Nanostructured Metal Oxides as Heterogeneous Environmental Catalysts

Abbas Khalil[1], Department of Chemistry, United Arab Emirates University, Al-Ain, UAE.

Introduction

Inorganic solids fabricated in nanometer-sized particles have recently attracted a great deal of attention due to the significantly unique properties such materials exhibit as compared to their bulk counterparts. Fabrication of solids in ultra fine particles is always accompanied with very unique characteristics including, high surface areas, high porosity, and significant surface chemical reactivity, which lead to a variety of unique properites. These unique properties hold promises for remarkable performance in several important applied fields, including catalytic, magnetic, mechanical and biological applications.[1]

Recent work on the fabrication of oxide nanometer-sized particles and their employment as adsorbents and catalysts for the oxidation and removal of some volatile organic compounds has shown very promising results.[2-7] Several oxides have been found to adsorb and react with a variety of compounds that are of concern as environmental pollutants including, chlorinated hydrocarbons[2,]3 and other organic and inorganic volatile compounds including warfare chemicals[5].

One of our recent significant findings in this field was the discovery of a catalytic role for iron oxide dispersed on nanoparticles of magnesium oxide, which has shown remarkably enhanced reactivity toward the adsorption and decomposition of some chlorinated hydrocarbons.[6] This finding has stimulated our continuous research involving iron oxides.

In this presentation, the synthesis of nanoscale particles of alumina, iron oxides, and nanocomposites containing iron oxides will be presented. Adsorptive and catalytic behavior of these oxides toward some volatile organic compounds will be discussed.

Results and Discussion

High-surface-area catalysts of alumina, iron(III) oxide, and iron oxide-containing composites were prepared. Sol-Gel method was employed to prepare Al_2O_3 and Al_2O_3/Fe_2O_3 nanocomposites. Nanoparticles of iron oxides were prepared via forced precipitation of iron ions in an alcoholic media starting with iron(III) chloride, dissolved in 2-propyl alcohol, as a precursor. Initially a red soluble product was obtained, which resulted in a fine precipitate of ferrihydrite upon the addition of sodium t-butoxide (Na-t-OBu) in ethanol solution. Heat-treatment of the resulting ferrihydrite under dynamic vacuum at temperatures between 200 and 400 ºC has selectively resulted in γ-Fe_2O_3. Characterization by FTIR, XRD, TGA, TEM, and N_2 adsorption analysis has revealed nanometer-sized particles, 4-7 nm, with relatively high surface areas. Surface areas were in the range of 90-120 m^2/g for samples heat-treated at 400 ºC. Mesoporous structure was indicated from the nitrogen adsorption isotherms with total pore volume in the neighborhood of 0.3 cc/g. The observed thermal stability of maghemite phase is believed to be a result of the nanoscale structure of the particles as compared to the known behavior of bulk maghemite, which converts to hematite as heated at temperatures above 200 ºC.[7]

Analogous precipitation of iron ions in water is known to lead to crystalline goethite, α-FeOOH or hematite[7], which makes this new synthetic route unique in selectively producing maghemite with relatively high surface area and porosity. Although the mechanism of γ-phase formation is still not very well understood, it is evident that the use of an organic solvent plays an important role in controlling the mechanism. One possible mechanism involves partial reduction of Fe^{3+} ions as a result of the presence of carbonaceous species giving magnetite (Fe_3O_4) which converts to γ-Fe_2O_3 of the same spinel structure.
Our studies on the adsorptive potential and catalytic behavior have shown that the high-surface-area Al_2O_3, γ-Fe_2O_3 and composite systems containing iron oxides with either alumina or magnesium oxide possess a considerable potential to adsorb and react with CCl_4, producing metal chloride and carbon dioxide as the main carbon product. Corresponding commercial samples (low surface areas) have shown much weaker reactivity. The presence of small amounts of iron oxide in the composite systems has shown a significant enhancement in their reactivity toward carbon tetrachloride. These preliminary results are the driving force of an ongoing research involving iron oxides, in attempts to prepare more reactive iron oxide systems and to understand the catalytic role of iron oxides.

References

1. Klabunde, K. J, *Nanoscale Materials in Chemistry*, John Wiley and Sons, New York, **2001**.
2. Lucas, E.; Decker, S.; Khaleel, A.; Ponce, A.; Li, W.; Carnes, C; Klabunde, K. J., *Chem. Eur. J.* **2001**, 7, 12, 2505.
3. Khaleel, A.; Dellinger, B., *Environ. Sci. Technol.* **2002**, 36, 1620-1624.
4. Khaleel, A., Kapoor, P. N. and Klabunde, K. J., *Nanostructured Materials*, **1999**, 11, 4, 459.
5. Decker, S. P.; Klabunde, J. S.; Khaleel, A., Klabunde, K. J., *Environ. Sci. and Technol.* **2002**, 36, 4, 762-768.
6. Klabunde, K. J.; Khaleel, A.; Park, D., *High Temperature and Materials Science* **1995**, 33, 99-106.
7. Flynn, Jr. C. M., *Chem. Rev.*, **1984**, 84, 31.