deposited onto the ceramic fiber surfaces in the paper-structured composites. The BET surface area of the bead catalyst, which was prepared by the impregnation method via a protocol described in the literature [20], was much larger than that of the paper catalyst due to the smaller amount of gamma-alumina sol. The Ru-free paper composite was composed of alumina fiber and alumina sol with a ratio of 9:1 by weight.



Fig. 3 Optical images of paper-structured catalysts before (left) and after (right) Ru(OH)x synthesis.



Fig. 4 XRD spectra of (a) alumina bead, (b) beaded catalyst with Ru(OH)x, (c) ceramic fiber, (d) alumina sol calcined at 600°C, (e) paper composite calcined at 600°C, (f) paper-structured catalyst with Ru(OH)x. Triangles: gamma-alumina (ICDD no. 10-0425), squares: theta-alumina (ICDD no. 11-0517).

 Table 1 Fundamental characteristics of bead and paper catalysts, and catalytic efficiencies in a non-flow batch reactor.

Sample	Component	Crystalline phase	BET surface area ^[a]	Ru content ^[b]	Ru in reactor ^[c]	TOF ^[d]
			[m ² /g]	[wt%]	[mmol]	$[h^{-1}]$
Bead catalyst			180	0.24	0.045	46
	Alumina bead	Gamma-alumina	165			
Paper catalyst			34.8	0.91	0.045	41
	Paper composite ^[e]	Theta-alumina Gamma-alumina	29.0			
	Alumina fiber	Theta-alumina	14.2			
	Alumina sol	Gamma-alumina	150			

Reaction temperature 358 K; gentle stirring; 100 ml/min oxygen purge; 4.8 mmol benzyl alcohol in 0.5 mol toluene. [a] Brunauer–Emmett–Teller surface area; [b] Ru amount per catalyst; [c] Ru amount in a batch reactor; [d] Turnover frequency value, calculated at *ca*. 13% conversion 20 min after the reaction started; [e] Ru-free paper composite composed of alumina fiber and alumina sol with a ratio of 9:1 by weight.

The direct synthesis of $Ru(OH)_x$ on paper-structured composites was conducted using as-formed gamma-alumina crystals as a scaffold for $Ru(OH)_x$. The synthesis was carried out in two steps. First, paper composites were immersed in an aqueous solution of $RuCl_3$ and the Ru precursor was absorbed onto the fibers. The composites were then dried and immersed again in an aqueous solution of $RuCl_3$ at pH 13. During the second step, $Ru(OH)_x$ crystals grew from the Ru precursors on the paper-structured matrix. In this manner, $Ru(OH)_x$ -containing paper-structured catalysts were obtained. Ru content of paper-structured catalysts was 0.91 wt%, measured by AAS analysis (Table 1). Beaded catalysts that $Ru(OH)_x$ covered the surface layer of the alumina beads with a diameter of 3 mm [20] had the Ru content of 0.24 wt%. No Ru-related crystalline peaks were detected in the XRD profiles because the fine nanoparticles of $Ru(OH)_x$ highly dispersed on the catalyst support exhibited no diffraction as reported [20].

Figure 5 compares the pore size distributions determined by the mercury intrusion method. For the paper-structured catalysts, a clear peak at about 30 μ m was observed, and the porosity reached *ca*. 60%. The micrometer-ordered porous structure of fiber network was also confirmed by SEM image, as displayed in Fig. 6. In contrast, there were no significant peaks greater than 1 μ m for the beaded catalysts and their porosity was less than 20%.



Fig. 5 Pore size distribution curves of paper-structured (squares) and beaded (triangles) catalysts.



100 µm

Fig. 6 SEM image of paper-structured catalysts.

The geometric surface area of the paper composites was calculated using the data from mercury intrusion analysis. Cumulative pore area distribution above 1 μ m was used as the apparent geometric surface area and it was estimated to be about 90,000 m²/m³. The geometric pore area of the beaded catalysts was calculated to be 2,000 m²/m³ from the spherical diameter of 3 mm, because mercury intrusion data showed nearly zero pore area above 1 μ m. The very high values of geometric surface area obtained were reasonable, using the proposed equation [10]:

$$S_V = \frac{4(1-\varepsilon)}{d_f},\tag{1}$$

where S_V is the geometric surface area, ε the porosity, and d_f the characteristic length (fiber diameter). In the case of paper-structured catalysts, the calculated S_v was *ca.* 98,500 m²/m³ while ε was 63% and d_f was about 15 µm.

3-3-2 Catalytic behavior of paper-structured catalysts

The catalytic behavior of paper-structured catalysts was evaluated by the alcohol oxidation performance in the fixed bed reactor, as shown in Fig. 1. Aromatic and aliphatic alcohols were used for the catalytic reaction test. These alcohols were converted to their corresponding aldehydes and ketones *via* stoichiometric oxidation reaction and almost no by-products were detected by GC analysis. The reaction rates and efficiency were determined as TOF values and total conversion ratio. The results are listed in Table 2. In the case of benzyl alcohol and derivatives, a TOF representing a 12.75% yield of benzaldehyde (equivalent to

12.75% alcohol conversion with an initial feed of 5.6 mmol) on the 0.105 mmol Ru species for 0.03 h was estimated to be 224 h⁻¹. The TOF values around 200 obtained from benzyl group alcohols were comparable to powder catalysts tested in a batch reaction [20]. A high TOF value, indicating efficient reactivity, was achieved in a fixed bed reaction by $Ru(OH)_x$ containing paper-structured catalysts. The TOF values for aliphatic alcohols were lower than those of benzyl groups, as previously reported [20].

Entry	Substrate	Product	Conversion	Time	TOF ^[a]
			[%]	[h]	[h ⁻¹]
1	Benzyl alcohol	Benzaldehyde	>99	2	223
2	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	>99	2	192
3	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	>99	2	185
4	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	>99	2	207
5	1-Octanol	1-Octanal	50	6	44
6	2-Octanol	2-Octanal	65	6	76

Table 2 Catalytic conversion behavior of various alcohols over paper-structured catalysts.

Reaction temperature 358 K; liquid flow rate 10 ml/min; gas flow rate 100 ml/min. [a]

Turnover frequency value.

3-3-3 Residence time distribution analysis

To characterize the hydrodynamic behavior of the porous paper-structured catalysts, RTD studies were carried out by tracer measurement in a cold flow model, as illustrated in Fig. 2. Numerous RTD studies have been carried out for industrial fixed bed reactors, such as trickle beds [22] and monoliths [23]. In terms of fibrous catalytic materials, woven mesh structures [24], ceramics and metal forms have been investigated [25–27]. However, relationships between catalytic behavior and hydrodynamics have not been investigated for structured catalysts having micrometer-ordered pores originating from a fiber network. Although RTD measurements have been performed using water as a liquid phase and KCl solution as an electrolyte tracer in almost all of this prior work, 2-propanol (20.8 mN/m) was used as a liquid phase in this study to minimize surface tension compared with water (72.8 mN/m).

