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DOE/PC/91304--T8

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Quarterly Report

LOW SEVERITY UPGRADING OF F-T WAXES WITH SOLID SUPERACIDS

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Prepared for the Department of Energy
Grant No. DE-FG22-91PC91304
September 1, 1993, through November 30, 1993

January 31, 1994

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SUMMARY

During the last quarter we characterized the acidity of platinum-promoted solid superacids by TPD (temperature-programmed desorption) and investigated the effect of sulfate concentration on the activity of $Pt/ZrO_2/SO_4$ catalysts for isomerization and hydrocracking of n-hexadecane. The activities of Pt/ZrO_2 promoted by different anions (SO_4^{2-}, MoO_4^{2-} and WO_4^{2-}), to give $Pt/ZrO_2/SO_4$, $Pt/ZrO_2/MoO_4$ and $Pt/ZrO_2/WO_4$, were compared and the results related to their acidity and acid strength determined by TPD. TPD was an effective tool for the rapid evaluation of the acidity of metal-promoted solid superacids; this technique provided a good indication of the activity of the bifunctional solid superacids. The activity of the $Pt/ZrO_2/SO_4$ catalyst at 160°C was compared with a $Pt/\gamma\text{-}Al_2O_3$ reforming catalyst at 160°C and also at 400°C (350 psig H_2), respectively. The $Pt/\gamma\text{-}Al_2O_3$ catalyst was not effective at 160°C but gave a 6.2 wt% conversion of the n-hexadecane to isomerized and cracked products at 400°C.

The isomerization and hydrocracking of long-chain paraffins over metal-promoted solid superacids were carried out in the presence of selected aromatic compounds. It appears that the presence of aromatics changes the surface acidity of the catalyst, resulting in higher molecular weight products (from C_4-C_9 to C_{10}-C_{16}) from n-hexadecane. This finding is important in obtaining a more desirable product distribution from hydrocracking of F-T waxes.

EXPERIMENTAL

TPD Characterization

TPD experiments were performed using a fixed-bed reactor with a modified GC (Varian 3300) as detector. Before introducing the adsorbate, the catalyst was preheated at 450°C for one hour in dry air. The adsorptions were conducted by introducing pyridine into the reactor through a saturator at 160°C. He was used as carrier gas. After adsorption, the He flow was continued for an additional 20 minutes to remove excess pyridine. The reactor temperature was then raised at a rate of 10°C min^{-1} to 800°C, and maintained at this temperature for 10 minutes. The desorbed gases were analyzed by a thermal conductivity detector (TCD) and occasionally analyzed by GC-MS (HP-5970 II).

Effect of Sulfuric Acid Concentration on Activity of $Pt/ZrO_2/SO_4$ Catalysts

$Pt/ZrO_2/SO_4$ catalysts with different sulfate contents were prepared by sulfation of $Zr(OH)_4$ with various concentration of sulfuric acid. The $Zr(OH)_4$ was prepared by hydrolyzing aqueous solutions of $ZrOSO_4 \cdot 3H_2O$ with 28.5 wt% NH_4OH solution at room temperature. The precipitates were washed, dried at 100°C overnight and further treated by 0.5-6.0 N H_2SO_4 solution for one hour at room temperature using 15 ml of solution per gram of solid. Platinum was impregnated after sulfation. All the catalysts were then calcined at 600°C for three hours. The activity of these catalysts was measured by isomerization and hydrocracking of n-hexadecane at 160°C and 350 psig H_2 in a microreactor.

Anion-Modified Pt/ZrO_2 Catalysts

The procedures employed in the preparation of $Pt/ZrO_2/MoO_4$ and $Pt/ZrO_2/WO_4$ catalysts were similar to those employed in preparing the $Pt/ZrO_2/SO_4$ catalyst, except for the incorporation of MoO_4^{2-} and WO_4^{2-} ions. A $Pt/ZrO_2/WO_4$ catalyst was obtained by impregnating $Zr(OH)_4$ with aqueous ammonium metatungstate followed by removal of water at 110°C. Platinum was then impregnated and the catalyst calcined in air at 800-850°C for 2 hours. The $Pt/ZrO_2/MoO_4$ catalyst was obtained by impregnating $Zr(OH)_4$ with molybdic acid followed by impregnation with Pt and calcination in air at 650°C. The elemental Mo and W contents in the two catalysts were each 5.0 wt%.

