1 of 1

100-1-11-177 JUL 13 1993 100-1-11-177 100-1-11-177

LOW SEVERITY UPGRADING OF F-T WAXES WITH SOLID SUPERACIDS

Quarterly Report

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SUMMARY:

During the last quarter ZrO_2/SO_4 based catalysts containing Pt, Ni, and Mn/Fe metals were characterized by in situ FT-IR. A mixed oxide catalyst, $\text{Pt}/\text{ZrO}_2/\text{HfO}_2/\text{SO}_4$, was studied using a temperature programmed desorption (TPD) technique. Using in situ FT-IR analysis, a peak at $1370\text{--}1385\text{ cm}^{-1}$, believed to be associated with the structure of the active sites, was detected upon evacuation of moisture. The shift of this peak after pyridine adsorption is a measure of the acid strength of the solid superacids. The larger the shift, the greater is the acid strength since this shift is caused by strong interactions between the basic pyridine and acid sites. The acid strength of ZrO_2/SO_4 based catalysts containing Pt, Ni, and Mn/Fe were compared in relation to their performance in isomerization and hydrocracking of long-chain paraffins. The generation and elimination of protonic acid sites in response to the presence of molecular hydrogen were observed by monitoring the IR spectra of adsorbed pyridine. By heating in the presence of molecular hydrogen, Bronsted acid sites were generated and Lewis acid sites weakened. It is likely that platinum is responsible for the dissociation of molecular hydrogen to generate protonic acid sites, the remaining hydride ions attach to Lewis acid sites.

The isomerization and hydrocracking of n-pentane were examined by in situ FT-IR. It was found that the intensity of protonic acid sites was weakened as n-pentane was introduced into the IR cell, indicating that protonic acid sites tend to donate a proton to n-paraffins. There was no evidence of olefinic intermediates. It is likely that, as we previously proposed, isomerization and hydrocracking over $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ catalyst proceed through initial protonation of n-alkanes to form carbonium ions which are then isomerized and hydrocracked.

EXPERIMENTAL:

The design of an in situ FT-IR analytical system was reported last quarter. The acid strength of a series of ZrO_2/SO_4 based catalysts was measured in this system. A self-supported catalyst wafer (0.1 mm) placed in an IR cell with CaF_2 windows was pretreated at 150°C for 2 hours in a flow of He. After cooling the sample to room temperature in the presence of He, the IR cell was evacuated for 30 minutes to remove He and moisture. The sample wafer was then exposed to pyridine at 150°C for 20 minutes followed by evacuation for another 30 minutes. The amount of pyridine introduced into the IR cell can be controlled and measured. All IR spectra were recorded on a Mattson NU-10000 infrared spectrometer (Mattson Instruments, Inc.).

The approximate amount of protonic acid sites and Lewis acid sites on the catalyst surface was determined from the absorbance of bands at 1450 cm^{-1} and 1490 cm^{-1} , attributed to pyridine chemisorbed on Lewis acid sites and Bronsted acid sites, respectively. The resolution of the IR instrument is 4 cm^{-1} . The spectra were collected at different time intervals to identify the transformation of surface intermediates.

TPD experiments were performed using a modified GC instrument (Varian 3300). Before introducing the sample, the catalyst was dried at 400°C for one hour. The amount of pyridine adsorbed was controlled by adjusting the temperature of the saturator. After adsorption, the He flow was continued for an additional 30 minutes to remove excess adsorbate. The cell temperature was then raised at a rate of 15 K min^{-1} to 900 K. The desorbed gases were analyzed by a thermal conductivity detector.

RESULTS AND CONCLUSIONS:

Characterization of Acid Strength of ZrO_2/SO_4 Based Catalysts by In Situ FT-IR

It is difficult to measure the acidity and acid strength of ZrO_2/SO_4 based catalysts by Hammett indicators since they are colored. The TPD technique has been applied to characterization of ZrO_2/SO_4 based catalysts^[1]; it provides a quantitative measure of the number of acid sites (acidity). The acid strength is the potential of the acid sites, determined by their abilities in donating a proton or withdrawing an electron. TPD cannot furnish accurate information about acid strength since the desorption spectra for ZrO_2/SO_4 based catalysts are too broad. To remedy this, an in situ FT-IR technique was used to measure the acid strength of the catalysts at cell temperatures in order to relate acid strength with catalytic activity.