The RTD function E(t), was determined by experimental methods using a nonreactive tracer. From the measured concentration distribution of the tracer C(t), we can derive the following well-known equation for a pulse tracer input (2):

$$E(t) = \frac{C_t(t)}{\int_0^\infty C_t(t)dt}.$$
 (2)

The step-change RTD function F(t) is obtained as follows:

$$F(t) = \int_0^t E(t)dt \,. \tag{3}$$

Experiments were performed at a liquid feed flow rate of 10 ml/min and three different gas feed flow rates of 10, 30 and 60 ml/min. To exclude the effect of tracer absorption and desorption, packing materials were treated once by tracer solution before measurement (to

saturate the surfaces with any minor, non-specific adsorption of the tracer). The RTD curves of paper composites and ceramic beads are shown in Fig. 7. For the paper composites, RTD curves were uniformly distributed over time and similar for the three gas flow rates. Conversely, the ceramic beads showed early peaks in the RTD curves, with asymmetric tailing. For the gas feed flow rates, slight differences in the peaks were observed, whereby increasing the gas flow rates narrowed the dispersion in the RTD profiles, thus decreasing the axial diffusion in the liquid phase.



Fig. 7 Effect of gas flow rate on residence time distribution, paper-structured composites (A) and ceramic beads (B).

The mean residence time t_m and the variance σ^2 are given by equations (4) and (5):

$$t_m = \int_0^\infty t E(t) dt \tag{4}$$

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t) dt \,. \tag{5}$$

The liquid-phase Peclet number (*Pe*) was obtained by matching the variance of the RTD curve to the axial dispersion model with closed boundary conditions [28]:

$$\sigma^{2} = \frac{2}{Pe} - \frac{2}{Pe^{2}} \left(1 - e^{-Pe} \right).$$
 (6)

Figure 8 compares the mean residence time and Peclet numbers of paper composites and ceramic beads. Mean residence time is an important value for the characterization of a flow-type chemical reactor. In the case where unintentional dead volumes exists, mean residence time is clearly smaller than the theoretical value. There were large differences between paper-structured composites and ceramic beads. For the paper-structured composite, the gas feed rate did not influence the mean residence time, whereas the mean residence time decreased with increasing gas flow rate in the case of ceramic beads. The Peclet number was obtained as follows:

$$Pe = \frac{u_L L}{D},\tag{7}$$

where L is the characteristic length, u_L the liquid superficial velocity, and D is the mass diffusion coefficient. Peclet number describes the ratio between transport by convection and that by diffusion. A higher Peclet number indicates a reduced effect of diffusion on transport. For the ceramic beads, the Peclet number of the liquid phases increased with increasing gas flow rate. In contrast, little effect was observed with the paper composites. From the trends of both mean residence time and Peclet number, ceramic beads showed the typical pattern of liquid-phase maldistribution and by-pass flow. Paper-structured composites, in contrast, possessed good liquid wettability and smooth diffusion compared with ceramic beads because the porous fiber network contributed to uniform gas/liquid flows.



Fig. 8 Mean residence time (A) and Peclet number (B) of paper-structured composites (squares) and ceramic beads (triangles).

3-3-4 Alcohol oxidation behavior

Microstructure-dependent catalytic reactions were investigated in detail by comparing the catalytic efficiencies of paper-structured and beaded catalysts, respectively, with or without micrometer-size pores. Table 1 shows similar TOF values of benzyl alcohol oxidation by each catalyst in a non-flow batch system, in which the same Ru amounts (0.045 mmol) were supplied. Thus, there was nearly no difference in the catalytic efficiency found in the non-flow system. Both reactions proceeded with low efficiency, possibly due to the poor diffusion of oxygen to the reaction medium in a flask, resulting in the heterogeneous gas–liquid mixed flow. The microstructures of catalyst supports had no contribution to the catalytic reaction at a steady state.

Figure 9 demonstrates the time-course conversion profiles of benzyl alcohol during the

oxidation reaction in a flow system with Ru(OH)_x containing paper-structured catalysts and bead catalysts, for gas feed flow rates of 10 to 100 ml/min in the fixed bed reactor. For paper-structured catalysts, a higher flow rate of gas markedly induced a higher oxidation efficiency for benzyl alcohol. In contrast, bead catalysts were less affected by the gas feed flow rate. Figure 10 compares the TOF values of paper and pellets. The TOF values for paper-structured catalysts distinctly increased with increasing gas feed rate, while those of beaded catalysts remained almost constant. In comparison with bead catalysts, paper-structured catalysts showed more than four times higher TOF values at a gas feed flow rate of 100 ml/min. Table 3 compares the TOF values of various liquid-phase alcohol oxidations in fixed-bed reactors. Paper-structured catalysts showed efficient catalytic activity, unlike conventional column reactors and microreactors.



Fig. 9 Effect of gas flow rate on alcohol conversion over paper-structured (A) and beaded (B) catalysts.



Fig. 10 Comparison of TOF values for paper-structured (squares) and beaded (triangles) catalysts.

Entry	Catalysts	Supportin Materials	ng materials Shape	Reactor type	T ^[a] [K]	P ^[b] [atm]	Flow rate Liquid [ml/min]	e Gas [ml/min]	$TOF^{[c]}$ $[h^{-1}]$	Ref.
1	Pt	Carbon	Monoliths	Column reactor (23 mm i.d.)	383	12	1.7	82	16	[29]
2	Ru	Al ₂ O ₃	Powder	Micro reactor $(3 \times 3 \text{ mm})$	388	8	2	20	270	[30]
3	Fe ₂ O ₃ NPs ^{[d}	Al/Si ^[e]	Powder	Micro reactor (4 mm i.d.)	393	35	0.2	5	14	[7]
4	Ru	HAp ^[f]	Powder (MFEC)	Column reactor (30 mm i.d.)	303	1	1	-	N.A.	[31]
5	Ru	Al ₂ O ₃	Powder	Micro reactor $(3 \times 3 \text{ mm})$	363	25	1	N.A.	97	[32]
6	Ru	Al ₂ O ₃	Wet laid paper	Column reactor (23 mm i.d.)	358	1	10	100	223	This work

Table 3 Recent studies on the liquid-phase aerobic alcohol oxidation in fixed-bed reactors.

