

Correlation between Acidic Properties of Nickel Sulfate Supported on TiO₂-ZrO₂ and Catalytic Activity for Acid Catalysis

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Solid acid catalysts play an important role in hydrocarbon conversion reactions in the chemical and petroleum industries.¹⁻³ The acidic property of metal sulfate often gives high selectivity for diversified reactions such as hydration, polymerization, alkylation, cracking, and isomerization.^{2,4} However, structural and physicochemical properties of supported metal sulfates are considered to be in different states compared with bulk metal sulfates because of their interaction with supports.⁵ Nickel sulfate catalysts supported on titania-zirconia have not been reported up to now. This paper describes the correlation between acidic properties of nickel sulfate supported on TiO₂-ZrO₂ and catalytic activity for acid catalysis. For the acid catalysis, the cumene dealkylation was used as a test reaction.

The coprecipitate of Ti(OH)₄-Zr(OH)₄ was obtained by adding aqueous ammonia slowly into a mixed aqueous solution of titanium tetrachloride and zirconium oxychloride (Ti/Zr = 1, Junsei Chemical Co.) at room temperature with stirring until the pH of mother liquor reached about 8. The catalysts containing various nickel sulfate (Junsei Chemical Co.) contents were prepared by adding an aqueous solution of nickel sulfate to the Ti(OH)₄-Zr(OH)₄ powder followed by drying and calcining at high temperatures for 1.5 h in air. This series of catalysts are denoted by their weight percentage of NiSO₄. For example, 10-NiSO₄/TiO₂-ZrO₂ indicates the catalyst containing 10 wt% NiSO₄.

FTIR spectra were obtained in a heatable gas cell at room temperature using Mattson Model GL6030E FTIR spectrophotometer. Cumene dealkylation was carried out at 400-450 °C in a pulse micro-reactor connected to a gas chromatograph. Fresh catalyst in the reactor made of 1/4 inch stainless steel was pretreated at 400 °C for 1 h in the nitrogen atmosphere. Packing material for the gas chromatograph was Benton 34 on chromosorb W and column temperature was 130 °C. Catalytic activity for cumene dealkylation was represented as mole of benzene converted from cumene per gram of catalyst. Conversion was taken as the average of the first to sixth pulse values.

The absorption of asymmetric stretching frequency of S=O bonds is commonly found in the range of 1360-1410 cm⁻¹. Infrared spectra of 20-NiSO₄/TiO₂-ZrO₂ after evacuation at 25-600 °C for 1 h are shown in Figure 1. There are sharp bands at 1350-1380 cm⁻¹ accompanied by four broad

but split bands at 1213-1215, 1100-1121, 1059-1073, and 995-1010 cm⁻¹, indicating the presence of two kinds of sulfated species. The bands at 1350-1380 cm⁻¹ corresponds to the asymmetric S=O stretching frequency of sulfate ion bonded to TiO₂-ZrO₂ under the dehydrated condition, while the latter four bands are assigned to bidentate sulfate ion coordinated to TiO₂-ZrO₂.^{6,7} These results are very similar to those of other workers.⁶⁻⁸ However, the frequency shift of this band is different depending on the evacuation temperature, as shown in Figure 1. At 25 °C an asymmetric stretching band of S=O bonds was not observed because the water molecules are adsorbed on the surface of 20-NiSO₄/TiO₂-ZrO₂.^{6,7} The bands at 1630 cm⁻¹ are due to the H₂O adsorbed on the surface. However, from 100 °C the band began to appear at 1350 cm⁻¹, and the band intensity increased with the evacuation temperature and the position of band shifted to a higher wavenumber up to 500 °C. However, at 600 °C the band intensity decreased without further band shift because of desorption of sulfate ion. It is likely that the

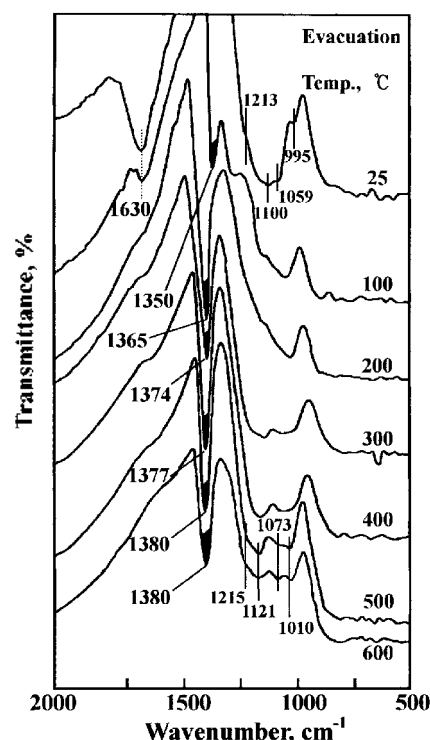


Figure 1. Infrared spectra of 20-NiSO₄/TiO₂-ZrO₂ evacuated at different temperatures.

