Catalysis Letters 61 (1999) 83–87

Cobalt-containing smectite-like mesoporous material as a new type of catalyst for hydrodesulfurization of thiophene

Masahiko Arai [a,*], Yui Minato [a], Kazuo Torii [b] and Masayuki Shirai [a]

[a] Institute for Chemical Reaction Science, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan
[b] Tohoku National Industrial Research Institute, Nigatake, Miyagino-ku, Sendai 983-8551, Japan

Received 12 March 1999; accepted 27 May 1999

Cobalt-containing mesoporous smectite-like material (SM(Co)) was prepared by a hydrothermal method and used as a catalyst for hydrodesulfurization (HDS) of thiophene. It is active by itself and produces mainly butenes and a small amount of n-butane. When platinum is added to this material, the HDS activity is enhanced by 50%, while the product distribution does not change so much. The platinum-loaded sample should have two types of active sites, one originally present in the smectite-like material and the other with platinum, the latter being different in nature from a sample of platinum supported on silica gel. Thus, the SM(Co) and Pt/SM(Co) samples are new types of HDS catalysts.

Keywords: hydrothermal synthesis, smectite, hydrodesulfurization, thiophene

1. Introduction

Mesoporous materials like FSM-16 [1] and MCM-41 [2] are interesting components for heterogeneous catalysts [3]. The porosity of these materials is so well organized that they can have narrow pore size distribution. Previously, we developed a hydrothermal method to synthesize mesoporous smectite-like materials [4–6]. Compared with FSM-16 and MCM-41 these synthetic smectite-like materials can have wide variations in the chemical composition and porosity depending on precursors and synthetic conditions. They can include different di- and trivalent metal cations in the lattices of their octahedral sheets. In addition, some synthetic smectite-like materials are stable at high temperatures up to 600 °C. These features make them to be good catalysts with and without additional active components like platinum and palladium. They have been demonstrated to be solid acid/base catalysts in 2-propanol decomposition [7], acetonitrile hydrogenation [8], and butene isomerization [9], size-selective catalysts in hydrogenation of NBR polymer [10], and multifunctional catalysts in butane hydrogenolysis and ethylene hydrogenation [11].

In the present work, we have prepared a cobalt-containing mesoporous smectite-like material and applied it for thiophene hydrodesulfurization (HDS). It has been found that the material itself is active and produces butenes with a small amount of n-butane. The activity increases by loading platinum with ion exchange and hydrogen treatment; however, the selectivity does not change so much. The catalytic performance is compared with those of silica-supported cobalt and platinum catalysts and cobalt-loaded catalyst with smectite-like material including magnesium for cobalt in the octahedral sheet. Recently, Hayashi et al. used several commercially available smectite-like materials as supports for cobalt catalysts [12], in which cobalt was loaded from outside, in contrast to our catalyst in which cobalt is introduced during the preparation of the smectite-like material and where it exists in the inner lattice of the octahedral sheet. They reported higher thiophene HDS activities of cobalt catalysts supported on smectite clay minerals compared with an alumina-supported catalyst. In the literature there are a number of works on HDS reactions, as described in some recent reviews [13–15]. We will report the performance of new types of HDS catalysts in this communication.

2. Experimental

2.1. Catalyst preparation

Cobalt-containing smectite-like material was prepared in similar procedures as used previously [4–6]. A water glass ($SiO_2/Na_2O = 3.22$) solution (60 ml) was mixed with a sodium hydroxide solution (1 M, 45 ml). A cobalt chloride solution (1.5 M, 60 ml) was added dropwise to this solution while stirring the mixture, producing a Co–Si precipitate, in which the Si : Co atomic ratio was adjusted to 8 : 6 by using the desired volumes and concentrations of those solutions. After filtration and washing with water, water was added again to the precipitate and the pH of this slurry was adjusted to 6.1 by adding sodium hydroxide solution. Then the slurry was thermally treated in an autoclave under autogaseous pressure at 200 °C for 2 h. The material obtained was dried under dynamic evacuation at 80 °C for 5 h and calcined in air at 300 °C for 1 h. This sample was observed to have a surface are of 380 m^2/g, a total

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[*] To whom correspondence should be addressed.

pore volume of 0.34 ml/g, and an average pore diameter of 3.6 nm from nitrogen adsorption and desorption measurements.