[a] Reaction temperature; [b] Reaction pressure; [c] Turnover frequency; [d] Fe₂O₃ nano-particles; [e] Aluminosilicate; [f] Hydroxyapatite.

To understand such unique phenomena, liquid film thicknesses on the catalyst surfaces were calculated. From the RTD measurement data, the total liquid holdup in the catalyst bed can be determined according to the following equation:

$$\varepsilon_L = \frac{u_L t_m}{L},\tag{8}$$

where, ε_L is the liquid holdup and u_L is the superficial velocity. Under the assumption that the static liquid holdup spreads over the entire specific surface area, the apparent thickness of the

liquid film can be obtained as follows [25]:

$$e = \frac{\varepsilon_L}{S_V},\tag{9}$$

where, e is the liquid film thickness and S_v is the geometric surface area. Figure 11 compares the liquid hold ups and the liquid film thicknesses of two catalysts, paper and beads, at various gas feed flow rates. The liquid film thicknesses of the paper-structured catalysts were one order of magnitude smaller than those of the beaded catalysts. These trends in liquid film thickness may explain the differences observed in catalytic reactivity between the paper-structured and beaded catalysts.



Fig. 11 Effect of the gas flow rate on liquid hold up (A) and liquid film thickness (B) of paper-structured composites (squares) and ceramic beads (triangles).

Generally, the gas velocity has a positive effect on the catalyst wetting efficiency under the trickle flow regime at a fixed liquid velocity, because the liquid film thickness decreases with gas velocity through spreading of the liquid phase over the external catalyst surface area [33, 34]. From a practical viewpoint, complete wetting of the liquid phase is not achieved at lower gas flow rates under general reaction conditions. Therefore, an increased gas velocity possibly affected the thinning of the liquid film.

Other reports on micrometer-ordered reactors concluded that the liquid-side mass transfer coefficient increases with an increase in the superficial gas velocities for a fixed superficial liquid velocity [35]. The annular flow determining the gas-liquid interfacial mass transfer in microchannels may be significantly different from similar processes in large channels. In this study, paper-structured catalysts possessing a micrometer-ordered pore structure exhibited similar results, probably because the increased relative gas velocity at liquid surface has a positive effect on mass transfer in the liquid phase, *via* turbulence and convective flow within the paper-structured catalysts.

3-4 Conclusions

Paper-structured $Ru(OH)_x$ catalysts with a ceramic fiber network were prepared by a wet papermaking technique. As-prepared paper catalysts possessed a porous micrometer-ordered structure and large geometric surface areas. The paper-structured catalysts exhibited high catalytic efficiency for selective aerobic oxidation of various aromatic and aliphatic alcohols to their corresponding aldehydes and ketones, in a fixed-bed, multiphase reactor. Residence time distribution measurement in a cold flow model showed superior liquid wettability and axial diffusion effects in paper-structured catalysts, compared with ceramic beads. Catalytic reactivity is expected to be associated with the hydrodynamic behavior for uniform liquid diffusion into the paper-structured catalyst surface, attributed to the formation of a thin liquid film layer, resulting in efficient oxidation at the multiphase gas-liquid-solid interface.

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Solvent-free alcohol oxidation via paper-structured catalysts: Flow dynamics and reaction kinetics

Abstract

Pd-containing paper-structured catalysts with micrometer-size pores have been prepared by a high-speed and low-cost papermaking technique. The paper-structured catalysts showed high catalytic activity and selectivity for solvent-free benzyl alcohol oxidation in a microfluidic reaction system, and in a fixed-bed gas–liquid–solid multiphase reactor. Kinetic and mechanistic studies of various reaction conditions revealed that the catalytic reactivity and selectivity were associated with the microfluidics in the paper-structured networks. Uniform distribution of liquid phase gave high reactivity, and the high selectivity of the oxidation pathways was ascribed to efficient gas–liquid–solid mass transfer within the thin liquid layer interface over the fiber networks.



4-1 Introduction

The oxidation of alcohols to their corresponding ketones, aldehydes and carboxylic acids is one of the most important transformations in organic synthesis. In addition, oxidation will likely play an important role in the development of value-added chemicals from natural feedstocks. Several classes of alcohols including monoalcohols, polyols and 5-hydroxymethylfurfural (HMF) have been successfully obtained from natural plants. Primary monoalcohols such as ethanol, octanol, benzyl alcohol and cinnamyl alcohol have been used as key intermediates in the chemical and pharmaceutical industries. Fatty alcohols, i.e., monohydric aliphatic alcohols of six or more carbon atoms, are widely used in many commodities. In addition to these common alcohols, HMF, polyol glycerol and glucose have received attention as green raw materials. Oxidation of these alcohols can give functional materials from biomass to replace petroleum as the main source of chemicals [1-3]. From a Green Chemistry viewpoint, alcohol oxidation should be conducted at relatively low temperature in the liquid phase, using a less toxic solvent or solvent free conditions, and the use of a cleaner oxidant, such as O₂, instead of metal oxidants [4]. However, this brings significant challenges in processing, such as the risk of hydrocarbon-oxygen explosions, the need for careful control of the reaction, and improvements in mass transfer limitations in multiphase interphases [5].

Selectivity is another key issue in alcohol oxidations. Preventing over-oxidation of the products is a tremendous challenge, as they are often more sensitive to be oxidation than the reactants [6]. Partial oxidations are therefore a scientific challenge with direct industrial

relevance. Optimizing the selectivity should be the most important goal and preventing the formation of waste should be the key objective for sustainable chemistry [7]. The oxidation of a primary alcohol proceeds first to an aldehyde and subsequently to a carboxylic acid. The oxidation of an alcohol to an aldehyde over a heterogeneous metal catalyst likely occurs in three steps. First, the alcohol is absorbed on the metal surface, producing an absorbed metal alkoxide. Second, β -hydride elimination occurs to produce a carbonyl species and a metal hydride. Finally, the metal hydride is further oxidized by dioxygen to regenerate the metal surface [1]. For the liquid phase oxidation of alcohol, the reaction rate is limited by oxygen transfer to the catalyst surface. Oxygen is typically introduced into the liquid through air bubbles. Since oxidation reactions occur in the liquid phase, either in the bulk liquid phase or in the thin liquid film which surrounds a solid catalyst, adequate mass transfer of oxygen is critical because the solubility of oxygen in organic compounds is low [8].

