DOI:10.16262/j.cnki.1005-0841.2009.02.003

An Advance in Complete Oxidation of Formaldehyde at Low Temperatures

Hua Tian Junhui He
(Functional Nanomaterials Laboratory, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China)

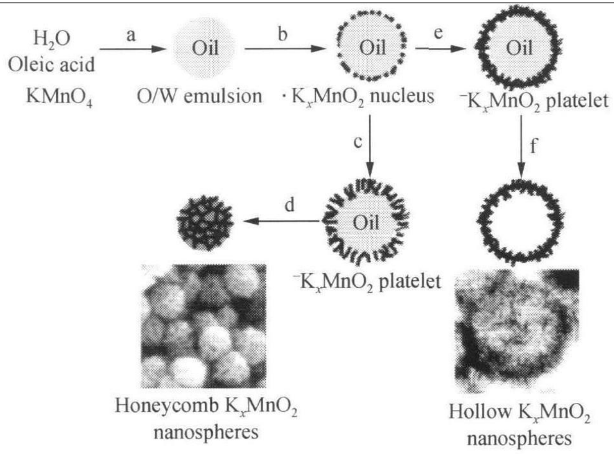
Editor's comments *Formaldehyde (HCHO) emitted from chemical manufacturing plants including methanol-gasoline/diesel fuel vehicles and the construction and decoration materials is one of the major air pollutions, which induces photochemical pollution and hazards human health. Great efforts have been made for the reduction or control of the emission of HCHO to satisfy the stringent environmental regulations. Now, a new study supported by the National Natural Science Foundation of China reports mesoporous manganese oxide with novel nanostructures for the decomposition of HCHO. The obtained manganese oxide nanomaterials showed high catalytic activities for oxidative decomposition of HCHO at low temperatures. Complete conversion of HCHO to CO_2 and H_2O were achieved, and no harmful by-products were detected in effluent gases. The catalytic activities of these nanomaterials are significantly higher than those of previously reported manganese oxide octahedral molecular sieve (OMS-2) nanorods, MnO_x powders, and alumnina-supported mangnaese-palladium oxide catalysts. These results provide a new route for the removal of HCHO and other air pollutions.*

Key words Manganese oxide, honeycomb nanosphere, hollow nanosphere, formaldehyde, oxidation

The indoor environment plays an important role in human health, because people generally spend more than 80% of their time in indoors, which contributes a higher risk from inhalation of pollutants than outdoors. Formaldehyde (HCHO) emitted from the construction and decoration materials is one of the most dominant volatile organic compounds (VOCs) in the indoor environment. Previous research indicated that serious health problems including nasal tumors, irritation of the mucous membranes of the eyes and respiratory tract, and even lethiferous diseases such as nasal cancer can be caused if people are exposed to an indoor environment polluted with elevated HCHO levels for an extended length of time.[1-3]

Currently effective removal of HCHO is attracting much attention. The catalytic decomposition of HCHO has been achieved in the temperature range 90—500℃. Facile decomposition of HCHO at low temperature, however, is still a challenge though there are increasing concerns on HCHO in the indoor environment. Catalytic oxidation is a promising approach as HCHO can be oxidized to CO_2 over catalysts at lower temperatures than thermal oxidation.[4,5] MnO_x powders, MnO_2 octahedral molecular sieve (OMS-2) nanorods, and alumina-supported manganesepalladium oxides ($Mn\text{-}Pd/Al_2O_3$) were used as catalysts for decomposition of HCHO, and the latter two catalysts showed high activities at low temperatures.[6,7] Very recently, Sinha A. *et al.*[8] reported that mesostructured 2.8 wt% $Au/\gamma\text{-}MnO_2$ nanoparticle composites could be used for extensive air purification.

Control over the size, shape, and structure of inorganic nanomaterials to search for new properties has become one of the major objectives of nanoscale science and technology, because of their structure, size and shape-dependent characteristics and novel chemical properties.[9,10] Different MnO_2 morphologies have so far been prepared, including rods, wires, tubes, urchin-like microstructures, etc. However, few works were reported on nanostructures of layered MnO_2, such as birnessite-type MnO_2 (A_xMnO_2, where $A=H^+$ or metal cation). A_xMnO_2 is a layered structure consisting of edge-sharing MnO_6 octahedra with an interlayer spacing of ca. 0.7 nm.[11] Recently, Our group prepared novel mesoporous nanospheres of layered manganese oxide (K_xMnO_2) with honeycomb and hollow nanostuctures via a facile approach at room temperature.[12] The catalytic activities of these manganese oxide nanostructures showed a 100% conversion of HCHO to $CO_2 + H_2O$ at 80℃. It was the first report of catalytic decomposition of HCHO by mesoporous layered K_xMnO_2 nanomaterials at such low temperatures.