As shown later, this cobalt-containing material has smectite-like structure, and it will be abbreviated with SM(Co). In addition, magnesium-containing smectite-like material (SM(Mg)) prepared in similar procedures and a porous silica gel (Aldrich Davisil grade 646 SiO_2) were also used for comparison. The surface area, total pore volume, and average pore diameter were 485 m^2/g, 0.40 ml/g, and 3.3 nm for SM(Mg) and 300 m^2/g and 1.15 ml/g for the porous silica gel (from Aldrich's catalog book and no data for the pore diameter). These materials were used as catalysts and supports.

Cobalt was loaded to SM(Mg) and SiO_2 by wet impregnation using a cobalt acetate solution. The supports were kept immersed in the precursor solution overnight and the solvent was removed by evaporation at 50 °C under reduced pressure. The cobalt-loaded samples were then calcined in air at 500 °C for 3 h. Platinum was loaded to SM(Co), SM(Mg), SiO_2 and Co/SiO_2 by ion exchange using a tetraammine platinum dichloride solution. These were immersed in the precursor solution at pH 11 for several days while shaking. After decantation, the samples obtained were dried in air at room temperature and then under vacuum at 120 °C for 3 h.

2.2. Thiophene HDS

A fixed-bed flow quartz reactor was used to conduct HDS reactions at atmospheric pressure. A weighed amount of catalyst (about 0.1 g) was treated by passing pure hydrogen at the desired temperature for 3 h and the reaction was started by introducing a reaction mixture of thiophene (2.9 vol%) and hydrogen through the catalyst bed at 22 ml/min. The reaction was first conducted at 350 °C for a few hours until the rate of reaction became stable. Then the reaction was conducted at different temperatures between 350 and 450 °C, and the rate of reaction was determined at 5 min after the catalyst sample reached the desired temperature. The reaction temperature was changed randomly by heating and cooling the sample, and reproducible results were obtained at the same temperatures. The reaction products were analyzed by an online gas chromatograph with flame ionization detector. The amounts of hydrocarbons were measured but not hydrogen sulfide.

2.3. Characterization

The structure of materials synthesized was examined by X-ray diffraction (XRD) with Cu Kα or Fe Kα X-ray beam, extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES). These EXAFS and XANES measurements were carried out at the BL-10B station (Si(311)) of Photon Factory of High Energy Accelerator Research Organization at Tsukuba. The detailed procedures of EXAFS measurements are described elsewhere [11].

3. Results and discussion

Figure 1 shows typical time profiles of HDS reactions at 350 °C for SM(Co) and 5 wt% Co-loaded SiO_2 samples treated with H_2 at 400 °C. One can see stable conversion and product distribution from the start of reaction for these two samples and this was also common to the other samples prepared. Under the reaction conditions used, only C_4 hydrocarbons were observed to form.

Table 1 compares the catalytic performance of various samples prepared, which were treated with H_2 at 400 °C. It is interesting that SM(Co) is active by itself, in contrast to SM(Mg) and SiO_2 that are practically inactive. The activity of SM(Co) is much higher than those of the Co-loaded SiO_2 and SM(Mg) samples and it is also more active compared with the 1 wt% Pt-loaded SiO_2 sample. The SM(Co) sample produces mainly butenes with a minor product of n-butane, similar to the Co-loaded samples. It is significant from a practical point of view that unsaturated C_4 hydrocarbons are the main products. The addition of Pt in 1 wt% enhances the activity of SM(Co) by about 50%, while it does not change the product distribution so much. The product distribution with Pt/SM(Co) as well as SM(Co) is very different from that of Pt/SiO_2 giving a saturated C_4 hydrocarbon, n-butane, as a main product. The addition of Pt indicates the same effect on the activity of the Co/SiO_2 sample. Table 1 also includes apparent activation energies (E_a) for those samples. SM(Co) is similar to Co/SM(Mg)