There are many, intricate problems in applying multiphase catalytic reactions. The reaction rate is dependent on the slowest step of all the processes, such as mass transfer from the bulk liquid to the liquid-solid interface, gas diffusion into the liquid layer, or reactivity on the surface of the solid catalysts. In these cases, the results, especially selectivity, cannot be controlled by the reaction parameters, for example, by controlling the reaction temperature and starting concentrations of reactants. To solve these problems, microstructured reactors (MSR) or microfluidic reactions show promise as a solution. MSR are defined as reactors with small dimensions, at a micrometer scale, and they have the potential to save both cost and time in process development [9]. The small dimensions of MSR enhance the diffusion speed of both

heat and molecules. Furthermore, the high surface to volume ratios of MSR greatly improve mass and heat transfer performance [10]. Because of the outflow of products, over reactions must be avoided, and pseudo-stoichiometric catalysts and substrate conditions in a continuous flow can increase the reactivity and selectivity [11]. The selectivity in a chemical processes is often determined by reaction kinetics. However, for fast reactions conducted in batch reactors, theoretical kinetics do not always hold, because of local deviations in concentration due to inefficient mixing. Therefore, such reactions cannot be controlled well in batch reactors. When a reaction is conducted in a microreactor, the kinetic regime can be obtained in shorter reaction times because of the fast mass transfer, and therefore kinetic based selectivity is obtained, and less waste is produced [12, 13]. Besides the kinetic parameters, the mean residence time and residence time distribution (RTD) in the reactor strongly influence the product yield and selectivity. To get a maximal yield of an intermediate product for consecutive reactions, the RTD in the reactor should be narrow. The abovementioned short diffusion time of MSR is expected to achieve a narrow RTD. Isothermal conditions combined with short residence time and narrow RTD are the main purpose of using MSR [14].

Fibrous catalysts have been categorized as microstructured catalysts based on fibers, which allow high catalytic effectiveness and a low pressure drop. Beneficial aspects for catalytic applications include the high surface to volume ratio and the high void fractions offered by these characteristic structures. Fibrous catalysts are often described as having good mass transfer; however, few papers covering fluidic properties have been reported [15, 16]. In previous studies, fibrous catalysts made of inexpensive ceramic fibers were developed by a
high-speed and low-cost papermaking technique. As-prepared wet laid structures, termed paper-structured catalysts, are easy to fabricate, easy to handle, possess micrometer-size pores, and show excellent performance both in gas and liquid phase reactions [17–20]. Ruthenium hydroxide (Ru(OH)_x) was synthesized on the alumina/silica fiber surfaces of paper composites, and provided the selective oxidation of benzyl alcohol to benzaldehyde in a fixed-bed gas-liquid-solid multiphase reactor [21]. RTD measurement in a cold flow model showed superior liquid wettability and axial diffusion in these catalysts. High catalytic reactivity is possibly associated with the uniform microfluidic flow in the paper-structured catalysts [22]; however, there remain some theoretical issues. In this study, palladium catalyst species were synthesized onto the alumina/silica fibers by established papermaking technique, and applied to the aerobic oxidation of benzyl alcohol under solvent free conditions. The relationship between microfluidic behavior and reaction selectivity has been investigated by comparing various reaction conditions.

4-2 Experimental

4-2-1 Materials

Ceramic fibers (B80L, Al₂O₃: 80% and SiO₂: 20%, Denki Kagaku Kogyo Kabushiki Kaisha, Tokyo, Japan) were cut to an average length of 0.5 mm. An alumina sol (520, Nissan Chemical Industries Ltd., Tokyo, Japan) was used as an inorganic binder to improve the physical strength of the papers, and to load the catalyst species onto the sol components. Two types of polymer flocculants were used as retention aids; cationic polydiallyldimethylammonium chloride (PDADMAC; molecular weight: ca. 3×10^5 , charge density: 5.5 meq. g⁻¹, Sigma-Aldrich Co., Ltd., St Louis, MO, USA) and anionic polyacrylamide (A-PAM; A125S, molecular weight: ca. 1×10^7 , charge density: 3.2 meq. g⁻¹, MT Aquapolymer Inc., Tokyo, Japan). Pulp fibers were obtained by beating commercial bleached hardwood kraft pulp into 300 ml of Canadian Standard Freeness with a Technical Association of Pulp and Paper Industry (TAPPI) standard beater (2505, Kumagai Riki Kogyo Co., Ltd., Tokyo, Japan). Commercial ceramic beads (KHS-24, Sumitomo Chemical Co., Ltd., Tokyo, Japan) were used as catalyst supports. Pd catalysts in a beaded form were prepared as described in the literature [23]. Other chemicals were reagent grade and used without further purification.

4-2-2 Catalyst preparation

Paper-structured catalysts were fabricated by a wet papermaking process as described previously [17–22]. An outline of the papermaking procedure can be summarized as follows. A water suspension of ceramic fibers was mixed with PDADMAC (0.5 wt% of total solid), alumina sol, A-PAM (0.5 wt% of total solid) and pulp fibers (0.25 g of total solid) in that order, with 3-min intervals between each step. The mixture was then solidified by dewatering using a 200-mesh wire. The wet-state sheet was pressed at 350 kPa and dried at 105°C. The obtained sheet ($2 \times 10^4 \text{ mm}^2$) consisted of ceramic fibers (5.0 g), alumina sol (2.8 g) and pulp fibers (0.25 g). The sheets were cut into disk shaped pieces and calcined at 600°C for 5 h to remove organic compounds and to improve their physical strength by binder sintering.

The on-paper synthesis of the Pd catalysts on the paper-structured matrix was carried out as follows. First, the paper composite disks (diameter: 23 mm) were immersed in an aqueous solution of palladium chloride (PdCl₂; 9.4 mM, 50 mL) at 80°C under reduced pressure, and the solution pH was adjusted to 3 by the addition of an aqueous solution of hydrochloric acid (1.0 M). The disks were washed with deionized water, dried at 105°C for 1 h, and calcined at 400°C for 5 h under a nitrogen atmosphere [23].