A reforming catalyst, Pt/γ-Al_2O_3, containing 5.0 wt% of Pt was purchased from Aldrich Chemical, Inc. The catalyst was preheated at 400°C before reaction to remove physically adsorbed moisture.

RESULTS AND CONCLUSIONS

Characterization of the Acidity and Acid Strength of Metal-Promoted Solid Superacids

We define acidity and acid strength as follows: acidity is proportional to the number of acid sites while acid strength is the ability of a protonic acid site to donate a proton, or the ability of a Lewis acid site to attract electrons. We used TPD to measure both acidity and acid strength by relating them to the amount of pyridine desorbed and the temperature of desorption. We found that this was consistent with catalytic behavior in a microreactor.

A TPD spectrum for pyridine adsorption on $Pt/ZrO_2/SO_4$ is shown in Figure 1. An asymmetric peak at 230°C (within 200-300°C) was observed. This characteristic is consistent with in-situ FT-IR measurements. As shown in Figure 2, strong adsorptions of both Lewis (1491 cm^{-1}) and Bronsted acid sites (1548 cm^{-1}) appear upon saturation of $Pt/ZrO_2/SO_4$ catalyst with pyridine. The desorption of pyridine (decrease in peak intensity of the Lewis and Bronsted acid sites) starts at 200°C and is completed at 300°C. To assure that this peak is not generated by decomposition or from gases formed from the interaction between pyridine and catalyst, a gas sample was taken at 250°C during the TPD measurement. This sample was injected into a GC-MS (HP 5790 II) and found to contain only pyridine. The correspondence between TPD measurement and in-situ FT-IR analysis indicates that the TPD peak at around 230°C is an indication of the nature of Lewis and Bronsted acid sites. A small, broad and asymmetric peak at 430°C (within 350-490°C) was also observed. This suggests that the catalyst surface contains small amounts of nonuniform acid sites with higher acid strengths. GC-MS analysis showed that the gas sample taken at 450°C was a mixture of pyridine and SO_2, indicating that decomposition of sulfate groups begins at temperature near 450°C. It appears that the desorption temperature of the peak at (230°C) and its intensity are measures of acid strength and acidity of these metal-promoted solid superacids.

The catalytic isomerization and hydrocracking of n-hexadecane were used as test reactions to obtain a measure of the superacidic character of these anion promoted oxides; the results are summarized in Table 1. As expected, $Pt/ZrO_2/SO_4$, with both the highest acidity and acid strength, gives the highest conversion for hydrocracking of n-hexadecane. This correspondence between the acidity and activity indicates that TPD may be developed as an effective method to evaluate the superacidity of metal-promoted solid superacids.

Effect of the Concentration of H_2SO_4 on Catalytic Activity

It is generally believed that the strong acidity of sulfated solid superacids is generated from the induction effect of the SO_4^{2-} group in the catalyst. As shown in Figure 3, the sulfate contents of Pt/ZrO_2 treated with various concentrations of H_2SO_4 solutions do not change after calcination at 600°C for three hours. The activities of the $Pt/ZrO_2/SO_4$ catalysts treated with 1.0N to 4.0N sulfuric acid are almost the same. The decrease in activity for the sample treated with 6.0N sulfuric acid may be due to blocking of the surface with excess SO_4^{2-} during sulfation or modification of the catalyst caused by excess SO_4^{2-}.

