Study on the Catalytic Performance of Cu-Mn based Spinel Oxides for Benzene Oxidation under Microwave Irradiation

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Title　Study on the Catalytic Performance of Cu-Mn based Spinel Oxides for Benzene Oxidation under Microwave Irradiation
(マイクロ波照射下におけるCu-Mn系スピネル酸化物のベンゼン酸化触媒特性に関する研究)

区　　分　: 甲

Category

論 文 内 容 の 要 旨

Thesis Summary

(a) Cu-Mn oxides with different Cu/Mn ratios were successfully synthesized by precipitation-calcination method. Catalyst with a Cu/Mn molar ratio of 1:1 calcined at 400 °C exhibited the highest activity for benzene oxidation under microwave heating due to the reactivity of the oxygen species. The "thermal effect" of microwave heating tremendously lowers the reaction temperature, and the microwave irradiation effect is significant for highly crystallized particles. The reactions in the absence of gaseous oxygen indicate that the reaction mechanism is lattice oxygen species induces catalytic oxidation, and then gaseous oxygen migrates and replenishes into it. The possible oxygen activation process is $O_2 \rightarrow O^{2-}_{ads} \rightleftarrows O^{2-}_{latt}$. Kinetic studies suggest that the activation of oxygen species is important for oxidation reactions and that microwave irradiation facilitates this step.

(b) To further improve the catalytic activity, benzene oxidation reaction was efficiently proceeded over Co-doped Cu-Mn mixed oxides ($Co_xCu_{1-x}MnO_y$), and the effect of Co addition on the physicochemical properties and catalytic behavior were studied by experimental and theoretical analysis in detail. The existence of the spinel phase and the substitution of Co by Mn sites in Co-Cu-Mn oxides were characterized by XRD and XAFS spectra (Fourier and Wavelet transformed EXAFS, and XANES). Compared with the single oxides and pristine Cu-Mn mixed oxide, the Co-doped catalysts showed significantly higher benzene oxidation activities due to the enhanced reactivity of lattice oxygen species, the increased specific surface area, and the improved chemisorption of benzene. Complete benzene (400 ppm) degradation on $Co_{0.2}Cu_{0.8}MnO_y$ was achieved at a low temperature of 225 °C and space velocity of 60000 $mLg^{-1}h^{-1}$. Furthermore, this mode can also be applied to moisture conditions with high activity and stability. DFT calculations were carried out to investigate the interaction of the reactant and catalyst surface. The introduction of Co species in Cu-Mn spinel oxides took multiple parts in the reactions: (1) Compared with pristine Cu-Mn, Co substituted surface was much stronger for benzene adsorption, and the activated benzene reacted with lattice oxygen to form oxygen vacancies. The generated O defect will attack the adsorbed benzene to form more active benzene species; at the same time, benzene adsorption can further facilitate the formation of oxygen vacancies; (2) Co-doped Cu-Mn oxides showed lower oxygen vacancy formation energy, which will enhance the O_2 adsorption, dissociation, and replenishment in the lattice; (3) The H_2O molecule more inclined to bind at Co site, and did not completely cover the active site for benzene adsorption. These findings could provide a deep understanding of the effect of Co doping to conduct highly efficient oxidation catalysts and a facile and effective strategy for improving the catalytic properties of VOC removal.

(c) Furthermore, the benzene catalytic oxidation was carried out on the $Co_xMn_{1-x}CuO_y$ under microwave heating. The increasing concentration of Co enhanced the microwave heating performance. Under microwave irradiation, the complete benzene conversion was achieved at a relatively low temperature of 145 °C and microwave power (~50 W) on $Co_{0.4}Mn_{0.6}CuO_y$. This system can be also applied to catalytic reactions under humid conditions with high activity and stability. The combination of pre-adsorption and thermal oxidation processes improved the low concentrations of benzene removal based on the advanced adsorption capacity and microwave-improved rapid heating of the catalysts. A mixture of the $Co_{0.8}Mn_{0.2}CuO_y$ with high temperature-rise properties and the $Co_{0.4}Mn_{0.6}CuO_y$ with excellent catalytic properties showed even superior benzene oxidation properties under microwave heating. Thus, by controlling the composition of the Co-Cu-Mn spinel oxides, the high microwave absorption and VOCs oxidation properties were obtained, and these materials

can be applied to highly efficient VOCs removal processes.