4-2-3 Catalyst characterization

The specific surface areas of the catalysts were obtained from nitrogen absorption-desorption isotherms (Belsorp-mini, BEL Japan Inc., Osaka, Japan) and calculated by the Brunauer-Emmett-Teller (BET) method. Pore distribution analysis was carried out by mercury intrusion (Autopore IV 9500, Micromeritics Instrument Corp., Norcross, GA, USA). Pore size distributions were obtained from a pressure-cumulative mercury intrusion volume curve normalized by catalyst weight. The Pd content was determined by inductively coupled plasma optical emission spectrometer (ICP-OES; 720-ES, Agilent Technologies Inc., Santa Clara, CA, USA). Surface observation of the paper-structured catalysts was performed by scanning electron microscopy (SEM; JSM-6510, JEOL Ltd., Tokyo, Japan), and elemental mapping was obtained by energy dispersive X-ray spectrometry (EDS). Samples for scanning transmission electron microscopy (STEM; HD-2700, Hitachi High-Technologies Corp., Tokyo, Japan) were prepared before analysis by grinding the catalyst with an ion beam. Catalysts were nipped between silicon wafers with epoxy resin (G2, Gatan Inc., Pleasanton, CA, USA), then cured for 30 min at 120°C and polished by ion thinner (691 PIPS, Gatan Inc., Pleasanton, CA, USA). The samples were then subjected to an acceleration voltage of 200 kV. The chemical states of the catalyst components were analyzed by X-ray photoelectron spectroscopy (XPS; AXIS HSi spectrometer, Krato, Ltd., Manchester, UK). The XPS spectra were obtained using a monochromatic Al $K\alpha$ X-ray source (1486.6 eV) at 12 kV and 10 mA. The pass energy and step width in the photoelectron detection were set at 20 eV and 0.05 eV, respectively. Resulting spectra were calibrated to the C1s band at 285.0 eV.

4-2-4 Alcohol oxidation

Solvent-free benzyl alcohol oxidation was conducted using a fixed-bed external loop recycling reactor at atmosphere pressure [21, 22]. A schematic of the fixed bed reactor used in this study is illustrated in Fig. 1. Twenty disk-shaped paper-structured catalysts were stacked vertically (12.5 mm³) and placed on a perforated support in a stainless steel reactor vessel (23 mm inner diameter and 75 mm in height). In a similar manner, the catalyst beads were packed into the vessel, and then adjusted to a consistent total volume of 12.5 mm³. A liquid phase of benzyl alcohol (0.83 mol) was supplied by a pump (Hi-Cera Pump V, IWAKI Co., Ltd., Tokyo, Japan). Either oxygen, air or nitrogen was fed into the reactor by a mass flow controller (3200, Kojima Instruments INC., Kyoto, Japan). The reactor tube and supply pipes were heated to the reaction temperature by mantle and ribbon heaters, respectively. The supplied reactants after passing through the catalyst layers were returned to a gas/liquid separator. The gas phases were discharged from the system, and the liquid phases consisting of mixtures of substrate and

products were recycled. Feed flow rates of liquid and gas were set at 10-30 ml/min (liquid hourly space velocity: 48–144 h⁻¹), and 10–100 ml/min (gas hourly space velocity: 48–481 h^{-1}), respectively. The catalytic conversion of the alcohol and product selectivity were analyzed periodically by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) by sampling small aliquots from the outlet of the reactor. GC analysis was performed using a dimethylpolysiloxane column (DB-17ht, 30 m \times 0.25 mm \times 0.5 μ m, J&W Agilent Technologies Inc., Santa Clara, CA, USA) and flame ionization detector (GC6850, Agilent Technologies Inc., Santa Clara, CA, USA). GC/MS analysis was performed using a mass spectrometer detector (GC7890A with 5975C inert XLMSD, Agilent Technologies Inc., Santa Clara, CA, USA). The reactivity of each reaction was determined as a turnover frequency (TOF) and reaction selectivity. The TOF is defined as the number of moles of products per number of moles of catalyst per hour [23]. The TOF values were calculated based on the amount of catalyst loaded in the reactor and alcohol concentration in the outlet, at 30 min on-stream, as an equivalent alcohol conversion less than 10 %.



Fig. 1 Schematic of the external recycling loop reactor system.

4-3 Results and discussion

4-3-1 Characteristics of Pd/Al₂O₃ paper-structured catalysts

Paper-structured catalysts were prepared by a three-step fabrication process. First, the paper-structured composites were made by established low-cost and high-speed papermaking technique. Second, by calcining at 600 °C for 5 h, the paper composites were strengthened by sintering the alumina sol binder onto the ceramic fiber surfaces. This sintering process changes the crystalline structure of the alumina sol binder from boehmite to gamma-alumina. Finally, the direct synthesis of Pd-species on the paper-structured composites was performed using the gamma-alumina as a scaffold for the Pd-species [17–22]. The process for making the paper-structured catalysts is very simple and can be easily scaled up, compared with the manufacture of other microstructured catalysts or MSR. The BET surface areas of the original

ceramic fiber and paper-structured composites after calcination were 14.2 and 79.1 m² g⁻¹ respectively, as listed in Table 1. Gamma-alumina of high surface area was deposited onto the ceramic fiber surfaces in the paper-structured composite at a ratio of 35% by weight. The BET surface area of the bead catalysts was much larger than that of the paper-structured catalysts owing to the larger amount of gamma-alumina in the composition.

Sample	Component	Crystalline phase	BET surface area ^[a]	Pd content ^[b]	Pd in reactor ^[c]
			$[m^2 g^{-1}]$	[wt%]	[mmol]
Bead catalyst			180	1.5	1.13
	Alumina bead	Gamma-alumina	165		
Paper catalyst			80.5	0.49	0.19
	Paper composite ^[d]	Theta-alumina Gamma-alumina	79.1		
	Alumina fiber	Theta-alumina	14.2		
	Alumina sol	Gamma-alumina	150		

 Table 1 Fundamental characteristics of the bead and paper catalysts.

[a] Brunauer–Emmett–Teller surface area; [b] Pd amount per catalyst; [c] Pd amount in a batch reactor; [d] Pd-free paper composite composed of alumina fiber and alumina sol with a ratio of 65:35 by weight.

Optical images of the paper-structured catalysts and bead catalysts are shown in Fig. 2. These paper-structured materials were like cardboard, lightweight, flexible with 1.5 mm thickness, and easy to handle in practical uses. The paper-structured composites changed from white to yellow owing to the on-paper synthesis of Pd-species, which was also seen with the bead catalysts. ICP-OES analysis indicated that the Pd content of the paper-structured catalysts was 0.49 % by weight. Bead catalysts were prepared by the conventional impregnation method, as described in the literature [23–25]. The Pd content of the 3 mm diameter bead catalysts was 1.5 % by weight.







(c)





(d-1) Before reaction

(d-2) After reaction



Fig. 2 Optical images of the catalysts.

(a) Paper-structured composite, (b) Pd-containing paper catalyst, (c) alumina beads,

and (d) Pd-containing bead catalysts.

Fig. 3 profiles the pore size distribution as determined by the mercury intrusion method. Paper-structured catalysts possessed a sharp peak at about 30 μ m, while there was no significant peak greater than 1 μ m in the bead catalysts. The micrometer-ordered porous structure of the fiber network was also confirmed by SEM and EDS analysis, as shown in Fig. 4. EDS mapping displayed a uniform distribution of Pd-species on the paper-structured network. Fig. 5 shows the STEM image of the paper-structured catalysts. Very small Pd particles were dispersed in the gamma-alumina support with the diameter of several tens of nanometers.



