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Microporous and Mesoporous Materials 91 (2006) 53–58

MICROPOROUS AND MESOPOROUS MATERIALS

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Catalytic activity of mesoporous alumina for the hydrolysis and dechlorination of carbon tetrachloride

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Received 9 July 2005; received in revised form 1 November 2005; accepted 3 November 2005
Available online 4 January 2006

Abstract

Sol–gel-prepared mesoporous alumina (SG-Al_2O_3) was found to act as a potential catalyst for the complete dechlorination of carbon tetrachloride at temperatures $\geqslant 350$ °C in the presence of water. The main products were CO_2 and HCl at 400 °C and the deactivation of the catalyst by chlorination was inhibited. In the absence of water, however, lower reactivity was observed and the undesired $AlCl_3$, $COCl_2$, and Cl_2 by-products formed. The % conversion and the products profile were temperature dependent where higher % conversion and less $COCl_2$, $AlCl_3$ and Cl_2 were observed at higher temperatures.

Keywords: γ-Alumina; Catalytic dechlorination; Chlorinated hydrocarbons; CCl_4 decomposition

1. Introduction

Chlorinated hydrocarbons (CHC) are among the most hazardous organic compounds that get into the environment from different sources including chemical industrial plants, household chemicals such as detergents, chemical waste incinerators, and many other sources. Besides their severe toxic effects on humans, several CHC compounds, including CCl_4, are among the known ozone depleting gases [1]. As a result, controlling their emission, reducing their concentration and efficient disposal of them has become one of the challenging fields of environmental research in recent years.

Several methods have been reported for the destruction and abatement of CHC compounds including photocatalytic degradation, steam reforming [2], hydrodechlorination [3,4], and catalytic oxidation [5–15]. The most widely studied methods are catalytic oxidation and hydrodechlorination. Hydrodechlorination process is usually performed over noble metal-based catalysts in the presence of hydrogen or hydrogen supplying compounds. Major drawbacks in this process are the need for hydrogen or hydrocarbon storage and the use of noble metals. Hydrodechlorination of CCl_4 has been recently reported to take place over platinum-containing NaX zeolite with high activity and high selectivity to methane but the catalyst showed rapid deactivation [3].

Catalytic oxidation seems to be the most viable and economical approach for complete removal of such substances from the environment. Several heterogeneous catalytic systems, including noble metals [5,6], transition metal oxides [7–12], and zeolite-based catalysts [13–15], have shown significant reactivity toward the decomposition of CHC compounds where the desired reaction is the complete conversion to HCl and CO_2. The presence of excess chlorine over hydrogen in the CHC molecule usually prevents complete dechlorination and results in Cl_2 formation. The formation of HCl and Cl_2 makes the use of reactive metals ineffective where they result in chlorination and hence deactivation of the catalyst. On the other hand, transition metal oxide catalysts including oxides of V, Cr, Mn, Fe, Co, Ni, and Cu have shown significant reactivity toward CHC and higher resistance to chlorination and poisoning by Cl_2 and HCl [16].

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doi:10.1016/j.micromeso.2005.11.011

In previous studies, we have demonstrated that some reactive metal oxides and metal oxide composites fabricated in nanometer-sized particles have shown promising results [7,17,18]. Herein, recent results from a study on the role of the presence of water in the catalytic complete dechlorination of carbon tetrachloride by pure alumina are reported.

2. Experimental

2.1. Reagents and characterization techniques

CCl_4 (99.9% pure), aluminum isopropoxide (97%), and 2-propanol (95.5%) were purchased from Aldrich and used as received. Distilled deionized water was used in all reactions. Two types of alumina were employed, commercial alumina (C-Al_2O_3) and sol–gel prepared alumina (SG-Al_2O_3). C-Al_2O_3 (128 m^2/g) was obtained from Sasol North America Inc.

