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Preparation of highly active AlSBA-15-supported platinum catalyst for thiophene hydrodesulfurization

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Abstract

The catalytic activities of various noble metals (Pt, Pd, Rh, and Ru) supported on siliceous SBA-15 and Al-containing SBA-15 (AlSBA-15) for hydrodesulfurization (HDS) of thiophene at 350 °C were investigated. AlSBA-15 was prepared by a grafting method using aluminum isopropoxide ($Al(OC_3H_7)_3$) hexane solution. The HDS activity of Pt/AlSBA-15 catalyst was the highest among those of various supported noble metal catalysts, and this activity was higher than that of commercial $CoMo/Al_2O_3$ HDS catalyst. The catalysts were characterized by XRD analysis, hydrogen adsorption, 2-propanol dehydration, cumene cracking, and FT-IR. Dispersion of Pt on SBA-15 was remarkably enhanced by Al grafting. It was revealed that the acidity of AlSBA-15 was higher than that of SBA-15. Furthermore, Brønsted acid sites were observed on AlSBA-15. FT-IR spectra of thiophene adsorbed on AlSBA-15 indicate that thiophene molecules interact with Brønsted acid sites on the surface of AlSBA-15 and that the strength of this interaction was stronger than that of SBA-15. Based on these results, thiophene molecules activated on Brønsted acid site of AlSBA-15 and hydrogen molecules activate to form spillover hydrogen on Pt particles in Pt/AlSBA-15 catalyst in the HDS of thiophene.

Keywords: Acid rain prevention; Hydrodesulfurization; Thiophene; SBA-15; Noble metal catalyst

1. Introduction

The damage to nature and environment by acid rain on a global scale is a serious problem. Sulfur oxides (SO_x) are produced by combustion of organic sulfur compounds in petroleum and coal used for boilers and engines of power plants and cars. Hydrodesulfurization (HDS) of petroleum feedstock is an important process in the petroleum industry to produce clean fuels [1–4]. However, recently, the development of highly active HDS catalysts, which exhibit higher activity than commercial $CoMo/Al_2O_3$ HDS catalysts, have been claimed in the petroleum industry to produce fuels with lower sulfur content [5,6]. It has been accepted that noble metal catalysts are potentially new HDS catalysts for petroleum [7–12]. The authors have also investigated the development of highly active noble metal HDS catalysts supported on zeolites [13–15,22].

Recently, mesoporous silicates such as FSM-16, MCM-41, and SBA-15, which have larger pore diameters and higher surface areas than zeolites, have attracted wide attention as new materials for catalysts and catalyst supports. Some attempts have been made to develop new HDS catalysts based on mesoporous silicates [16–19]. In previous papers, we have reported that noble metals, especially platinum, supported on mesoporous silicates such as FSM-16 [20] and MCM-41 [21,22], showed high activity in the HDS of thiophene, and noble metals supported on mesoporous silicates can potentially be used as new HDS catalysts for petroleum feedstock. Furthermore, the catalytic activity of Pt/MCM-41 for the HDS of thiophene was enhanced by Al-modification of the MCM-41 surface and Brønsted acid sites in Pt/Al-modified MCM-41 catalyst play an important role in the HDS of thiophene [23,24]. Generally, the Brønsted acid site of mesoporous silicate is generated by incorporation of Al atoms into the silicate framework. Mesoporous silica

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SBA-15, which has a larger pore diameter than MCM-41, can be synthesized using triblock copolymer and strong acidic media. However, because the Al source dissolves in strong acidic media when used in the synthesis of SBA-15, direct incorporation of Al atoms into the framework of SBA-15 is not efficient. Thus, it is expected that the catalytic activity of Pt/SBA-15 for HDS reaction is enhanced by alumination of siliceous SBA-15 support using aluminum isopropoxide.

In the present work, we examined the catalytic performance of noble metals supported on SBA-15 and AlSBA-15 for the HDS of thiophene to develop highly active mesoporous silicate catalyst for HDS of petroleum feedstock. Furthermore, we studied the reaction mechanism in the HDS of thiophene over highly active Pt/AlSBA-15 catalyst.

