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Synthesis and Photocatalytic Activity of Mesoporous SiO_2-TiO_2

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ABSTRACT

Mesoporous SiO_2-TiO_2 was synthesized by sol-gel method using $Si(OC_2H_5)_4$, $Ti(OC_2H_5)_4$ and stearyltrimethylammonium chloride. By using acetylacetone as the capping agent of $Ti(OC_2H_5)_4$, homogeneous SiO_2-TiO_2 composite was obtained. Spherical mesoporous SiO_2-TiO_2 was also synthesized by sol-gel method using W/O emulsion under microwave irradiation. The specific surface area of these mesoporous SiO_2-TiO_2 materials decreased when Ti/Si molar ratio was higher than 0.1, which indicated that Ti was homogeneously distributed in mesoporous SiO_2 matrix at $Ti/Si \leqq 0.1$. Photocatalytic activity of mesoporous SiO_2-TiO_2 materials was investigated by degradation of methylene-blue in water under UV light irradiation. Mesoporous SiO_2-TiO_2 was effective for the adsorption-decomposition of methylene-blue.

KEYWORDS

Mesoporous silica, titania, spherical particle, sol-gel, photocatalyst

1. Introduction

Mesoporous silica is useful as adsorbents in gas or liquid phase and catalyst support. Regularly-oriented mesoporous structure is formed by a sol-gel process using the self-assembly of organic surfactant as template [1]. The gas adsorbability of mesoporous silica is remarkably enhanced by addition of other metal oxides, especially TiO_2, forming acidic points [2-4]. Although the sol-gel method using metal alkoxides is easy to synthesis mesoporous silica composite, there is a problem in the difference of hydrolysis rate between various starting alkoxides. The authors have studied the process factors on formation of SiO_2-TiO_2 mesoporous materials from Si and Ti alkoxides, and found that the way for homogenization is the partial hydrolysis of Si alkoxide before the addition of Ti alkoxide [4-6].

We have also synthesized spherical mesoporous silica materials by microwave-emulsion method [7]. In the microwave-emulsion method, n-hexane was used as oil phase, because n-hexane does not absorb microwave, and aqueous solution including silica source and template of mesopores as water phase. When microwave is irradiated to the W/O emulsion, water phase is heated selectively and sol-gel reaction proceeds in water phase, resulting in formation of spherical mesoporous silica.

In this study, homogeneous SiO_2-TiO_2 mesoporous materials were synthesized by using acetylacetone as capping agent of Ti alkoxide. In addition, spherical mesoporous SiO_2-TiO_2 was synthesized by microwave-emulsion method and the photocatalytic activity was compared with bulk sample.

2. Experimental Procedure

2.1 Synthesis of mesoporous SiO_2 and SiO_2-TiO_2

Mesoporous SiO_2 and SiO_2-TiO_2 were synthesized by sol-gel method using $Si(OC_2H_5)_4$ (TEOS; Wako Pure Chemical Industries, Ltd.) and $Ti(OC_2H_5)_4$ (TEOT; Merck KGaA, Co.).

First, TEOT was capped with acetylacetone to control the reactivity, because the hydrolysis rate of TEOT was higher than that of TEOS. TEOT was mixed with acetylacetone in dry N_2 at the ratio of TEOT to acetylacetone = 1:2 in mol. After stirring for 30min, TEOS, stearyltrimethylammonium chloride (C_{18}TAC; Nacalai Tesque, Inc.) as template and diluted HCl water (pH=2) were added to the capped TEOT solution, and then heated at 50 ℃. The composition was set at TEOS:C_{18}TAC:H_2O=1:0.2:20 in mol. The Ti/Si molar ratio in the composite was changed from 0.1 to 0.5. After sol-gel reaction was proceeded completely, the gel was calcined in air at 500 ℃ for 4 h at 2 ℃/min in order to remove the organic template.

