Sulfated Zirconia in SBA-15 Structures with Brønsted Acidity as Observed by ^{1}H MAS NMR Spectroscopy

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Introduction

Owing to the environmental restrictions throughout the world, non-polluting and atom-efficient catalytic technologies are much important now. The use of highly corrosive, hazardous and polluting mineral acids, such as HF and H_2SO_4 is commonly employed in the today's petrochemical and refinery industries.

In an effort to replace those acids, zirconium oxide, or zirconia, when modified with sulfate ions, forms a highly acidic or superacidic catalyst that exhibits superior catalytic activity that can activate C-C and C-H bonds of alkanes at relatively mild conditions. Thus, S-ZrO_2 and modified S-ZrO_2 form an important class of catalysts.

The commercial zirconia has a rather low surface area of 50 m^2/g or even less. Inclusion of sulfated zirconia in the mesoporous silicas provides a proper catalyst for many industrially important acid catalyzed reactions. The combination of silica and zirconia, not only increases the surface area of zirconia, but also improves the acidity by providing a fine distribution of acid sites in the silica framework.

In this study we report liquid like acidity of the high surface area sulfated zirconia in the mesoporous silica (SBA-15) structure. SBA-15 type mesoporous materials have higher stability than other mesoporous silicas due to their thicker walls, which enables the introduction of other metals into the framework. The sulfated zirconia incorporated SBA-15 type catalysts were prepared at different zirconia loadings (5-30 mol%ZrO_2). Zirconia was introduced in the form of $ZrOCl_2 \cdot 8H_2O$ during the preparation of SBA-15 and calcined at 500°C. Subsequent sulfation introduced superacidic character to the material. Catalysts were characterized by XRD, BET, and TEM. Besides, the effect of the inclusion of sulfated zirconia to SBA-15 on the acidic properties was investigated by means of ^{1}H MAS NMR.

Materials and Methods

Pure SBA-15 was prepared according to literature.[1] In the preparation of the ZrO_2 included SBA-15, the zirconia was introduced at an appropriate amount simultaneously with silicon source in the form of $ZrOCl_2 \cdot 8H_2O$ during the preparation of SBA-15. The catalysts were calcined in air flow at 500 ˚C for 5h. Finally, the sulfated catalysts were prepared by sulfating in a 0.25 M H_2SO_4 solution.

Results and Discussion

BET results indicate that the preparation of 5 mol % ZrO_2 loading with high surface area (313m^2/g) was accomplished. XRD results showed the formation of ZrO_2 crystals after 25mol% loading. In other words, the ZrO_2 crystals are finely distributed in the mesoporous silica framework up to this loading. TEM images revealed that even at 15mol% ZrO_2 loading the mesoporous hexagonal structure of SBA-15 was retained.

Figure 1a, 1c shows the ^{1}H MAS NMR spectra of the SBA-15 samples with zirconia and without zirconia. A sharp ^{1}H resonance line at 10.6 ppm was observed in the ^{1}H MAS NMR spectra of the samples including zirconia after sulfation (Figure 1 d). This signal is close to the acid signal observed in liquid superacids. This seems to support the idea that sulfated zirconia is not only an oxidant but also a good proton donor, a controversial subject in catalysis. The relative intensity of this line exhibited a maximum with zirconia loading at 25 mol% ZrO_2, which coincided with the appearance of the crystalline zirconia phases in the XRD results. Further increase in zirconia content resulted in a decrease in the intensity of the acid line at 10.6 ppm. Thus, there is an optimum for ZrO_2 loading between 15 and 25%.

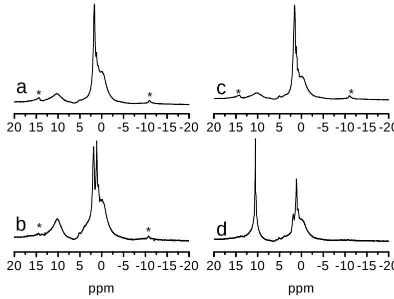

Figure 1. ^{1}H MAS NMR taken at Avance-400 with MAS spinning frequency of 5 kHz at 300 K for dehydrated a) SBA-15, b) sulfated SBA-15, c) SBA-15 with 5% ZrO_2, d) sulfated SBA-15 with 5% ZrO_2. * stands for the spinning side bands. The ppm scale is with respect to liquid TMS.

Significance

Our measurements on hydrated and dehydrated sulfated zirconia included SBA-15 samples have clearly revealed the formation of superacid proton sites. Thus, they are promising catalysts for the industrial applications where strong acidity is essential in hydrocarbon conversion reactions.

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References

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