It is known that moisture has a strong influence on the catalytic activity of ZrO_2/SO_4 based catalysts^[2]. As shown in Figure 1, the $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ catalyst shows a strong absorption at 1616 cm^{-1} , ascribed to the bending vibration of $-\text{OH}$ in water. In the presence of water, four absorption bands are observed at 1208 , 1137 , 1048 and 981 cm^{-1} , but no absorption is identified in the region of 1250 cm^{-1} - 1400 cm^{-1} . On raising the temperature to 150°C , an absorption at 1336 cm^{-1} appears and gradually shifts to 1370 cm^{-1} . It is reported^[3] that this strong absorption at 1370 cm^{-1} is typical of the highest oxidation state of sulfur, S^{6+} . We believe that the surface sulfur species represented by the 1375 cm^{-1} band is responsible for the high catalytic activity in the acid-catalyzed reaction. This spectral change indicates that the removal of molecular water has resulted in a structural transformation from a chelating complex to an inorganic sulfate.

About 90% of water originally present on the $\text{Pt}/\text{ZrO}_2/\text{SO}_4$ catalysts can be removed by heating in the presence of He for two hours. The $\text{S}=\text{O}$ band always appears from 1370 cm^{-1} to 1390 cm^{-1} depending on the composition of the catalyst. The position of this peak varies

slightly, but the intensity and the changes of this peak may be related to acidity or acid strength of solid superacids. We found that the peak at 1370 cm^{-1} shifted to a lower wave number after pyridine adsorption. IR spectra of pyridine adsorbed on the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst followed by purging with He are shown in Figure 2; the $\text{S}=\text{O}$ band at 1378 cm^{-1} shifts to 1338 cm^{-1} after the catalyst is exposed to pyridine. The shift is caused by the strong interaction of pyridine with the $\text{S}=\text{O}$ bond resulting in blocking of the acid sites. The shifts are quite different for different catalysts. It is reasonable to postulate that the larger the shift, the greater the acid strength. As a result, the acid strength of ZrO_2/SO_4 based catalysts was estimated by measuring the extent of the shift after pyridine adsorption.

As shown in Table 1, the ZrO_2/SO_4 catalyst exhibits the highest acid strength but lowest conversion for isomerization and hydrocracking of n-hexadecane because the catalyst is deactivated by coking. As expected, addition of platinum to ZrO_2/SO_4 decreases the acid strength but gives the highest activity for isomerization and hydrocracking of n-hexadecane. Obviously the presence of Pt promotes hydrogen transfer on the catalyst surface. The catalyst containing Mn and Fe exhibits a lower acid strength than $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst in keeping with its behavior in isomerization and hydrocracking of n-hexadecane. $\text{Ni/ZrO}_2/\text{SO}_4$ catalyst shows a similar acid strength to $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst but the activity is not comparable. This is due to the different abilities of Pt and Ni to dissociate molecular hydrogen and generate protons and hydride ions which help promote hydrogen transfer on the surface.

The IR spectra of $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst, on which pyridine has been adsorbed, followed by heating in the presence of hydrogen, are shown in Figure 3. Heating in the presence of molecular hydrogen caused the peak intensity at 1450 cm^{-1} (Lewis acid sites) to decrease, and the peak intensities at 1490 cm^{-1} (Bronsted + Lewis acid sites) and 1540 cm^{-1} (Bronsted acid

sites) to increase. The interaction between molecular hydrogen and Pt/ZrO₂/SO₄ caused an increase in the number of protonic acid sites on the surface. In contrast, for ZrO₂/SO₄ and Ni/ZrO₂/SO₄ catalysts, the ratio of Lewis to Bronsted acid sites remains constant during heating in the presence of hydrogen (Figures 4 and 5), confirming that Pt possesses a strong ability to dissociate molecular hydrogen to form H⁺ and H⁻. This property of protonic acid sites may allow us to control the surface acidic properties by adjusting the hydrogen pressure and Pt loading, thus controlling the catalytic activity. In practice, we do find that the catalytic activity of Pt/ZrO₂/SO₄ catalyst for isomerization and hydrocracking of long-chain paraffins increases markedly with increase in hydrogen pressure and Pt loading.

In situ isomerization of n-pentane was determined at 150°C in a microreactor; more than 60 wt% conversion to isopentane was achieved. As shown in Figure 6, a typical isoparaffin absorption at 2870 cm⁻¹ is observed immediately after n-pentane is introduced into the cell. It is interesting that protonic acid sites are weakened by an increase of intensity in isopentane absorption, indicating that protonic acid sites likely donate protons to n-pentane. In Figure 7, a new absorption band at 1464 cm⁻¹ is believed to be related to the reaction intermediates but its nature is still undetermined. It is clear that no olefinic intermediates are formed in the reaction. In addition, a slight shift of the S=O band from 1382 cm⁻¹ to 1475 cm⁻¹ indicates that n-pentane interacts with the active structure.