2.2 Synthesis of spherical mesoporous SiO_2 and SiO_2-TiO_2

Microwave-emulsion method was applied to synthesize the spherical mesoporous SiO_2 and SiO_2-TiO_2. The procedure has already been reported as ref.[7]. Figure 1 shows the flow chart for synthesis of spherical mesoporous SiO_2-TiO_2. In order to prepare oil phase of W/O emulsion, n-hexane was mixed with 10 wt% of polyglycerol polyricinalate (PP) as emulsifier. On the other hand, TEOS was added to capped-TEOT solution prepared as above and mixed with diluted HCl water (pH=2) including C_{18}TAC. After stirring for 1.5 h at 50 ℃, partially hydrolyzed TEOS-TEOT solution was obtained. The composition was set at TEOS:C_{18}TAC:H_2O=1:0.28:56 in mol. The Ti/Si molar ratio in the composite was changed from 0.1 to 1.0. The water phase, prepared by addition of 5 ml of H_2O to the partially hydrolyzed TEOS-TEOT solution, was mixed with oil phase under stirring, resulting in W/O emulsion. The microwave heating process was performed by using the MARS5X (CEM Co.) microwave digestion system. The reaction was carried out in a sealed Teflon vessel under stirring with a magnetic stirrer and the reacting temperature was set at 60 ℃ for 30 min. After heating, the precipitate was separated by centrifugation. The produced powder was washed

with ethanol and distilled water, and then dried at 100 ℃. In order to remove the organic residue, the dried products were calcined at 500 ℃ for 4 h at 2 ℃/min in air.

2.3 Characterization

The morphology of products was observed by scanning electron microscopy (SEM; S-5200, Hitachi Co.). The specific surface area and average pore size of calcined products were determined from N_2 adsorption isotherm by the BET method (Belsorp 18SP, BelJAPAN, Inc.). Acidity was measured by amine titration in benzene using *p*-dimethylaminoazobenzene as an indicator. Photocatalytic activity was determined by degradation of methylene-blue in water under UV light irradiation. Black light (FL6-BLB, Toshiba Lighting and Technology, Co.) was used as light source and the wavelength was 352 nm. The absorption spectrum of methylene-blue was measured at λ = 664 nm with a UV-Visible spectrometer (U-3300, Hitachi Co.).

3. Results and discussion

Homogeneous SiO_2-TiO_2 mesoporous materials were synthesized by using acetylacetone as capping agent of Ti alkoxide. The typical SEM image of spherical mesoporous SiO_2-TiO_2 synthesized by microwave-emulsion method is shown in Fig. 2. Most particles were spherical and the particle size was 0.1-20 μm. Some broken particles were observed, indicating the formation of solid particles. As the Ti/Si molar ratio became higher, the morphology of particles changed to irregular. However, the XRD peaks of anatase and/or rutile were not detected even at Ti/Si=0.5. These results indicated that TiO_2 was not formed separately from SiO_2 network and homogeneous incorporation of Ti to Si-O network was achieved by using acetylacetone to control the hydrolysis rate of TEOT. Figure 3 shows the change in the specific surface area of bulk and spherical mesoporous SiO_2-TiO_2 with Ti/Si

molar ratio. In both cases, the specific surface area was kept high up to Ti/Si=0.1, and then decreased with an increase in Ti/Si molar ratio. In addition, N_2 adsorption isotherms of bulk and spherical samples at Ti/Si $\leqq$ 0.1 were Type IV. These results indicated that the mesoporous SiO_2 structure was maintained even in the presence of Ti less than Ti/Si=0.1. The BJH pore size of both samples at Ti/Si=0.1 was 3.4 nm. Acidity of bulk sample reached the maximum value at Ti/Si=0.1, and then decreased (Fig.4). This means that Ti was homogeneously distributed in Si-O network at Ti/Si$\leqq$0.1 like –Si-O-Ti-O-Si-. At Ti/Si>0.1, TiO_2 cluster began to generate in Si-O network like –Si-O-Ti-O-Ti-O-Si-, which led to a decrease in acidity. Furthermore, TiO_2 cluster may be isolated from Si-O network at Ti/Si>0.5. The same result was obtained in the case of spherical mesoporous SiO_2-TiO_2.

Photocatalytic activity of bulk and spherical mesoporous SiO_2-TiO_2 was determined by degradation of methylene-blue (MB) in water. The 20mg of powder sample was suspended in 100ml of 50 μM MB aqueous solution. The change of MB concentration by adsorption was pursued for 14 h under dark condition, and then that by photocatalytic decomposition for 7 h under UV light irradiation. Figure 5 shows the change in MB concentration with time. The adsorption and decomposition of MB were not observed on both bulk and spherical mesoporous SiO_2. In the case of SiO_2-TiO_2 materials, MB concentration significantly decreased within 14 h under dark condition, and then decreased with time under UV light irradiation. This means that MB adsorbed on acid point of SiO_2-TiO_2 samples and photo-decomposition proceeded on acid point under UV light irradiation. The morphology of mesoporous SiO_2-TiO_2 did not so much influence on the photocatalytic activity.

