Remarkable Enhancement of Catalytic Activity of FSM-16 by Modification with Ammonium Sulfate for Acid-Catalyzed Reactions

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Impregnation of FSM-16 with ammonium sulfate followed by optimized thermal pretreatments, especially by evacuation, leads to a remarkable enhancement in the catalytic activity of FSM-16 for acid-catalyzed reactions.

Recently, the synthesis of new materials such as MCM-41,[1] FSM-16,[2] SBA-15,[3] HMS,[4] etc. has become the focus of considerable interest. In view of the fact that these mesoporous materials exhibit relatively low acidity and as such insufficient activity for acid-catalyzed reactions, it is highly desirable to generate active acid sites. So far, the main mode for achieving this aim has been the isomorphous substitution of framework silicon with heteroatoms such as Al,[1] Ga,[5] Fe,[6] and so on. In addition, the method of grafting of various active moieties such as metal alkoxides onto mesoporous silica surface has been reported.[7]

In our previous work, a novel route for transforming mesoporous silica FSM-16 into an active catalyst by sulfiding with hydrogen sulfide after metal ion-exchange was reported.[8] We have also reported the remarkable enhancement of FSM-16 for 1-butene isomerization by the modification with iron (II) sulfate.[9] In this study, we report on the catalytic activity enhancement of FSM-16 by modification with ammonium sulfate for acid-catalyzed reactions.

The $[NH_4]_2SO_4$/FSM-16 catalyst was prepared by impregnating FSM-16 with a solution of ammonium sulfate to obtain a 5 wt% $[NH_4]_2SO_4$ loaded sample. The sample was then dried at 100 °C for 2 h followed by two pretreatment methods (viz: A and B). Method A involved calcination at 100-500 °C for 3 h in air, while in method B, the catalyst was evacuated at 200-500 °C for 2 h after calcination at 200 °C. Isomerization of 1-butene and cyclopropane were conducted in a closed-circulation reactor system made of Pyrex glass at 25 °C and 100 °C, respectively. In both cases, the initial pressure of reactant was 40 Torr (5.33kPa) while the catalyst weight was 50 mg. Product analysis system consisted of a gas chromatograph equipped with a TCD and a 4 m propylene carbonate column cooled at 0 °C. Thermogravimetric/differential thermal analysis (TG/DTA) and infrared (IR) spectroscopy of adsorbed pyridine were employed for characterization of the catalysts.

The catalytic activities of $[NH_4]_2SO_4$/FSM-16 (A and B) for 1-butene isomerization are shown in Figure 1. It can be observed that the catalysts prepared by method A exhibit maximum activity after calcination at 300 °C which is comparable to those of FSM-16. On the other hand, a remarkable increase in activity of catalysts prepared by method B was seen after evacuation at 300 °C and it was quite close to the value obtained for the $FeSO_4$/FSM-16 described in our previous paper.[9] Almost similar results were obtained in the isomerization of cyclopropane.

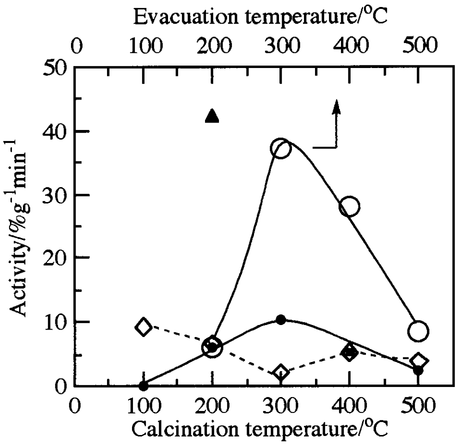

Figure 1. Activity of FSM-16 and $(NH_4)_2SO_4$/FSM-16 (A and B) for 1-butene isomerization at 25 °C.
● $(NH_4)_2SO_4$/FSM-16 (A) ○ $(NH_4)_2SO_4$/FSM-16 (B)
▲ $FeSO_4$/FSM-16 ◇ FSM-16

The TG/DTA profiles recorded for the unsupported $[NH_4]_2SO_4$, FSM-16 and $[NH_4]_2SO_4$/FSM-16 are presented in Figure 2. The TG profile for $[NH_4]_2SO_4$ reveals two steps of weight losses, one around 300 °C and the other near 400 °C. The first step, which is accompanied by an endothermic DTA peak, can be attributed to the evolution of the ammonia from $[NH_4]_2SO_4$. The second step mainly involves the decomposition of the sulfate anion. The TG profile for FSM-16 shows a weight loss below 120 °C which is due to the desorption of

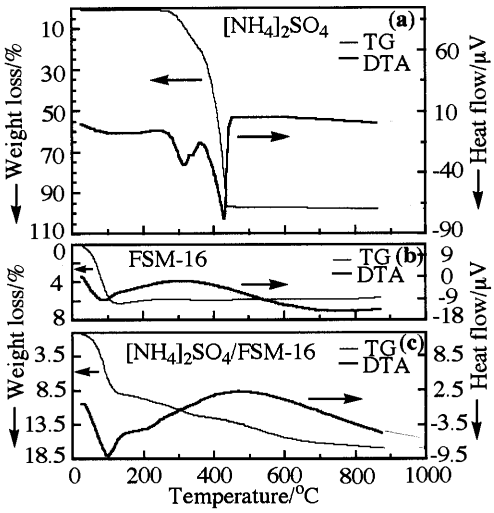

Figure 2. TG/DTA profiles.