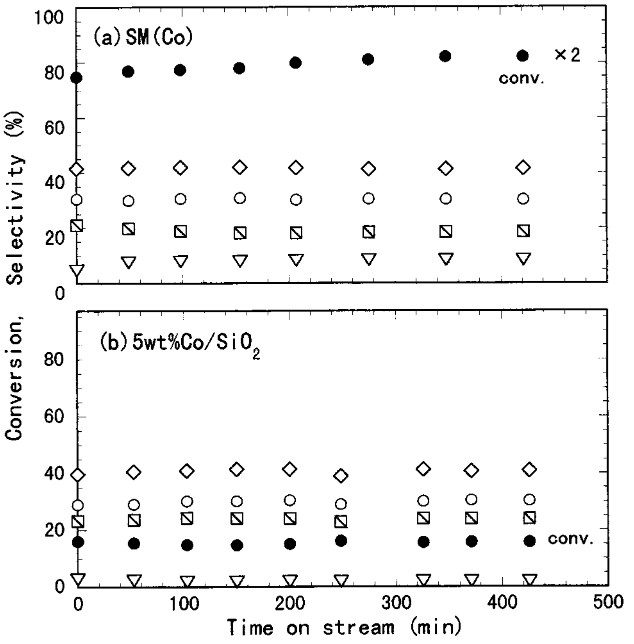

Figure 1. Typical time course of thiophene HDS reactions at 350 °C for (a) SM(Co) and (b) 5 wt% Co-loaded SiO_2 samples after the treatment with H_2 at 400 °C. (●) Conversion, (◇) *trans*-2-butene, (○) *cis*-2-butene, (⧅) 1-butene, (▽) n-butane.

Table 1
Results of HDS reactions of thiophene over various catalysts.

Catalyst	Conversion[a] (%)	Selectivity[a] (%)				E_a[b] (kJ/mol)
		n-butane	1-butene	*Trans*-2-butene	*Cis*-2-butene	
SM(Co)	41	8	18	42	30	18.9 ± 8.5
1%Pt/SM(Co)	60	15	17	39	28	11.4 ± 1.3
SM(Mg)	in[c]	–	–	–	–	–
5%Co/SM(Mg)	25	6	21	42	30	17.9 ± 7.0
SiO_2	<1	–	–	–	–	–
5%Co/SiO_2	16	2	24	41	30	26.8 ± 5.7
35%Co/SiO_2	23	5	23	41	30	22.4 ± 3.1
1%Pt/SiO_2	36	80	4	8	6	32.1 ± 2.0
1%Pt/35%Co/SiO_2	40	10	20	40	30	22.2 ± 6.4

[a] Data at 350 °C.
[b] Apparent activation energy measured from 350 to 450 °C with 90% confidence limit.
[c] Inactive.