Comparison of the Activity of $Pt/ZrO_2/SO_4$ and Pt/Al_2O_3 catalysts in Hydrocracking Paraffins

Pt/Al_2O_3 has been used commercially as a cracking and reforming catalyst. This catalyst is effective only at high temperatures (>500°C). We compared the activity of the $Pt/\gamma\text{-}Al_2O_3$ catalyst with platinum-promoted solid superacids at 160°C, and 350 psig. The results are summarized in Table 2. At 160°C, the $Pt/\gamma\text{-}Al_2O_3$ is inactive; however, about a 6.2 wt% conversion was observed at 400°C with $Pt/\gamma\text{-}Al_2O_3$ catalyst yielding cracked products containing normal and monobranched paraffins. At 160°C on a $Pt/ZrO_2/SO_4$ catalyst, an 83.8 wt% total conversion was reached and the products contained highly branched paraffins. Considering that both catalysts contain platinum, it is obvious that the acidity of ZrO_2/SO_4 plays a key role in hydrocracking of paraffins. The difference in product distribution obtained from the catalysts implies that the reactions occur through different pathways.

Effect of Aromatics on the Product Distribution from Hydrocracking of Paraffins

F-T waxes contain mainly paraffins with small amounts of olefins. It is well known that upgrading of paraffins on solid superacids involves carbocation intermediates. These carbocations may be captured by electron rich compounds such as aromatics. We found that paraffins alkylated aromatic rings , a reaction of great interest.

This finding led to an exploration of the effect on product distribution of the addition of aromatics to long-chain paraffins. The results are shown in Table 3. The presence of 5 wt% of toluene significantly inhibits isomerization and hydrocracking activity of the $Pt/ZrO_2/SO_4$ catalyst; total conversion drops from 75.4 wt% to 25.4 wt%. Evidently, the electron-rich toluene captures protonic acid sites responsible for hydrocracking of paraffins.

The presence of toluene changed the product distribution, giving a 52.2% selectivity to isohexadecane. Toluene weakens the acidity of the $Pt/ZrO_2/SO_4$ catalyst, preventing further cracking. In a batch reactor, the competitive adsorption of aromatics and paraffins on protonic acid sites is difficult to control; aromatics will occupy most of the protonic acid sites, inhibiting the protonation of paraffins. Use of a continuous flow fixed-bed reactor may give different results since the residence time of aromatics and paraffins on the catalyst surface can be monitored.

FUTURE WORK

ZrO_2, ZrO_2/SO_4 and $Pt/ZrO_2/SO_4$ derived from ZrO_2 aerogels synthesized under CO_2 supercritical conditions will be provided by Carnegie Mellon University and will be tested as catalysts for isomerization and hydrocracking of n-hexadecane. Their activity will be compared with $Pt/ZrO_2/SO_4$ catalysts prepared by conventional methods. These catalysts will be characterized by TPD and in situ FT-IR to gain insights into the nature of the acidity and acid strength of metal-promoted solid superacids.

TPD measurements will be continued with weak basic compounds such as benzene and xylene as adsorbents to probe surface acidities. The TPD measurement coupled with in-situ FT-IR analysis will be carried out to provide a better understanding of the chemistry occurring on metal-promoted solid superacids.

A kinetic model will be derived and fitted with experimental data. This model will be used to help define the reaction chemistry involved in isomerization and hydrocracking of long-chain paraffins.

Table 1. Effect of Anion Functional Groups on Catalytic Activity and Acidity of Pt/ZrO_2

Catalysts	n-C_{16} conversion (wt%)	Acidity (mol/g)	T_d^* (°C)
$Pt/ZrO_2/SO_4$	83.9	0.358	290.2
$Pt/ZrO_2/WO_4$	1.0	0.144	283.0
$Pt/ZrO_2/MO_4$	none	0.085	257.3

* Desorption temperature at maximum intensity.

Table 2. Comparison of Hydrocracking Activity of $Pt/ZrO_2/SO_4$ and Pt/γ-Al_2O_3 Catalysts

Catalysts	Reaction Conditions and Product Type	
$Pt/ZrO_2/SO_4$	160°C, 350 psig of H_2, 60 min, total conversion 83.8 wt%	Selectivity: (multibranched) C_4-C_9 71.2 C_{10}-C_{13} 18.6 iso-C_{16} 10.2
Pt/γ-Al_2O_3	160°C, 350 psig of H_2, 60 min, no conversion	-----
	400°C, 350 psig of H_2, 60 min, total conversion 6.2 wt%	Selectivity: (monobranched and normal) C_4-C_9 44.5 C_{10}-C_{14} 23.0 C_{16} 32.5

