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Novel tough catalyst supports for reactions involving HF

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Abstract

Metal fluorides are more stable than metals and metal oxides; therefore, no oxides can be applied as catalyst supports for the reactions in which hydrogen fluoride is involved. The authors observed that metal phosphates are not reactive to HF at higher reaction temperatures such as 973 K. Hence, the decomposition of $CClF_2CClF_2$ was studied over Pt-supported SiO_2, Al_2O_3, and $AlPO_4$-based catalysts. Hydrodehalogenation proceeded and CHF_2CClF_2 and C_2H_6 were formed as major products, small amounts of CHF_2CHF_2, CH_2FCClF_2, CH_2FCF_3, and CH_4 were also formed. Pt/SiO_2 was the most active; however, SiO_2 reacted with HF and the SiF_4 formed sublimated. Following these, Al_2O_3 was the most active; however, it reacted with HF to form AlF_3 and was deactivated. Similar hydrodehalogenation proceeded over $Pt/AlPO_4$ and $Pt/(CePO_4–AlPO_4)$. The crystal structure of these catalysts did not change during the catalytic reaction, although the reduction of specific surface areas (SSA) was observed. Therefore, $AlPO_4$ and Ce containing $AlPO_4$ are suitable as catalyst supports in reactions in which HF is involved. XPS showed that the electronic effects of $AlPO_4$ lie between that of SiO_2 and Al_2O_3. A good linear relationship is found to exist between the initial reaction rates per unit surface area of Pt metal supported on the supports and the binding energy of supported Pt. This suggests that the more cationic the Pt, the more easily it could abstract Cl^- from $CClF_2CClF_2$.

Keywords: $AlPO_4$; Catalyst support; Hydrogen fluoride; CFCs; Halogenated hydrocarbons

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1. Introduction

So far, several effective catalysts for the decomposition of chlorofluorocarbons (CFCs) have been studied. Reported catalysts are classified as (1) metal oxides: Al_2O_3, $SiO_2–Al_2O_3$ [1–3], $TiO_2–SiO_2$ [4–6], ZnO, V_2O_5, and Cr_2O_3 supported on γ-Al_2O_3, and $WO_3/Al_2O_3–ZrO_2$ [7–9]; (2) zeolites: H-Y and Na-Y zeolites, H-Mordenite [10–12]; and (3) others: H_2SO_4 supported on TiO_2 and supported on $CuSO_4$ [13], Fe_2O_3/active charcoal [1], and Au/Al_2O_3 [14]. Most investigations dealt with the catalytic activity and products distribution within a short duration; however, a decline in the activity was reported. Although the reason for the decline was not elucidated in the paper, halogenation of the components of catalysts is considered to be the cause of deactivation. This can be ascribed to the fact that, in the decomposition of CFCs, HCl, HF, Cl_2, and/or F_2 will be formed, since the Gibb's free energies of the fluorides are lower than those of the corresponding metal oxides and metals.

During the last few years, the authors have studied a number of metal phosphates and sulfates. We found that metal phosphates including $Zr_3(PO_4)_4$, $CePO_4$, and $AlPO_4$, especially Ce-added $AlPO_4$, are active during the decomposition of CFCs in the presence of water vapor [15–23]. $Zr_3(PO_4)_4$ and $AlPO_4$-based catalysts, in particular, showed a high activity and long catalyst life [24–32]. $AlPO_4$ was very stable and fluorination did not proceed in the presence of HF at 1000 °C.

In the case of hydrogenation of fluorine-containing compounds, HF is formed in the reaction. Metals and noble metals supported on the oxides such as SiO_2, Al_2O_3, and TiO_2, are well-known as catalysts for hydrogenation and

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hydrodefluorination of fluorine-containing hydrocarbons. These oxide supports will gradually fluorinate to the corresponding fluorides and deactivate if HF is formed in the reaction.

Metal phosphates have a strong resistance to reaction with HF; therefore, metal phosphates will be the effective catalyst supports for the reactions involving HF. The application of $AlPO_4$-based compounds to catalyst supports for the Pt catalyst in the hydrodehalogenation of $CClF_2CClF_2$ as a model reaction is studied in this paper.