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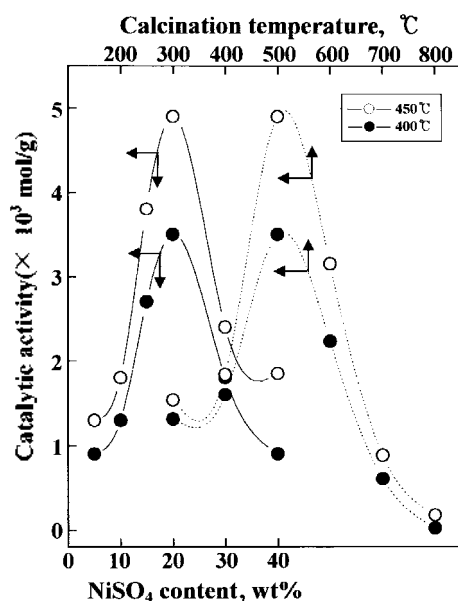


Figure 2. Variations of catalytic activity for cumene dealkylation as functions of NiSO_4 content and calcination temperature of 20- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$.

surface sulfur complexes formed by the interaction of oxides with sulfate ions in highly active catalysts have a strong tendency to reduce their bond order by the adsorption of basic molecules such as H_2O .^{6,7,9} Consequently, as shown in Figure 1, an asymmetric stretching band of S=O bonds for the sample evacuated at lower temperature appears at a lower frequency compared with that for the sample evacuated at higher temperature because the adsorbed water reduces the bond order of S=O from a highly covalent double-bond character to a lesser double-bond character. The strong ability of the sulfur complex to accommodate electron from a basic molecule such as H_2O is a driving force in generating superacidic properties.^{6,7,9} This superacidic property is attributable to the double-bond nature of the S=O in the formed by the interaction between NiSO_4 and $\text{TiO}_2\text{-ZrO}_2$.

It is interesting to examine how the catalytic activity of acid catalyst depends on the acidic property. The catalytic activities of catalysts calcined at 500 °C for the cumene dealkylation are measured and the results are illustrated as a function of NiSO_4 content in Figure 2, where reaction temperatures are 400-450 °C. In view of Table 1 and Figure 2, the variations in catalytic activity for cumene dealkylation are well correlated with the changes of their acidity measured by the ammonia chemisorption method,⁹ showing the highest activity and acidity for 20- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$. It has been known that cumene dealkylation takes place on relatively strong acid site of the catalysts.¹⁰ Good correlations have been found in many cases between the acidity and the catalytic activities of solid acids. For example the rates of both the catalytic decomposition of cumene and the poly-

Table 1. Acidity for $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$ containing different NiSO_4 contents and for 20- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$ calcined at different temperatures

Catalyst	Acidity, $\mu\text{mol/g}$	Calcination Temperature of 20- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$, °C	Acidity, $\mu\text{mol/g}$
$\text{TiO}_2\text{-ZrO}_2$	168	300	320
5- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$	243	400	335
10- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$	279	450	348
15- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$	347	500	356
20- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$	356	600	308
30- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$	329	700	130
40- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$	305	800	56

merization of propylene over $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts were found to increase with increasing acid amounts at strength $H_0 \leq +3.3$.¹¹ Catalytic activities of 20- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$ are also plotted as a function of calcination temperature for cumene dealkylation in Figure 2. The activities increased with the calcination temperature, giving a maximum at 500 °C and then the activities decreased. Comparing Figure 2 and Table 1, catalytic activity closely correlates to the acidity of 20- $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$ catalysts calcined at different temperatures and the asymmetric stretching frequency of S=O bonds. The decrease of catalytic activities above 500 °C can be probably attributed to the fact that the surface area and acidity above 500 °C decrease with the calcination temperature.

The existence of both Brønsted and Lewis acid site was shown by the infrared spectra of ammonia adsorbed on $\text{NiSO}_4/\text{TiO}_2\text{-ZrO}_2$.

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