Fig. 3 Pore size distribution curves for the paper catalysts (square) and bead type catalysts (triangle).



Fig. 4 SEM and EDX mapping images of the Pd-containing paper catalyst.

(a) SEM image (b) EDX mapping of Al, and (c) EDS mapping of Pd.



100 nm

Fig. 5 STEM image of the Pd catalyst.

4-3-2 Solvent-free aerobic oxidation of benzyl alcohol

Among the alcohols, benzyl alcohol is one of the most studied examples for the selective oxidation to aldehydes. Benzyl alcohol undergoes a variety of reactions depending on the reaction conditions and the type of catalyst. Selectivity and the catalytic mechanism must be understood to assist catalyst design and fine-tuning. To achieve high selectivity in a particular reaction, it is important to understand all the parallel and consecutive reaction pathways. The reaction pathways of benzyl alcohol oxidations and the standard enthalpy of the formation of products from benzyl alcohol are shown in Fig. 6 [26]. Oxidation of benzyl alcohol (1) leads to benzaldehyde (2), benzoic acid (3) and benzyl benzoate (4). Side reactions such as disproportionation to form toluene (5), benzaldehyde and H₂O have been observed. Dehydration to form dibenzyl ether (6) and self-condensation to form anthracene and stilbene may occur. These reactions are active only under particular reaction conditions, for example, the disproportionation reaction is feasible because of the slightly negative overall enthalpy of the reaction. Anthracene and stilbene are found at high temperatures in the gas phase. In contrast, at low temperatures, the liquid phase oxidation of benzyl alcohol, many products including benzoic acid, benzyl benzoate, dibenzyl ether and toluene were formed although the main product was benzaldehyde. Benzaldehyde is formed by the oxidation of benzyl alcohol in the presence of an oxidant. Benzyl benzoate is formed either by the reaction between benzoic acid and benzyl alcohol or by the oxidation of a hemiacetal intermediate (7). Benzaldehyde dibenzyl acetal (8) was possibly formed by the dehydration reaction between a hemiacetal and benzyl alcohol [27, 28, 29, 30]. Fig. 7 (A) shows the time-course reaction profiles of the benzyl alcohol oxidation using paper-structured catalysts. The reaction was conducted at 373 K, 20 ml/min liquid and 100 ml/min gas feed flow rate. Benzyl alcohol was converted to benzaldehyde and toluene immediately, and the amount of undesirable products formed by side reactions increased with time. The major product of the benzyl alcohol oxidation was benzaldehyde and toluene in an equilibrium amount. Benzaldehyde can be

formed by two reaction pathways; one is by oxidation and another is through the disproportionation of benzyl alcohol. Fig. 8 shows the XPS spectra of Pd 3d region of paper-structured catalysts as prepared, and after the reaction. For the as-prepared catalysts, the peaks of binding energy were observed at 337.4 eV and 343.0 eV, corresponding to Pd²⁺ 3d_{5/2} and $Pd^{2+} 3d_{3/2}$. For the catalysts after the oxidation reaction of benzyl alcohol, the peaks of binding energy at 335.8 eV and 340.9 eV were assigned to $3d_{5/2}$ and $3d_{3/2}$ orbitals of metallic Pd⁰. Thus, the changes in the valance state of palladium species in the paper-structured catalysts occurred during the oxidation of benzyl alcohol. Optical images of the paper-structured catalyst and bead catalysts also showed a color change due to the palladium (Fig. 2, b-2 and d-2). These phenomena have been investigated previously [23]. The initial reduction of palladium oxides can only be caused by adsorbed benzyl alcohol. The most reasonable explanation is that β -C–H bond in the benzyl alkoxide breaks at the palladium sites and this active hydrogen subsequently reduces palladium oxide. Meanwhile, the benzaldehyde is released from the catalyst surface into the liquid phase as an oxidized product. After the Pd-species are reduced, the oxidation of benzyl alcohol will continue via the classical three-step oxidation pathways: (1) the alcohol absorbs onto the metal surface, producing an absorbed metal alkoxide; (2) β-hydride elimination to produce a carbonyl species and a metal hydride; and (3) the metal hydride is further oxidized by dioxygen to regenerate the metal surface [1, 26, 31].



Fig. 6 Reaction pathways of the benzyl alcohol oxidation.



Fig. 7 Catalytic behavior during the benzyl alcohol oxidation.

(A) Paper-structured catalysts, (B) bead catalysts, (1) benzyl alcohol, solid circles; (2) benzaldehyde, open circles; (3) benzoic acid, open diamonds; (4) benzyl benzoate, solid diamonds; (5) toluene, solid triangles; (6) dibenzyl ether, solid squares; and (8) benzaldehyde dibenzyl acetal, solid triangles.



Fig. 8 XPS spectra of the paper-structured catalyst (a) as prepared, and (b) after the oxidation reaction.

4-3-3 Kinetics study on microfluidic reaction

Microstructure-dependent gas-liquid-solid multiphase catalytic reactions, named microfluidic reactions, were investigated in detail by comparing the catalytic efficiencies and selectivity using paper-structured catalysts, with bead catalysts without micrometer-size pores, as shown in Fig. 3. Fig. 7 compares the time-course conversion profiles of benzyl alcohol oxidation with Pd-containing paper-structured catalysts with the bead catalysts. As mentioned above, benzyl alcohol was oxidized to benzaldehyde, while at the same time, disproportionation occurred to form toluene and benzaldehyde, and other side reactions might proceed. Compared with the paper-structured catalysts, bead catalysts showed slow alcohol

conversion rates and the formation of benzaldehyde dibenzyl acetal (8) in larger quantity. Table 2 and Fig. 9 compare the differences in the catalytic oxidation behaviors. Conversion, selectivity and by-product ratio (**BP**) have been defined as follows:

$$Conversion = (1 - [Residual alcohol] / [Initial Alcohol]) \times 100 [\%]$$
(1)

$$Selectivity = (Aldehyde yield) / (Conversion) \times 100 [\%]$$
⁽²⁾

By-products ratio

= (Dibenzyl ether yield + Benzaldehyde dibenzyl acetal yield) / (Conversion) × 100 [%]

(3)