Table 3. Effect of Toluene on Product Distribution in Hydrocracking of n-hexadecane

Temperature		160°C
Pressure		350 psig
Reaction Time		60 minutes
Feed/Catalyst		6.0
	Product Distribution	
	Absence of Toluene	Presence of Toluene (5wt%)
Total Conversion	75.4 wt%	25.4 wt%
Selectivity:		
C_4-C_9	67.8	27.4*
C_{10}-C_{13}	23.4	20.4
iso-C_{16}	9.8	52.2

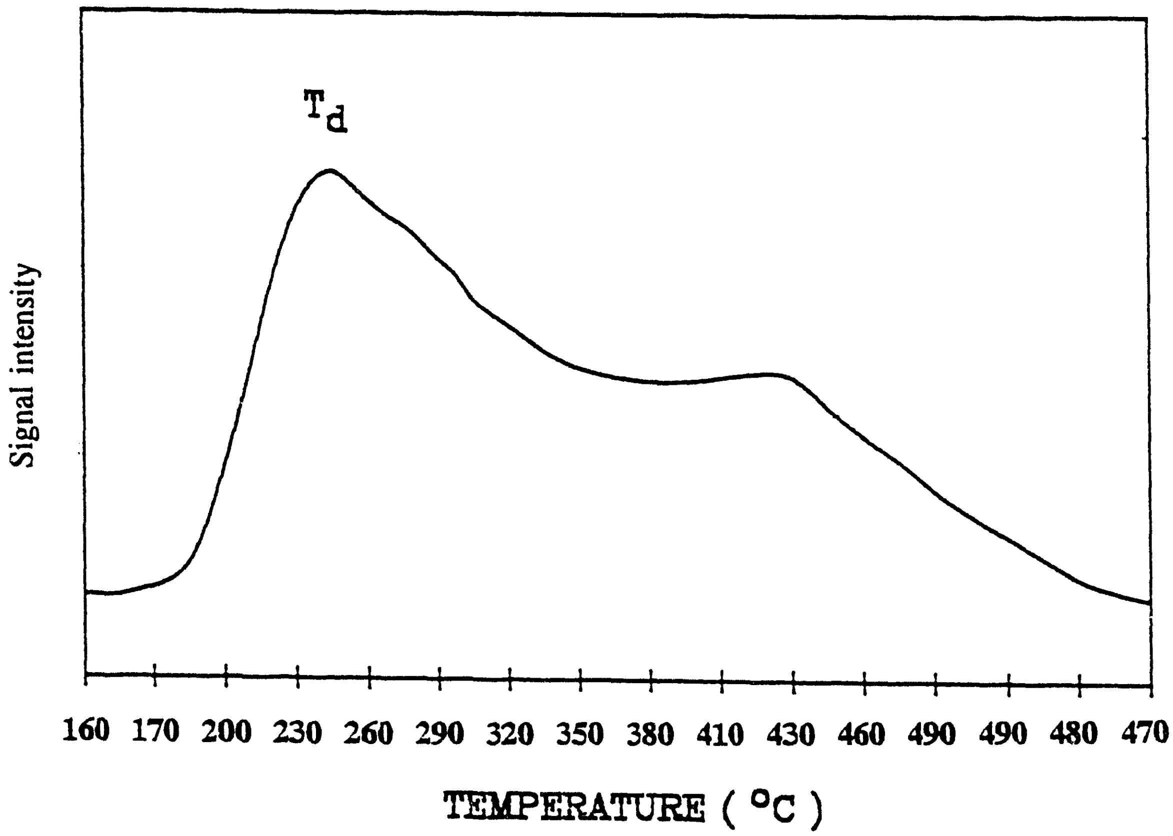