2. Experimental

2.1. Preparation of catalysts

Aluminum phosphate was prepared by the precipitation method described below. An aqueous solution of 10 wt.% ammonium hydroxide was slowly added into an aqueous solution composed of stoichiometric amounts of aluminum nitrate (0.5 M) and 85% orthophosphoric acid, with constant stirring until the pH of the solution reached 4.5. The precipitate obtained was washed with pure water and filtrated. The powder obtained was pressed into a cylindrical form, crushed, and sieved into 14–32 mesh granules and finally it was calcined at 1000 °C for 5 h in air. Ce-added $AlPO_4$ was prepared using a solution containing Ce nitrate together with Al nitrate and phosphoric acid. Ce-added $AlPO_4$ was determined to be a mixture of $CePO_4$ and $AlPO_4$ by X-ray diffraction (XRD) (Rigaku RINT-2500HF system). The formed support was denoted as $CePO_4$–$AlPO_4$ (Ce/Al = 1/9) in this paper. $AlPO_4$-based supports were added to an aqueous solution of tetraammineplatinum nitrate, $[Pt(NH_3)_4](NO_3)_2$ (about 1.00 g/l), while the mixture was continuously stirred for 1 h; then the water was evaporated by a rotary evaporator. The obtained powder was calcined at 450 °C for 1 h. The powder was then pressed, crushed, and sieved to 16–32 mesh and was finally reduced by H_2 stream (30 cm^3/min) at 400 °C for 2 h in the reactor.

2.2. Experimental procedure

The catalytic reactions were carried out under atmospheric pressure using a continuous flow reaction system with a fixed-bed reactor, which is shown elsewhere [21]. The reaction conditions are depicted in the footnotes under the tables. The mixture of $CClF_2CClF_2$ and hydrogen was fed to a 16 mm diameter tubular flow reactor made of stainless steel. The reaction products were analyzed using a Shimadzu GC-14ATP gas chromatograph (GC) (thermal conductivity detector, TCD) with a Parapak Q column (4 mm i.d. × 7 m) and a molecular sieve 5 Å (4 mm i.d. × 3 m) column and a Shimadzu GCMS-QP5050A mass spectrometer. Analysis of the products by GC was carried out 1 h after reaching the required temperature. The standard concentration of gaseous feed is 4.0 mol% $CClF_2CClF_2$, 40.0 mol% H_2, and 56.0 mol% He; and the gas was fed to the catalyst bed at W/F = 5.4 g-cat s/cm^3.

2.3. Characterization of the catalysts

The XRD patterns were measured by a Rigaku RINT-2500HF system. The dispersion of supported Pt was determined by CO adsorption. The sample (0.60 g) in a He flow (30 cm^3/min) was heated to 500 °C and the flow was then changed to H_2; subsequently after 1 h, the sample was cooled to ambient temperature. The flowing gas was again changed to He and the CO pulse of about 4.0 μmol was introduced several times until no CO adsorption was observed. The specific surface areas (SSA) of the fresh and used catalysts were determined by the BET method (N_2 adsorption) using a Carlo Erba SORPTY-1750 analyzer. The specific surface areas of the Pt (1 wt.%)/$AlPO_4$ and Pt (1 wt.%)/$CePO_4$–$AlPO_4$ (Ce/Al = 1/9) catalysts were 67.9 and 26.9 m^2/g, respectively. XPS of the catalysts was measured with a Shimadzu ESCA-850.

3. Results and discussion

3.1. Catalytic activity of the Pt-supported catalysts for hydrogenation of $CClF_2CClF_2$

The activity valves of the hydrodehalogenation of $CClF_2CClF_2$ of Pt (0.5 wt.%) catalysts supported by four kinds of supports: SiO_2, Al_2O_3, $AlPO_4$, and $CePO_4$–$AlPO_4$ (Ce/Al = 1/9) are shown in Fig. 1 and the product distribution is shown in Table 1. As can be seen from the table, Pt/SiO_2 exhibited the highest activity. Reaction began at around 473 K and the conversion reached 91.8% at 573 K. The major products at 573 K were CHF_2CClF_2 (27.7%) and C_2H_6 (58.3%). Small amounts of CHF_2CHF_2, CH_2FCClF_2, CH_2FCF_3, and CH_4 were formed. When the temperature was increased to 623 K, the gas flow gradually decreased; then,

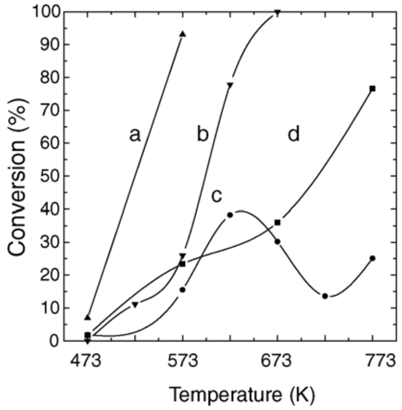

Fig. 1. Hydrodehalogenation of $CClF_2CClF_2$ over Pt catalysts supported on various supports: (a) Pt/SiO_2, (b) Pt/Al_2O_3, (c) Pt/$AlPO_4$ and (d) Pt/$CePO_4$–$AlPO_4$, Pt: 0.5 wt.%.