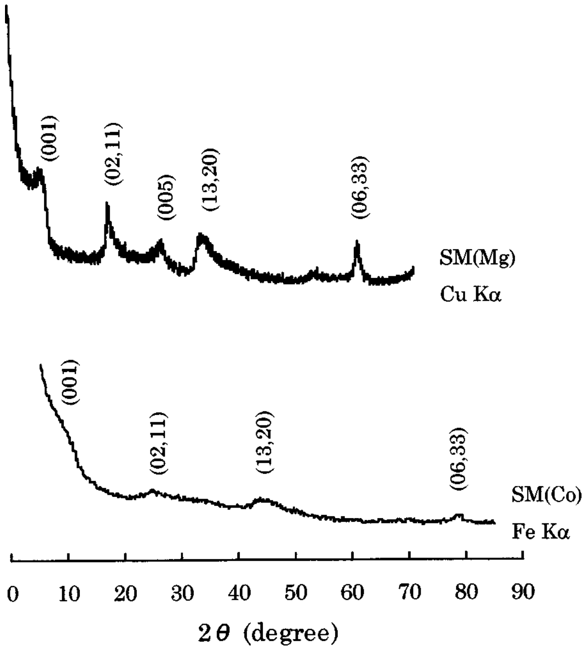

Figure 2. XRD patterns of SM(Co) and SM(Mg) samples.

but Pt/SM(Co) is different from the other samples. The E_a values of SM(Co) and Pt/SM(Co) are smaller than those of Co/SiO_2 and Pt/SiO_2; Pt/SM(Co) shows the smallest E_a value, which is small as compared with the values reported with other conventional monometallic and bimetallic catalysts using alumina and silica supports [14]. For Co/SiO_2, the addition of Pt does not change the E_a value.

Figure 2 shows XRD patterns for the SM(Co) and SM(Mg) samples prepared. These patterns are characteristic to smectite clay minerals [4–6], demonstrating that the two samples have the smectite-like structure. The degree of crystallization is not high and they include small and large crystal fragments of smectite-like structure. It is believed that smaller fragments function as pillars and these samples can be mesoporous materials. We also made XRD measurements after HDS reactions but no appreciable changes were observed.

Figure 3 shows XANES and EXAFS results for SM(Co) and reference samples. For Fourier transforms of Co K-edge EXAFS oscillations with SM(Co), one can see oxygen at the nearest position of 1.5 Å and cobalt in the next neighborhood at 2.6 Å, while direct Co–Co bonds are not seen. This spectrum of SM(Co) is different from those of Co metal and oxides but it is similar to synthetic Ni-containing smectite-like material as reported previously [11]. Figure 4 compares the EXAFS and XANES results for SM(Co) before and after HDS reaction. For the used SM(Co), the first peak shifts to a longer distance and the intensity of the second peak decreases, the spectrum being similar to that of CoS. Thus, the Co–S bond is likely to form during the reaction, but bulk CoS was not produced, as indicated by XRD measurements.

Although active sites of SM(Co) and Pt/SM(Co) as well as Co/SM(Mg) are not identified at present, we can mention the following. The HDS reaction should proceed through the adsorption of thiophene with its sulfur onto some sites of a catalyst. The SM(Co) sample does not have Co species that can be exposed and make direct contact with foreign gas molecules. The Co cation is present in the center of the octahedron. However, a foreign molecule like thiophene may be adsorbed in the hole in the triangular face comprising three oxygen atoms (some may be replaced with a hydroxyl group) of the octahedron. It may have interaction with Co and this would cause the formation of Co–S bonds, as strongly suggested by EXAFS results. Such catalytic sites should be present in a significant quantity for this material because its degree of crystallization is low and it has many edge faces. The Pt/SM(Co) sample is similar to SM(Co) in the product distribution but different in the total activity and E_a value. One possibility is that the addition of Pt produces additional active sites, the nature of which is different from those of SM(Co) and Pt/SiO_2. Those additional active sites with Pt should be effective for desulfurization of thiophene and the following hydrogenation into butenes but not for the complete hydrogenation into butanes. For Co/SiO_2, the addition of Pt also increases its activity but it does not affect the prod-