4. Conclusions

In this study, homogeneous SiO_2-TiO_2 mesoporous materials without the separate deposition of TiO_2 could be synthesized by using acetylacetone as capping agent of Ti

alkoxide. Spherical mesoporous SiO_2-TiO_2 was also synthesized by microwave-emulsion method. The results of specific surface area and acidity indicated that Ti was homogeneously distributed in Si-O network less than Ti/Si=0.1. The adsorption-decomposition of MB may proceed on the acid point.

References

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vrtuli and J. S. Beck, Nature 359 (1992) 710.

2. S. Zheng, L. Gao, Q. Zhang and J. Guo, J. Mater. Chem. 10 (2000) 723.

3. S. Zheng, L. Gao, Q. Zhang, W. Zhang and J. Guo, J. Mater. Chem. 11 (2001) 578.

4. X. Y. Li, M. Uehara, N. Enomoto and J. Hojo, Trans. Mater. Soc. Jpn. 26 (2) (2001) 499.

5. X. Y. Li, M. Uehara, N. Enomoto and J. Hojo, J. Ceram. Soc. Jpn. 109 (10) (2001) 818.

6. N. Enomoto, K. Kawasaki, M. Yoshida, X. Y. Li, M. Uehara and J. Hojo, Solid State Ionics, 151 (2002) 171.

7. M. Inada, A. Nishinosono, K. Kamada, N. Eenomoto, J. Hojo, J. Mater. Sci. 43 (7) (2008) 2362.

Figure legends

Fig. 1 Flow chart for synthesis of spherical mesoporous SiO_2-TiO_2.

Fig. 2 SEM images of spherical mesoporous SiO_2-TiO_2 at Ti/Si=0.1 synthesized by microwave-emulsion method.

Fig. 3 Change in specific surface area of bulk and spherical mesoporous SiO_2-TiO_2 with Ti/Si molar ratio.

Fig. 4 Change in acidity of bulk mesoporous SiO_2-TiO_2 with Ti/Si molar ratio.

Fig. 5 Change in MB concentration with time.

Figure

Fig.1

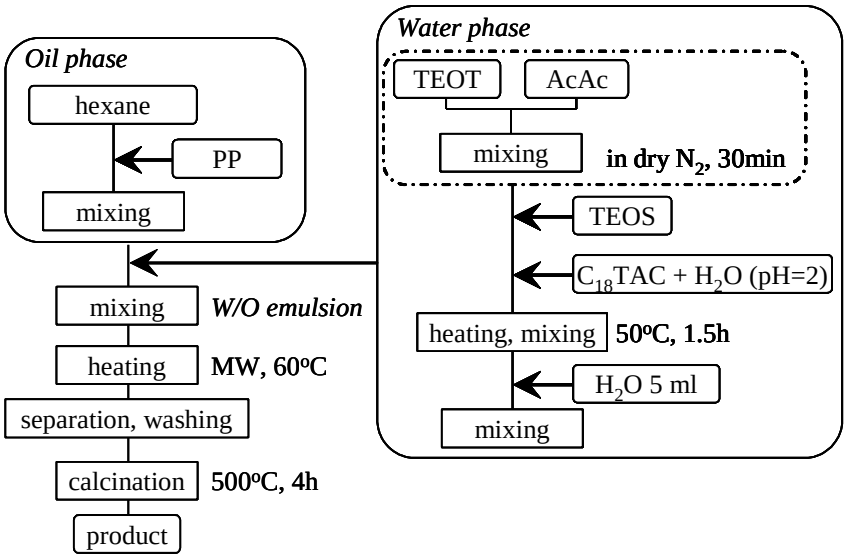

Oil phase
hexane
PP
mixing
Water phase
TEOT
AcAc
mixing
in dry N2, 30min
TEOS
C18TAC + H2O (pH=2)
heating, mixing
50ºC, 1.5h
H2O 5 ml
mixing
mixing
W/O emulsion
heating
MW, 60ºC
separation, washing
calcination
500ºC, 4h
product