Scheme 1 Plausible formation mechanism of honeycomb and hollow K_xMnO_2 nanospheres.

We used oleic acid (OA) as reducing agent of potassium permanganate ($KMnO_4$). In the reaction system, oleic acid formed a stable O/W emulsion (Scheme 1), in which the "Baeyer test for unsaturation" reaction[13] quickly occurred between $KMnO_4$ and oleic acid at the O/W interface and produced K_xMnO_2 nuclei there. At low $KMnO_4$ concentration, an unstable shell of loosely packed platelets formed (process c). Removal of oleic acid and formed cis-diol by ethanol resulted in collapse of the shell, giving honeycomb nanospheres. At high $KMnO_4$ concentration, large amounts of lamellar platelets were produced, and a robust shell of densely packed platelets formed (process e). After removal of oleic acid and formed cis-diol, hollow nanospheres were produced. The morphology and mesoporous character of the as-prepared nanomaterials are shown in Fig. 1 and Fig. 2, respectively.

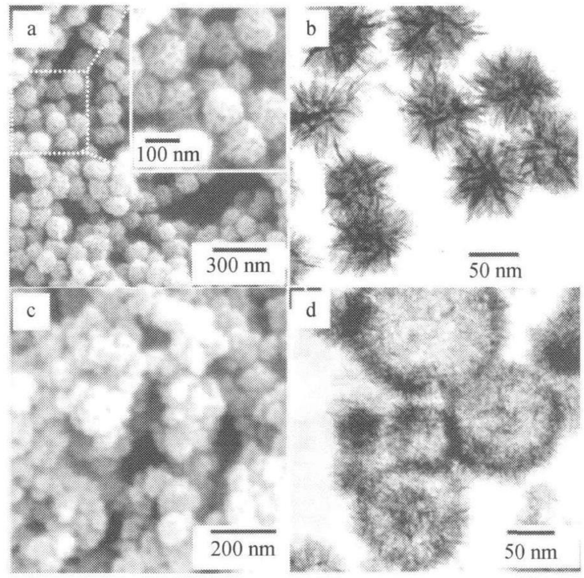


Fig. 1 SEM (a) and TEM (b) images of honeycomb K_xMnO_2 nanospheres ($KMnO_4$/OA = 1 : 5) and SEM (c) and TEM (d) images of hollow K_xMnO_2 nanospheres ($KMnO_4$/OA=1 : 1).

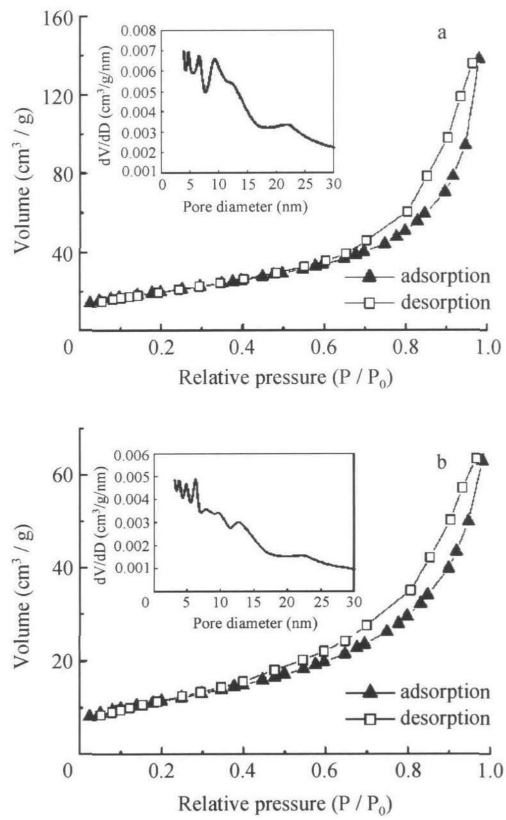


Fig. 2 Nitrogen sorption isotherms and pore size distributions (inset) of honeycomb (a) and hollow (b) K_xMnO_2 nanospheres.

These new nanomaterials had robust nanostructures and showed morphology-dependent catalytic activities for decomposition of formaldehyde. The HCHO conversion by the hollow K_xMnO_2 nanospheres (50 mg) increased to 100% when the temperature increased to 80℃, and that by the honeycomb nanospheres (70 mg), however, needed 85℃ to reach a 100% conversion, as shown in Fig. 3.

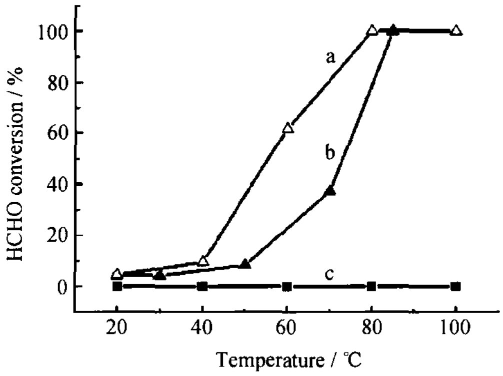


Fig. 3 HCHO conversion on control (■), honeycomb K_xMnO_2 nanospheres (70 mg) (▲), and hollow K_xMnO_2 nanospheres (50 mg) (△), respectively.