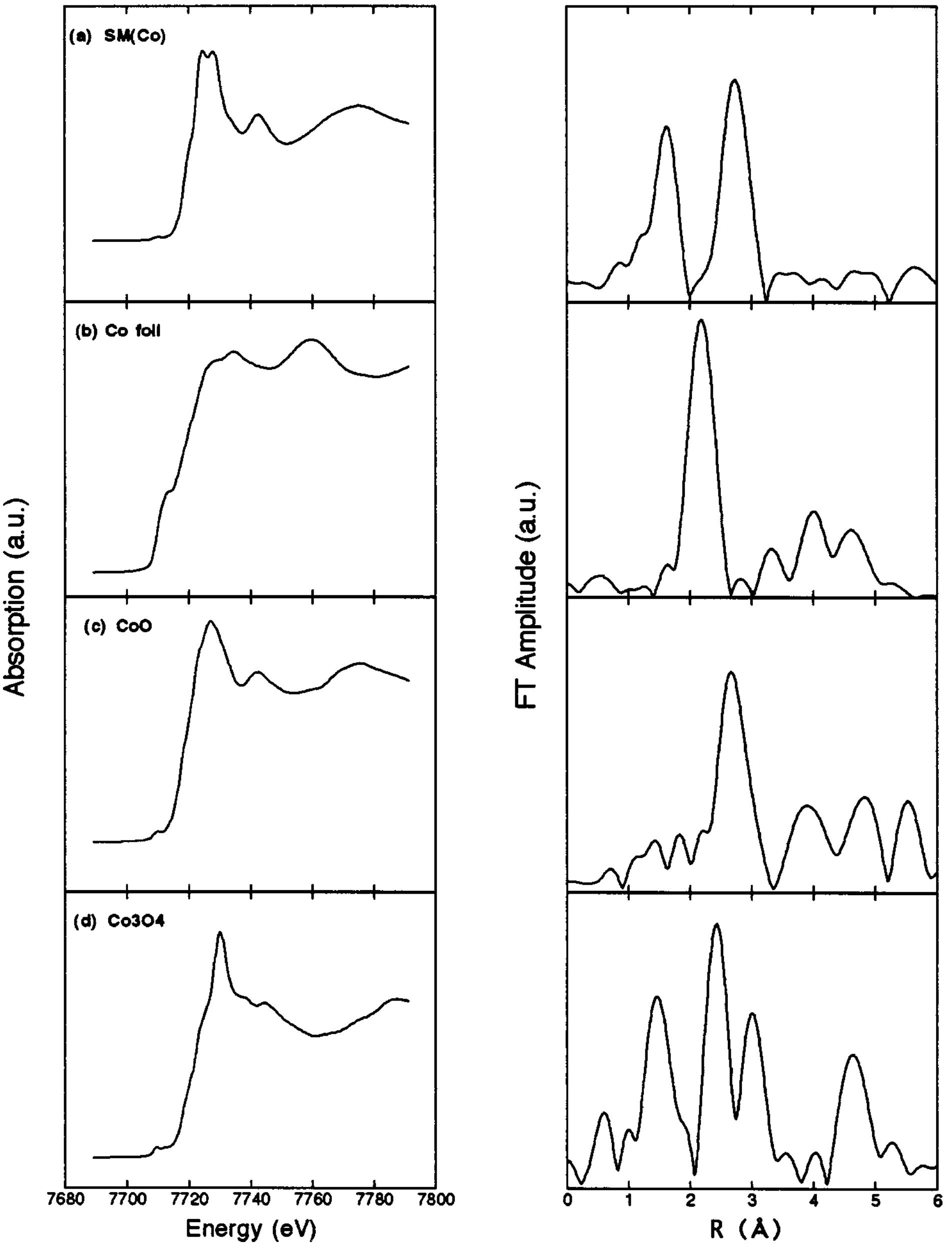

Figure 3. Co K-edge XANES spectra and Fourier transforms of the k^3-weighted Co K-edge EXAFS of SM(Co) and reference samples of Co metal, CoO and Co_3O_4.

uct distribution and activation energy. Thus one can assume that the addition of Pt increases the number of active Co species. Further research is now in progress to clarify those active sites for HDS catalysts of new types, SM(Co), Pt/SM(Co) and Co/SM(Mg) samples, by several spectroscopy techniques.