2. Experimental

2.1. Preparation of catalysts

Siliceous SBA-15 was prepared by conventional hydrothermal process, described earlier [38,39] using tetraethoxysilane ($Si(OC_2H_5)_4$, Aldrich Chemical Co.), triblock copolymer (poly(ethylene glycol)$_{20}$–poly(propylene glycol)$_{70}$–poly(ethylene glycol)$_{20}$, Dai-ichi Kogyo Seiyaku), and hydrogen chloride (HCl, Kanto Chemical Co.). The solid product was washed by water followed by drying at 100 °C and calcination in air at 557 °C for 8 h. AlSBA-15 (Si/Al = 15) was prepared by a grafting method using aluminum isopropoxide ($Al(OC_3H_7)_3$ (Kanto Chemical Co.)) dry hexane solution at room temperature for 24 h. The obtained sample was washed by dry hexane and was calcined at 400 °C for 2 h. Addition of sodium to AlSBA-15 support was also performed by an impregnation method using sodium hydroxide (NaOH, Wako Pure Chemical Industries) aqueous solution. After sodium impregnation, Na-added AlSBA-15 (Na–AlSBA-15) was dried at 120 °C and was calcined at 500 °C for 4 h. Supported noble metal catalysts were also prepared by an impregnation method using noble metal chloride ($H_2PtCl_6\cdot 6H_2O$, $PdCl_2$, $RhCl_3\cdot 3H_2O$, $RuCl_3\cdot 3H_2O$, Kanto Chemical Co.) aqueous solution; the amount of noble metal loading was 5 wt.%. $PdCl_2$ was dissolved in 1.0 mol l^{-1} HCl aqueous solution because $PdCl_2$ did not dissolve completely in water. After impregnation, the samples were dried at 120 °C followed by calcination at 500 °C for 4 h. The supported noble metal catalysts were treated by helium stream at 500 °C for 1 h and were reduced by hydrogen at 450 °C for 1 h before the reaction.

2.2. Hydrodesulfurization of thiophene

HDS of thiophene was performed at 350 °C under 0.1 MPa by a conventional fixed-bed flow reactor. Thiophene was introduced into the reactor by passing hydrogen (30 ml min^{-1}) through a thiophene trap cooled at 0 °C. Reaction conditions were as follows: catalyst weight = 0.1 g, H_2/thiophene = 30 mol mol^{-1}, W/F = 37.9 g h mol^{-1}. The reaction products were analyzed by gas chromatograph (FID) equipped with silicone DC-550 (2 m, 150 °C) and VZ-7 (4 m, 0 °C) columns, respectively. We used $CoMo/Al_2O_3$ (Nippon Cyanamid Co.) as a reference catalyst.

2.3. Characterization of catalysts

2.3.1. Nitrogen adsorption isotherm

The nitrogen adsorption isotherm at −196 °C was measured by using Micromeritics ASAP 2000. The specific surface areas of SBA-15 and AlSBA-15 were calculated by the BET method and the pore size distributions by the BJH method.

2.3.2. Dispersion of platinum

The dispersion of platinum on SBA-15 and AlSBA-15 was measured by XRD and hydrogen adsorption. XRD was performed using a Rigaku diffractometer with Cu Kα radiation. Adsorption of hydrogen on the supported Pt catalyst was performed using a glass vacuum system at 25 °C. The supported Pt catalysts were evacuated at 500 °C for 1 h followed by reduction with hydrogen (26.7 kPa) at 450 °C for 1 h and evacuation at the same temperature for 1 h before hydrogen adsorption.

2.3.3. Acidities of SBA-15 and AlSBA-15

The acidities of SBA-15 and AlSBA-15 were evaluated by 2-propanol (2-PA) dehydration (200 °C) and cumene cracking (400 °C) using a pulse reactor with helium carrier gas. In both reactions, catalysts (0.03 g) were charged into the reactor and were pretreated at 500 °C for 1 h before the reaction. 2-PA or cumene (0.2 μl) was introduced into the reactor using a microsyringe. The reaction products of 2-PA dehydration and cumene cracking were separated using a silicone DC-550 (2 m, 130 °C) column and a PEG-1000 column (2 m, 80 °C), respectively. However, the reaction products of 2-PA dehydration were trapped by liquid nitrogen and were flashed by boiling water before the separation. After the separation, the reactant and products were analyzed by thermal conductivity detector (TCD).

2.3.4. Measurement of FT-IR spectra

FT-IR spectra of pyridine and thiophene adsorbed on SBA-15 and AlSBA-15 were observed using a Jasco FT-IR spectrometer. The catalysts were evacuated at 500 °C for 2 h before the measurement.

3. Results and discussion

3.1. Textural properties of SBA-15 and AlSBA-15

The textural properties of SBA-15 and AlSBA-15 were characterized by XRD and nitrogen adsorption. In the XRD pattern of SBA-15, an intense peak at 0.92° and low-intensity peaks at 1.64° and 1.90°, which were attributed to a hexagonal structure, were observed (Fig. 1). After Al grafting, the XRD pattern of AlSBA-15 was the same as that of siliceous SBA-15. Fig. 2 shows the nitrogen adsorption isotherms of SBA-15 and AlSBA-15. SBA-15 shows that the amount of nitrogen adsorption sharply increased in the range of relative