Fig.2

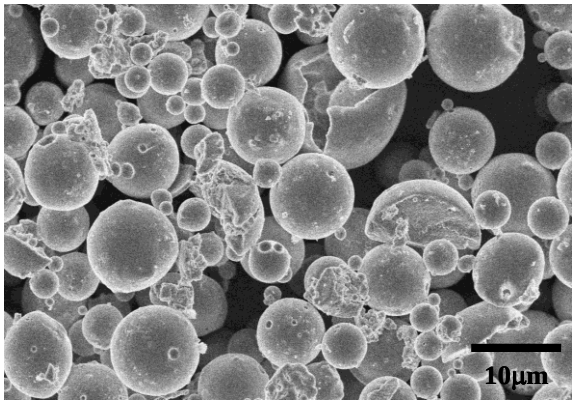
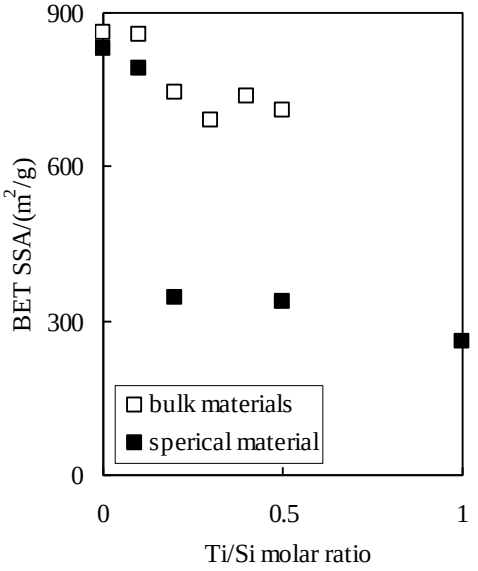


Fig.3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300
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BET SSA/(m2/g)
0
0.5
1
Ti/Si molar ratio
bulk materials
sperical material

Fig.4

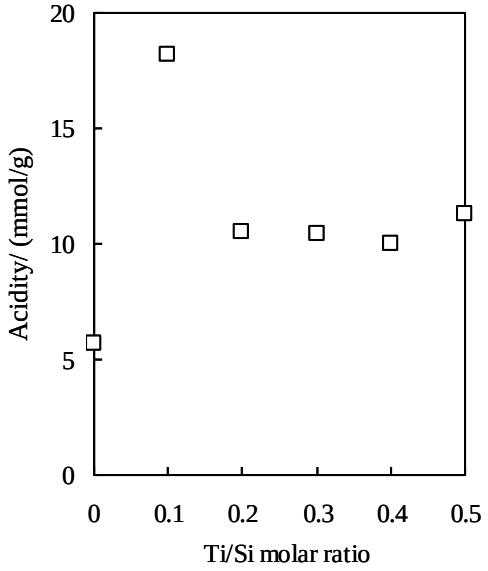
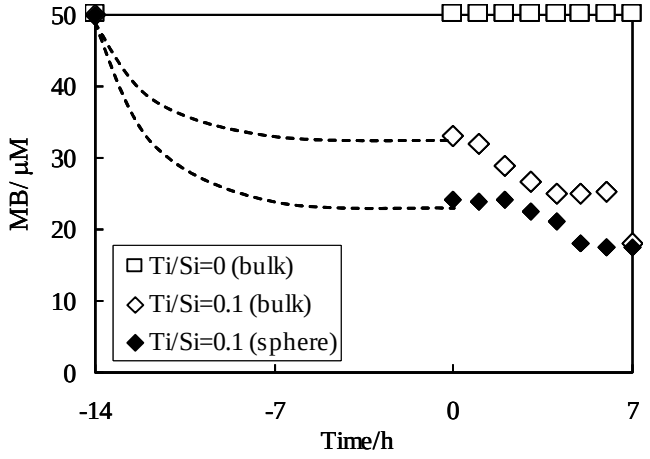


Fig.5


50
40
30
20
10
0
MB/ μM
-14
-7
0
7
Time/h
Ti/Si=0 (bulk)
Ti/Si=0.1 (bulk)
Ti/Si=0.1 (sphere)