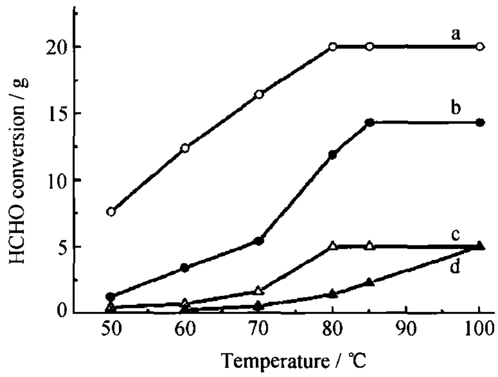


Fig. 4 HCHO conversion per gram of samples on MnO_x powder (▲), OMS-2 nanorods (△), honeycomb (●) and hollow (○) K_xMnO_2 nanospheres, respectively.

These decomposition temperatures are much lower than those achieved by using similar manganese oxide materials. We compared the catalytic activities of the current as-prepared K_xMnO_2 nanomaterials with previously reported materials. It was found that the catalytic activities of honeycomb and hollow K_xMnO_2 are much higher than those of MnO_x powder, OMS-2 nanorods, and even Mn-Pd/Al_2O_3 catalysts (Fig. 4). Therefore, these mesoporous K_xMnO_2 nanospheres with large surface area and high dispersity are convenient and effective catalysts, and may provide a promising approach for oxidation decomposition of indoor pollutants and other VOCs in environment. Future research efforts will be necessary to offer significant improvement over this approach. In fact, with the support of the National Natural Science Foundation of China, we are currently investigating more convenient methods to synthesize the catalysts.[14]

References

[1] Wang, L. *et al.*, Study of catalytic decomposition of formaldehyde on Pt/TiO_2 alumite catalyst at ambient temperature. *Journal of Hazardous Materials* 167, 399—405 (2009).

[2] Agency for Toxic Substance and Disease Registry, Public Health Service, U. S. Department of Health and Human Services, Toxicological Profile for Formaldehyde, NTIS Accession No. PB99-166654, p. 451, (1991).

[3] U. S. EPA, Characterizing Air Emissions from Indoor Sources, EPA report: EPA/600/F-95/ 005, U. S. Environmental Protection Agency, Washington, DC, (1995).

[4] Alvarez-Galván, M. C. *et al.*, Alumina-supported manganese- and manganese-palladium oxide catalysts for VOCs combustion. *Catalysis Communications* 4, 223—228 (2003).

[5] Imamura, S. *et al.*, Oxidative decomposition of formaldehyde on silver-cerium composite oxide catalyst. *Catalysis Letters* 24, 377—384 (2004).

[6] Tang, X. F. *et al.*, Synthesis and Catalytic Performance of Manganese Oxide Octahedral Molecular Sieve Nanorods for Formaldehyde Oxidation at Low Temperature. *Chinese Journal of Catalysis* 27, 97—99 (2006).

[7] Álvarez-Galván, M. C. *et al.*, Formaldehyde/methanol combustion on alumina-supported manganese-palladium oxide catalyst. *Applied Catalysis B: Environmental* 51, 83—91 (2004).

[8] Sinha, A. K. *et al.*, Mesostructured manganese oxide/gold nanoparticle composites for extensive air purification. *Angewandte Chemie International Edition* 46, 2891—2894 (2007).

[9] Hupp, J. T. *et al.*, Better living through nanopore chemistry. *Science* 309, 2008—2009 (2005).

[10] Chen, J. *et al.*, α-Fe_2O_3 nanotubes in gas sensor and lithium-ion battery applications. *Advanced Materials* 17, 582—586 (2005).

[11] Ma, Y. *et al.*, Syntheses of birnessites using alcohols as reducing reagents: effects of synthesis parameters on the formation of birnessites. *Chemistry of Materials* 17, 1972—1979 (1999).

[12] Chen, H. *et al.*, Self-assembly of novel mesoporous manganese oxide nanostructures and their application in oxidative decomposition of formaldehyde. *The Journal of Physical Chemistry C* 111, 18033—18038 (2007).

[13] Fessenden, R. J. and Fessenden, J. S., Organic Chemistry Willard Grant Press: Boston, MA, p. 413, (1979).

[14] Zhu, J. and He, J., Effects of reaction conditions on the structure, morphology and size of manganese oxide nanoparticles. *Aca Chimica Sinica* (2010), in press.