Characterization of Zirconium and Hafnium Bimetallic Oxides Catalysts By TPD

The Pt/HfO₂/SO₄ catalyst, expected to behave similarly to Pt/ZrO₂/SO₄ catalyst, gave lower conversions. However, the bimetallic oxides catalyst, Pt/ZrO₂/HfO₂/SO₄, exhibits different activities for isomerization and hydrocracking of long-chain paraffins, depending on the ratio of ZrO₂ to HfO₂ (Figure 8). XRD analysis has not revealed any interaction between

the two oxides. The crystalline structures of Pt/ZrO₂/HfO₂/SO₄ which have been identified are tetragonal ZrO₂ and HfO₂. We have found by TPD that an increase in the ratio of ZrO₂ to HfO₂ increases the number of acid sites (acidity) and is related to performance in isomerization and hydrocracking (Figure 8). The acid strength will be analyzed by in situ FT-IR in the near future.

FUTURE WORK:

The effect of olefins, hydride donors and water on superacid-catalyzed reactions will be studied using in situ FT-IR. The activities of various solid superacids will be related to their acid strength and acidity as measured by FT-IR and TPD.

A continuous flow fixed bed reactor will be used in kinetic studies of isomerization and hydrocracking of long-chain paraffins.

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Table 1. Comparison of the Acid Strength and Hydrocracking Activity of ZrO₂/SO₄ Based Catalysts Promoted with Different Metals

Catalyst	Activity, Conv. of n-C ₁₆	Acid strength, shift of S=O band after pyridine adsorption
ZrO ₂ /SO ₄	none, deactivated	1398 to 1330 cm ⁻¹ , 68 cm ⁻¹
Pt/ZrO ₂ /SO ₄	80.1 wt%	1378 to 1338 cm ⁻¹ , 40 cm ⁻¹
Mn, Fe/ZrO ₂ /SO ₄	none, deactivated	1370 to 1336 cm ⁻¹ , 34 cm ⁻¹
Pt/Mn, Fe/ZrO ₂ /SO ₄	66.2 wt%	-----
Ni/ZrO ₂ /SO ₄	27.5 wt%	1380 to 1334 cm ⁻¹ , 46 cm ⁻¹

Figure 1. Change in IR spectrum as sample is heated at 150°C with flow of helium. S=O band appears on removal of water.

Figure 2. The shift of S=O band of Pt/ZrO₂/SO₄ catalyst caused by pyridine adsorption (B=Bronsted, L=Lewis).

- (1) After preheating at 150°C under He for 60 minutes (1378 cm⁻¹).
- (2) Adsorption of pyridine for 20 minutes, 150°C (1338 cm⁻¹).
- (3) Adsorption of pyridine for another 10 minutes, 150°C (No S=O peak).
- (4) Desorption of pyridine on increase of temperature to 250°C.

Figure 3. The change of Bronsted/Lewis sites ratio on exposure to H₂.

Figure 4. The change in IR spectra due to S=O band of ZrO_2/SO_4 caused by pyridine adsorption.

- (1) After preheating at 150°C under He for 60 minutes.
- (2) Adsorption of pyridine for 20 minutes, 150°C .
- (3) Adsorption of H_2 for 20 minutes, 150°C .
- (4) Adsorption of H_2 for another 20 minutes, 150°C .
- (5) Desorption of pyridine on increase of temperature to 250°C .

Figure 5. The change in IR spectra due to S=O band of Ni/ZrO₂/SO₄ caused by pyridine adsorption.

Reaction conditions are the same as indicated in Figure 4.

Figure 6. The change in Bronsted/Lewis acid sites ratio over Pt/ZrO₂/SO₄ catalyst caused by introducing n-pentane.

Figure 7. The detection of reaction intermediate during isomerization of n-pentane pentane(150°C).

Figure 8. Upgrading of n-hexadecane with $\text{Pt}/\text{ZrO}_2/\text{HfO}_2/\text{SO}_4$ catalyst (160°C , 2.5MPa, 60 min). Acidity of the catalyst is indicated by the number next to the data point (mmol of pyridine adsorbed per gram of catalyst)

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