SG-Al_2O_3 was prepared via sol–gel method using aluminum triisopropoxide. In a typical experiment, aluminum triisopropoxide (3.0 g, 0.0147 mol) was dissolved in 2-propanol (250 mL) and toluene (50 mL). While stirring the solution, water (0.8 mL, dissolved in 15.0 mL 2-propanol) was added dropwise. A clear gel was obtained which was stirred for 6 h and then left standing for another 24 h for complete gelation. The solvent was removed from the gel by evaporation in a water bath at 90 °C followed by air drying for 12 h. Ultra-fine aluminum hydroxide powder was obtained which showed a specific surface area around 750 m^2/g. The hydroxide was converted to alumina by activation under dynamic vacuum at 500 °C. The powder was heated at a rate of 5 °C/min and held at 320 °C for 30 min, where most of the decomposition to oxide was found to take place [19], and at 500 °C for 4 h.

FTIR spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer. Powder X-ray diffraction (XRD) analyses were obtained using a Philips PW/1840 diffractometer with Cu-K_α radiation. BET surface area and porosity of SG-Al_2O_3 was measured by nitrogen gas adsorption at 77 K employing a Quantochrome Autosorb-1 volumetric gas sorption instrument.

2.2. Catalytic reactions

The catalytic reactions were studied using FTIR spectroscopy employing a fixed-bed flow reactor. In a typical experiment, 0.105 g (1.0×10^{-3} mol) alumina was placed in a U-shaped Pyrex tube (6 mm diameter) reactor and heated (10 °C/min) under He flow (20 mL/min) to the process temperature. A cylindrical heater around the reactor was used and the temperature was monitored by a temperature controller and a K-type thermocouple placed close to the sample. CCl_4 was injected in 10 μL pulses every 10 min alone or along with the desired amount of water (CCl_4:H_2O molar ratio = 1:2.5 or 1:1.25) into the carrier gas stream in the heated zone of the reactor. For FTIR analysis of the gaseous products, fixed amounts of the eluting gases after each pulse were transferred into a pre-evacuated gas IR cell equipped with KBr windows. The transfer line connecting the reactor and the IR cell was maintained at ~150 °C using a heating tape. Conversion degree was calculated by comparison with spectra obtained from background experiments where no catalyst was used. $AlCl_3$, if formed, condensed on the outlet of the reactor and was collected at the end of each experiment.

In some chosen experiments, the eluting gas stream was allowed to bubble in a trap containing 3.0 mL of KI aqueous solution (1.5 M) where Cl_2, if formed, would oxidize the iodide to iodine. The iodine was titrated with 0.05 M aqueous solution of sodium thiosulfate to determine the amount of chlorine. The amount of HCl produced was determined by titrating the same solution with 0.5 M NaOH. $AlCl_3$, if formed, condensed at the top of the reactor, cold zone, and was identified by XRD. The reproducibility of the results was within 10%.

3. Results and discussion

3.1. Preparation and characterization of SG-Al_2O_3

Mesoporous high-surface-area alumina was obtained with a specific surface area in the range of 500–550 m^2/g. The average pore diameter was between 65 and 90 Å and the total pore volume was around 1.3 $cm^3\ g^{-1}$. The XRD analysis of SG-Al_2O_3 samples preheated at 500 °C showed no diffraction patterns indicating highly amorphous powder. Samples heated at 600 °C showed diffraction patterns matching that of γ-alumina.

3.2. Catalytic dechlorination reactions

SG-Al_2O_3 showed relatively low reactivity toward CCl_4 at 400 °C in the absence of water. Only the first 10-μL pulse completely decomposed and about 95% conversion was observed in the second pulse. As more CCl_4 was introduced, the conversion degree declined gradually. The products observed included CO_2, HCl, Cl_2, $COCl_2$ (phosgene), $AlCl_3$, and coke (as indicated by the gray-black color of the catalysts after reactions).

In the presence of water (1:2.5 CCl_4:H_2O molar ratio), SG-Al_2O_3 acted as a potential catalyst for the complete dechlorination of CCl_4 at 400 °C producing only CO_2 and HCl. In a study where water was not used in the first 10 pulses (a total of 100 μL CCl_4), the conversion degree declined as discussed above. After the 10th pulse, water was added with some pulses where those mixed with water almost completely decomposed while others without water only partially decomposed showing a pattern that was nicely reproducible as shown in Fig. 1. In other experiments where water was added with every CCl_4 pulse, complete decomposition continued until a CCl_4:Al_2O_3 molar ratio as high as 2.5 was reached. The results from similar experiments where Cl_2 and HCl were