

Cryptomelane-Type of Manganese Oxide: A Hydrophobic Oxidation Catalyst

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Introduction

Manganese oxides have shown promising catalytic properties in total oxidation of CO and VOC, selective oxidation of alcohols and alkanes, as well as decomposition of H_2O_2 , O_3 and NO_x . However, rapid deactivation has occurred on most manganese oxide catalysts in high moisture content environment. Au and other precious metal coated catalysts have achieved good activity and stability in some processes such as oxidation of CO with co-existence of water vapor, but the high cost may limit its large scale applications.

In this work we have synthesized a cryptomelane type of manganese oxide (a 4.7Å tunneled MnOx), with excellent hydrophobicity and activity in oxidation of benzene, CO and ethanol, and studied the physical/chemical adsorptive properties, porosity, acid-base properties and the role of lattice oxygen in catalytic cycles. Other types of manganese oxide (birnessite, a layered MnOx and todorokite, a 6.9Å tunneled MnOx), ZSM-5 and $\text{Pt/Al}_2\text{O}_3$ have also been evaluated as comparison.

Materials and Methods

Different methods were employed to synthesize cryptomelane, todorokite and birnessite, including sol-gel, hydrothermal and solid state reactions. Materials were characterized with XRD, FESEM, FTIR, TGA, DSC, TPD-MS, TPSR-MS. Nitrogen physisorption experiments were done at 77K on an ASAP 2100 Physisorption apparatus and CO_2 physisorption experiments were carried out on an Autosorb-6 apparatus at 273K. Sorption of water, ethanol, or benzene or binary mixtures of the above adsorbates in static and flow environments were studied at room temperature with static weighing. Catalytic reactions were done in U-type reactor and glass frit reactor with helium as a carrier gas. The down stream gas was analyzed on GC and MS.

Results and Discussion

The structures of the studied materials were confirmed by XRD. Fig 1 shows water and benzene absorption on the studied materials. Absorption bands in the region 3000-3700 cm^{-1} and 3100 cm^{-1} were used to indicate the OH groups of hydrates or absorbed water, and C-H of benzene on the materials, respectively. Cryptomelane manganese oxide shows no absorption of water but only benzene. Under similar conditions other materials absorb both water and benzene. The results indicate that cryptomelane is more hydrophobic and has a higher affinity to benzene molecules.

Total oxidation of benzene was tested at 100 - 400°C, 0.1% - 3.5% benzene/air, and flow rate of 15 - 180 mL/min. The oxidation of benzene on OMS-2 started at 100°C with a conversion of 1.9%. As reaction temperature was increased, the conversion increased sharply, reaching 100% below 300°C, achieving a total oxidation of benzene, with $\text{CO}_2/\text{H}_2\text{O}$ as the only products. For catalysts birnessite and todorokite, oxidation of benzene started at 150°C and 200°C, respectively, a significantly higher temperature than that over OMS-2. Although

similar trends to those of OMS-2 with respect to temperature dependence were observed, both catalysts showed much lower activity than OMS-2, especially at lower temperatures.

CO reactions were done on the studied materials with and without the flow of oxygen. The trends of the activity change indicated lattice oxygen in cryptomelane framework is the active species for oxidation. A continuous supply of gaseous oxygen is important in recovering the lattice oxygen and maintains the catalytic cycle.

Significance

Manganese oxide with cryptomelane structure was found highly hydrophobic and catalytic active in a series of oxidation reactions. Such catalysts and their modified forms could be applied in control of industrial gas emissions, vehicle emissions and in-door air pollutants in the presence of water vapor.

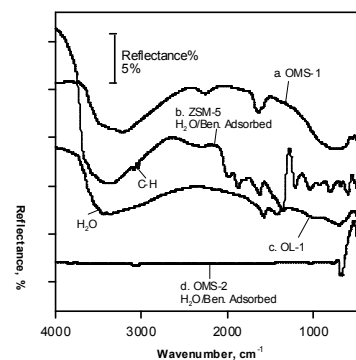


Figure 1 Diffuse Reflectance IR Spectra of OMS-1(a); ZSM-5(b); OL-1(c); and OMS-2(d).

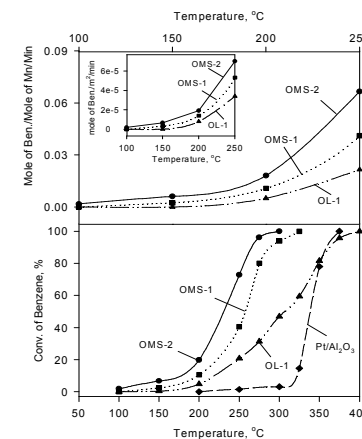


Figure 2 Total Oxidation of Benzene on Manganese Oxides and $\text{Pt/Al}_2\text{O}_3$.

References

1. Post, J. E.; Von Dreele, R. B.; Buseck, P. R. *Acta Crystallogr.* 1982, B38, 1056-1064.
2. DeGuzman, R. N.; Shen, Y. F.; Neth, E. J.; Suib, S. L.; O'Young, C. L.; Levine, S.; Newman, J. M. *Chem. Mater.* 1994, 6, 815-821.
3. Wang, J. Y.; Xia, G. G.; Yin, Y. G.; Suib, S. L.; O'Young, C. L., *J. Catal.* 1998, 176, 275-284.
4. Amorós, D. C.; Momge, J. A.; de la Casa-Lillo, M. A.; Solano, A. L.; *Langmuir* 1998, 14, 4589-4596.
5. Luo, J.; Zhang, Q.; Huang, A.; Suib, S. L., *Microporous and Mesoporous Mater.*, 2000, 35- 36, 209-217.