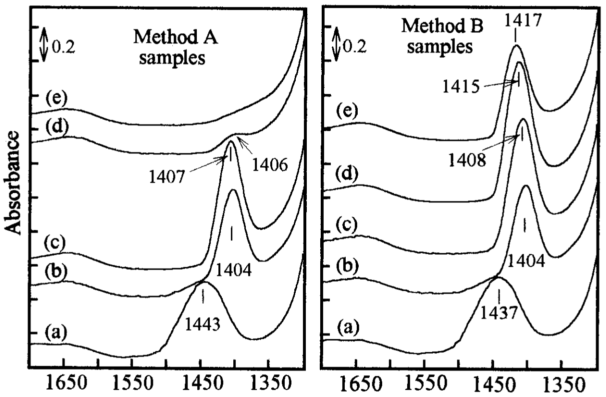

Figure 3. IR spectra of the SO_4^{2-} region of $(NH_4)_2SO_4$/FSM-16 (A and B). Evacuated at (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, and (e) 500 °C for 2 h each. (Methods A and B as described in text.)

adsorbed water. The supported sample exhibits an initial loss in weight similar to that of FSM-16, but it shows further decrease in weight as the temperature increases. It is evident that the rate of weight loss above 300 °C is much more slower for $[NH_4]_2SO_4$/FSM-16 than the unsupported $[NH_4]_2SO_4$. This indicates the relatively gradual decomposition of the salt in the supported form.

Figure 3 depicts the IR spectra of $[NH_4]_2SO_4$/FSM-16 (A and B). Absorption bands in the 1400-1415 cm^{-1} region were observed for both A and B samples thermally pretreated at 200-400 °C. These bands are assignable to the asymmetric stretching vibration of S=O bond of the sulfate species.[10] The sample calcined at 100 °C shows a very broad band centred around 1443 cm^{-1}, while a similar band is observed at 1437 cm^{-1}. The bands may be attributed to the bending vibration band of NH_4^+.[11] This assignment is supported by the presence of broad bands in the 3000-3300 cm^{-1} region (spectra not shown) associated with the N-H stretching vibrations. It was noted that increasing calcination temperature caused the disappearance of the broad band while the 1400 cm^{-1} region bands appeared. This can be related to the gradual decomposition of the supported salt which proceeds by initial removal of ammonia. The S=O peak intensity reached a maximum at 300 °C, after which it sharply decreased in the case of the method A catalysts. As shown, after calcination at 500 °C, no visible peak ascribed to sulfate species is observed.

In contrast, the evacuation of $[NH_4]_2SO_4$/FSM-16 (B) at even higher temperatures, for example, 500 °C, did not result in the complete disappearance of the S=O band (compare spectra (d) and (e) of A with the corresponding ones of B in Figure 3.) This suggests that direct calcination of $[NH_4]_2SO_4$/FSM-16 in air facilitates the decomposition of the $[NH_4]_2SO_4$ above 300 °C. Thus the thermal stability of the SO_4^{2-} species heated in vacuum is much higher than when calcined in air.

Figure 4 shows the spectra of adsorbed pyridine on (method A and B) catalysts after pyridine desorption by evacuation at 100 °C for 30 min. Bands were observed at 1547, 1490 and 1446 cm^{-1} in both cases. The 1547 cm^{-1} peak is attributed to the pyridinium ion associated with Brønsted acid site whilst 1446 cm^{-1} corresponds to coordinated pyridine at Lewis acid site. Thus both Brønsted acid sites and Lewis acid sites are present on $[NH_4]_2SO_4$/FSM-16. It was observed that in both cases (i.e., for A and B) the Brønsted acid band was much more intense than the Lewis acid band.

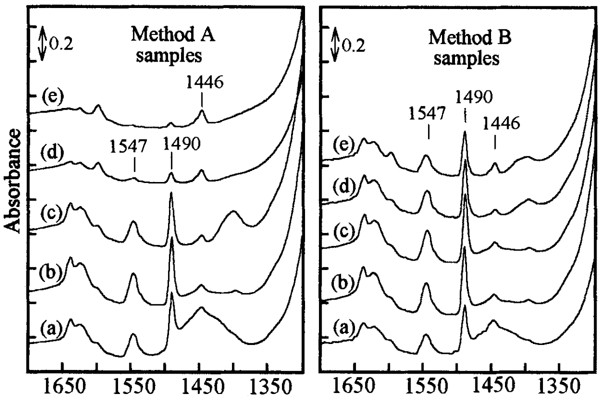

Figure 4. IR spectra of adsorbed pyridine on $(NH_4)_2SO_4$/FSM-16 (A and B) after desorption at 100 °C for 30 min. Evacuated at (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, and (e) 500 °C for 2 h before adsorption.

Among the method B catalysts, the sample evacuated at 300 °C exhibited the largest Brønsted acid peak. This sample also showed a relatively larger peak than its counterpart prepared by method A. These observations are partially in correlation with the catalytic activity for the 1-butene isomerization reaction especially, for the samples pretreated at 300 °C and above.

Calcination of $[NH_4]_2SO_4$/FSM-16 at 200 °C followed by evacuation at 300 °C markedly leads to enhanced catalytic activity for 1-butene and cyclopropane isomerization. Similar to our previous report,[9] it is assumed that the high activity is due to sulfate species so produced which interact with the SiOH group of FSM-16 and transform them into Brønsted acid sites by their inductive effect.

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