The residual alcohol and yield of each product were described as weight %, as determined by GC analysis. TOF values of the paper-structured catalysts were 10 times higher than that of the bead catalysts. For the paper-structured catalysts, increasing the gas feed flow rate increased the TOF values, conversion and selectivity. By contrast, bead catalysts were less affected by the gas feed flow rate. These phenomena were found in my previous studies, which reported a correlation between alcohol oxidation reactivity in a dilute solution [21] and hydrodynamic behavior in a cold flow model [22]. Efficient catalytic reactivity was possibly associated with the microfluidic behavior giving a uniform liquid diffusion onto the paper-structured catalyst surface, to form a thin liquid film layer about 10 µm in thickness [22]. The rate-limiting step in the alcohol oxidation is the oxygen transfer to the catalysts surface [8]. The oxygen transfer rate is generally a function of the diffusivity of the gas in the liquid and renewal rates of the liquid phase. As a consequence, it is strongly dependent on the thickness of liquid film and the degree of turbulence occurring in the reactor [32]. The thin liquid layer over the

micrometer-sized porous paper microstructure possibly promotes efficient oxygen transfer. Experimental studies of the microchannels have also showed that the liquid-side mass transfer coefficient increases with an increase in the superficial gas velocities for a fixed superficial liquid velocity [33]. Relativity differences between gas and liquid velocities lead to some turbulence in the thin liquid film, and this has a positive effect on the mass transfer. In this study, highly efficient oxidation of benzyl alcohol was also achieved, even in solvent-free conditions, via paper-structured catalysts.



Fig. 9 Effect of the gas flow rate on reactivity.

(A) TOF values^a, (B) conversion^b (triangles), selectivity^c (squares), and by-products ratio^d (diamonds) for the paper-structured catalysts (hollow) and beads catalysts (solid).
[a] Turnover frequency, (1 – [Residual alcohol] / [Initial Alcohol]) × 100, [c] (Benzaldehyde yield) / (Conversion), [d] (Dibenzyl ether yield + Benzaldehyde dibenzyl acetal) / (Conversion)

[b], [c], [d] values were calculated from the values at 4 h on stream, Reaction conditions; temperature 373 K, liquid flow rate 20 ml/min.

Entry	Catalysts shape	Reaction con	ditions	Flow rate		$\mathrm{TOF}^{\mathrm{b}}$	Conversion ^c	Selectivity ^d	BP^{e}
		T^{a}	Gas species	Liquid	Gas				
		[K]		[ml/min]	[ml/min]	[h ⁻¹]	[%]	[%]	[%]
1	Paper	373	O_2	20	100	2275	45	72	3
5		373	O_2	20	40	2291	31	68	9
3		373	O_2	20	20	1733	28	59	6
4		373	N_2	20	100	571	L	43	16
5		373	Air	20	100	1671	28	57	8
9		343	O_2	10	100	329	17	64	14
7		353	O_2	10	100	1900	51	72	2
8		363	O_2	10	100	1745	49	67	3
6		373	O_2	10	100	1402	49	59	С
10		383	0_2	10	100	3609	48	59	9
11	Beads	373	O_2	20	100	161	19	09	14
12		373	O_2	20	20	150	23	55	8
13		373	N_2	20	100	55	3	39	33
14		353	O_2	10	100	82	11	47	20
15		363	O_2	10	100	136	17	54	16
16		373	O_2	10	100	138	14	57	15
				- - : :		-	001		

Table 2 Catalytic oxidation behaviors in various conditions.

[a] Reaction temperature, [b] Turnover frequency, [c] (1 – [Residual alcohol] / [Initial alcohol]) × 100
[d] (Aldehyde yield) / (Conversion) × 100, [e] (Dibenzyl ether yield + Benzaldehyde dibenzyl acetal yield) / (Conversion) × 100
[b], [c], [d] values were calculated by the values at 4 h on stream

In addition to the reactivity, reaction selectivity was studied. Reaction pathways of benzyl alcohol oxidation shown in Fig. 6 can be divided to two parts, one is a pathway requiring oxygen and, another does not. The pathways that require no oxygen are shown in Fig. 10. Only three pathways are available without oxygen, disproportionation to form benzaldehyde and toluene, dehydration to form dibenzyl ether (6), and the dehydration reaction between a hemiacetal and benzyl alcohol to form benzaldehyde dibenzyl acetal (8). Benzyl hemiacetal (7) is unstable and immediately reacts with benzyl alcohol, and was not detected by GC and GC-MS analysis in this study. These two remaining products, dibenzyl ether (6) and benzaldehyde dibenzyl acetal (8), were classified as by-products (BP). When reactions were conducted under a nitrogen atmosphere (Table 2 entry 4 and 14), conversions and TOF values became low, and BP increased as compared with reactions under oxygen. More specifically, higher BP means the reaction pathways requiring oxygen is disfavored in some way. Using atmospheric air, i.e. a lower oxygen pressure, had a similar effect on reactivity and selectivity (Table 2 entry 5). Because the total flow volume of the gas phase was almost the same as with 100% oxygen, the liquid film thickness over the catalysts surfaces should be the same for these two reactions. However, the oxidative pathways were strongly reduced under atmospheric air. This phenomenon suggests that oxygen transfer in the liquid phase is very important in a multiphase oxidation reaction. Fig. 9 (B) compares gas flow rate to by-products ratio. For paper-structured catalysts, the increasing gas flow rate reduced the formation of the BP, while for bead catalysts it made negative effect. In my previous RTD studies, the mean residence time was smaller than the theoretical value, the liquid phase Peclet number (i.e. the ratio between transport by convection and that by diffusion) increased with increasing gas flow rate for bead catalysts. High Peclet numbers indicate a reduced effect of diffusion on transport. These trends in the residence time and Peclet number were typical of liquid phase maldistribution and by-pass flow, in contrast to the high wettability and smooth diffusion of the paper-structured catalysts [22]. Liquid phase maldistribution and stagnant flow resulted in large amounts of by-products, because of the inefficient contact between the gas-liquid-solid phases found with the bead catalysts. Poor contact between the liquid and solid phase tends to slow down the reaction rate of disproportionations with a small enthalpy of formation, in other words, the products needed high energy to be formed in the long contact times of the stagnant flow.



Fig. 10 Reaction pathways of benzyl alcohol in the absence of oxygen.