4. Conclusion

Synthetic Co-containing smectite-like material is an active catalyst for thiophene HDS reaction. This catalyst produces mainly butenes with n-butane as a minor product. The addition of Pt enhances its activity but does not influence the product distribution so much. In Pt-loaded catalyst, Pt may be additional active sites; however, these sites are different in nature from Pt/SiO_2, which gives n-butane as a main product.

Acknowledgement

The authors are thankful to Kuriko Aoki for her help during this study. This work was supported in part by Research for the Future Program of JSPS under the Project "Synthesis of Ecological High Quality of Transportation Fuels" (JSPS-RFTF98P01001). This work was carried out in part under the approval of the Photon Factory Advisory Committee (No. 97G022).

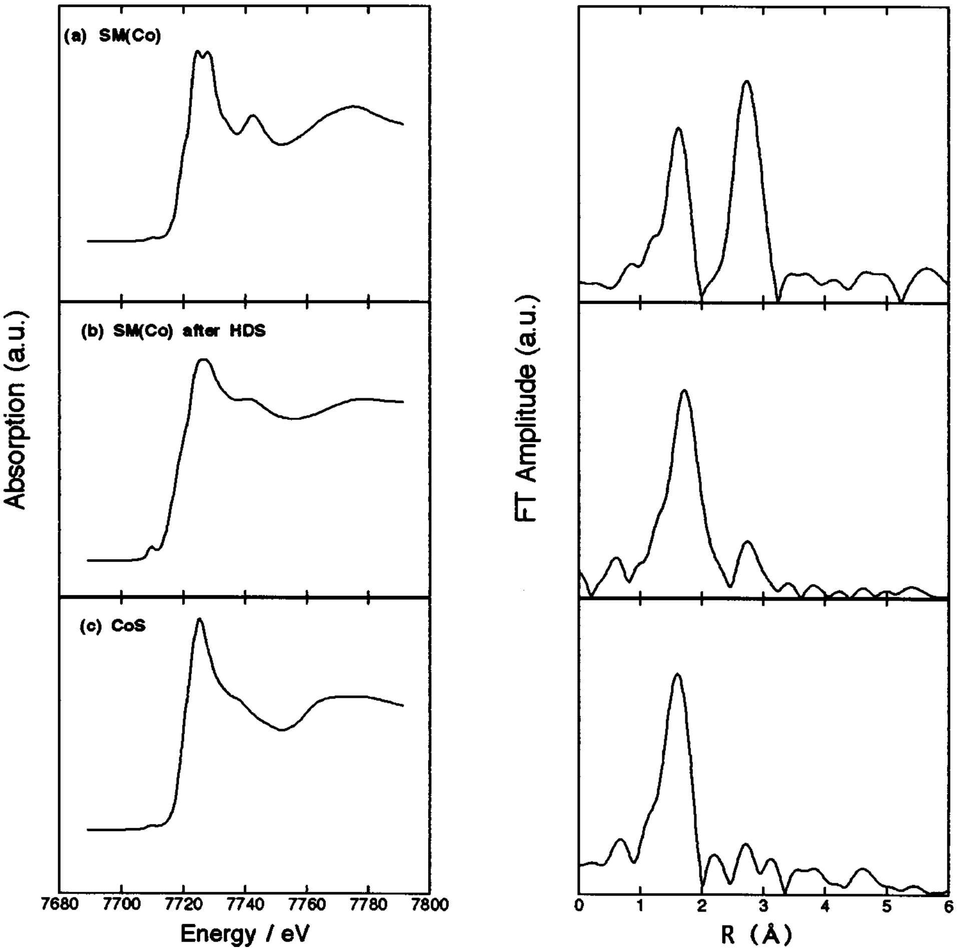

Figure 4. Co K-edge XANES spectra and Fourier transforms of the k^3-weighted Co K-edge EXAFS of SM(Co) before and after HDS reaction at 350 °C and a reference sample of CoS.

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