Fig. 11 compares the effects of the reactor external temperature on reactivity and selectivity. In general, higher external temperatures induce higher reactivity, because the amount of thermodynamically active species increases with increasing temperature. However, highly active species get over the activation energy barrier to form undesirable by-products and/or further oxidized products. The highest TOF was obtained at the external temperature of 383 K, with a slightly increase in by-product formation. Meanwhile, decreasing the external temperature from 373 K to 353 K increased the TOF and selectivity. Finally, the TOF value decreased at 343 K. To understand these phenomena, the thermal balance during the reaction must be considered. Oxidation reactions are exothermic and the oxidation of benzyl alcohol to benzaldehyde releases 219 kJ/mol of heat. For a reaction operating at 353 K (Table 2 entry 7), the generated heat was 1.2 kJ per pass from the experimental data of 6% conversion in the initial 12 min. If all the energy was used to raise the temperature of benzyl alcohol (specific heat capacity: 220 J/mol/K), the resulting temperature rise of benzyl alcohol was about 45 K. For the reaction operating at 373 K (Table 2 entry 7), the generated heat was similar. However, this external temperature was close to the boiling point of toluene (383 K, heat of vaporization: 33 kJ/mol), and the temperature rise in the substrate might induce the evaporation of toluene. The decreases in the TOF in Fig. 11 (A) could be considered the combined effect of the exothermic and endothermic thermal changes. Similar discussions have been made for gas phase oxidation of benzyl alcohol over metal fiber-based catalysts [34], and liquid phase oxidation of benzyl alcohol in microchannels [35]. The former study concluded there was rapid dissipation of reaction heat in fibrous networks. In the latter study, the reaction

was conducted with toluene as a solvent, and thus the evaporation of the toluene was neglected. The large surface to volume ratio of the microreactor allows for efficient heat transfer, preventing thermal runaway. In this study, micrometer-sized fiber-network pores and liquid flow over the microstructure exhibited high reactivity at a lower external temperature, probably because of the efficient heat and mass transfer. In addition, lower external temperatures resulted in higher selectivity, as shown in Fig. 11 (B). By contrast, bead catalysts showed only negative effects as the external temperatures decreased.



Fig. 11 Effect of the external temperature on reactivity.

(A) TOF values^a, (B) conversion^b (triangles), selectivity^c (squares), and by-products ratio^d (diamonds) for the paper-structured catalysts (hollow) and beads catalysts (solid).
[a] Turnover frequency, [b] (1 – [Residual alcohol] / [Initial Alcohol]) × 100, [c] (Benzaldehyde yield) / (Conversion), [d] (Dibenzyl ether yield + Benzaldehyde dibenzyl acetal) / (Conversion).

[b], [c], [d] values were calculated by the values at 4 h on stream,

Reaction conditions; liquid flow rate 10 ml/min, gas flow rate 100 ml/min.

The high reactivity and selectivity of paper-structured catalysts were obtained because of effective gas-liquid-solid contact and heat transfer in the micrometer-size porous network structure. The reactions requiring oxygen tended to improve with the more efficient mass transfer between phases, and uniform distribution of the liquid phase also resulted in relatively high selectivity.

4-4 Conclusions

Pd-containing paper-structured catalysts with micrometer-size pores were prepared by a high-speed and low-cost papermaking technique. The paper-structured catalysts showed high catalytic reactivity and selectivity for solvent-free benzyl alcohol oxidation with a microfluidic reaction system, in a fixed-bed gas-liquid-solid multiphase reactor. Kinetic and mechanism studies of various reaction conditions revealed that the catalytic reactivity and selectivity are associated with the microfluidics in the paper-structured networks. Uniform distribution of the liquid phase gave high reactivity because of the effective liquid–solid contact. High selectivity of oxidation pathways was ascribed to efficient oxygen gas transfer in the liquid phase by the microfluidic effect. Micrometer-sized paper-structured networks also had good effect on thermal diffusion inside the porous networks, and achieved preferable reaction conditions at a lower reaction temperature.

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Chapter 5

General conclusions

Chemical industries are demanding more environmentally acceptable processes, and products and practices that embrace the concept of green sustainable chemistry. Catalytic reactions between gas and liquid phases on a solid catalyst have attracted a lot of attention in both industrial and academic circles. Catalytic selective oxidation of alcohol in the liquid phase is one of the most important reactions to achieve by an environmentally friendly reaction, and there have been significant advances in the oxidation reactions using clean oxidants such as oxygen. In this study, multiphase microfluidic reactions were conducted over paper-structured catalysts with micrometer-size pores. The mechanism of the gas–liquid–solid multiphase catalysis was studied, to elucidate the unique reaction kinetics via paper-structured catalysts and to establish an efficient reaction process.

First, a ceramic paper matrix was prepared using a simple papermaking technique, and *in situ* synthesis of $Ru(OH)_x$ catalysts on the porous fiber-network structure of paper matrix was achieved. The as prepared $Ru(OH)_x$ -containing paper composites possessed a paper-like flexibility and porous microstructure because of the layered fiber networks. The paper catalysts demonstrated high catalytic efficiency in the aerobic alcohol oxidation from benzyl alcohol to benzaldehyde with high selectivity at a triple O₂-toluene/substrate-catalyst phase in a fixed bed external loop reactor. The $Ru(OH)_x$ paper catalysts showed significantly higher reactivity, as compared with conventional pellet and bead-type solid catalysts, especially for the initial conversion rates and durability for repeated uses, owing to the highly dispersed ruthenium hydroxide species on the porous paper composite microreactors.

In the next step, the hydrodynamic behavior of the fibrous paper-structured catalysts was

investigated in detail. Specifically, residence time distribution (RTD) studies were carried out by tracer monitoring in a cold flow model. RTD measurement in a cold flow model showed superior liquid wettability and axial diffusion effects in the paper-structured catalysts, compared with ceramic beads. Catalytic reactivity was associated with the hydrodynamic behavior giving a uniform liquid diffusion on the paper-structured catalyst surface, and attributed to the formation of a thin liquid film layer, and resulting in efficient oxidation at the multiphase gas–liquid–solid interface.

Furthermore, Pd-species containing paper-structured catalysts were prepared in a similar manner. The paper-structured catalysts showed high catalytic reactivity and selectivity for solvent-free benzyl alcohol oxidation, inherently involving complicated reaction pathways. Kinetic and mechanistic studies in various reaction conditions revealed that the catalytic reactivity and selectivity are expected to be associated with the microfluidics in the paper-structured networks. Uniform distribution of the liquid phase gave high reactivity, and high selectivity of oxidation pathways was ascribed to efficient gas–liquid–solid mass transfer and thermal diffusion within the thin liquid layer interface over the fiber networks.

In conclusion, paper-structured catalysts with micrometer-size pores achieved efficient microfluidic reaction fields in a traditional tubular reactor. Effective microfluidic reaction over the paper-structured catalysts realized both high reactivity and good selectivity in gas–liquid–solid three-phase reactions. Mass-transfer and catalytic reaction mechanism studies revealed the key factors inducing this unique reactivity. Paper-structured catalysts with paper-like flexibility can be used in practical applications, and are expected to be a promising catalytic

material for green sustainable chemistry and industries.

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