Figure 1. TPD spectrum of pyridine-adsorbed Pt/ZrO_2/SO_4 catalyst

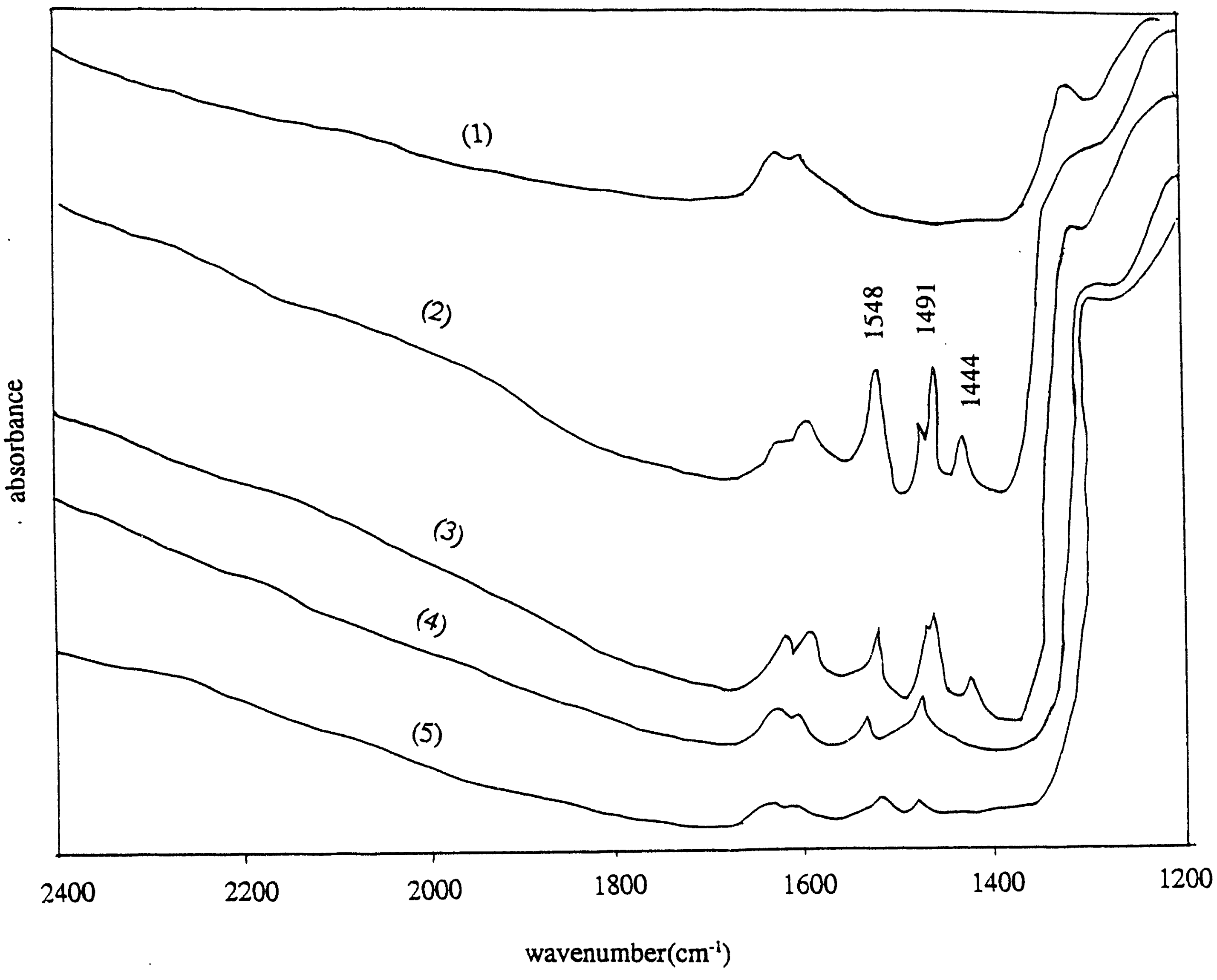

Figure 2. Desorption of pyridine from Pt/ZrO_2/SO_4 catalyst observed by in-situ FT-IR

(1) before introducing pyridine
(2) adsorption of pyridine at 150°C
(3) desorption of pyridine at 200°C
(4) desorption of pyridine at 250°C
(5) desorption of pyridine at 300°C

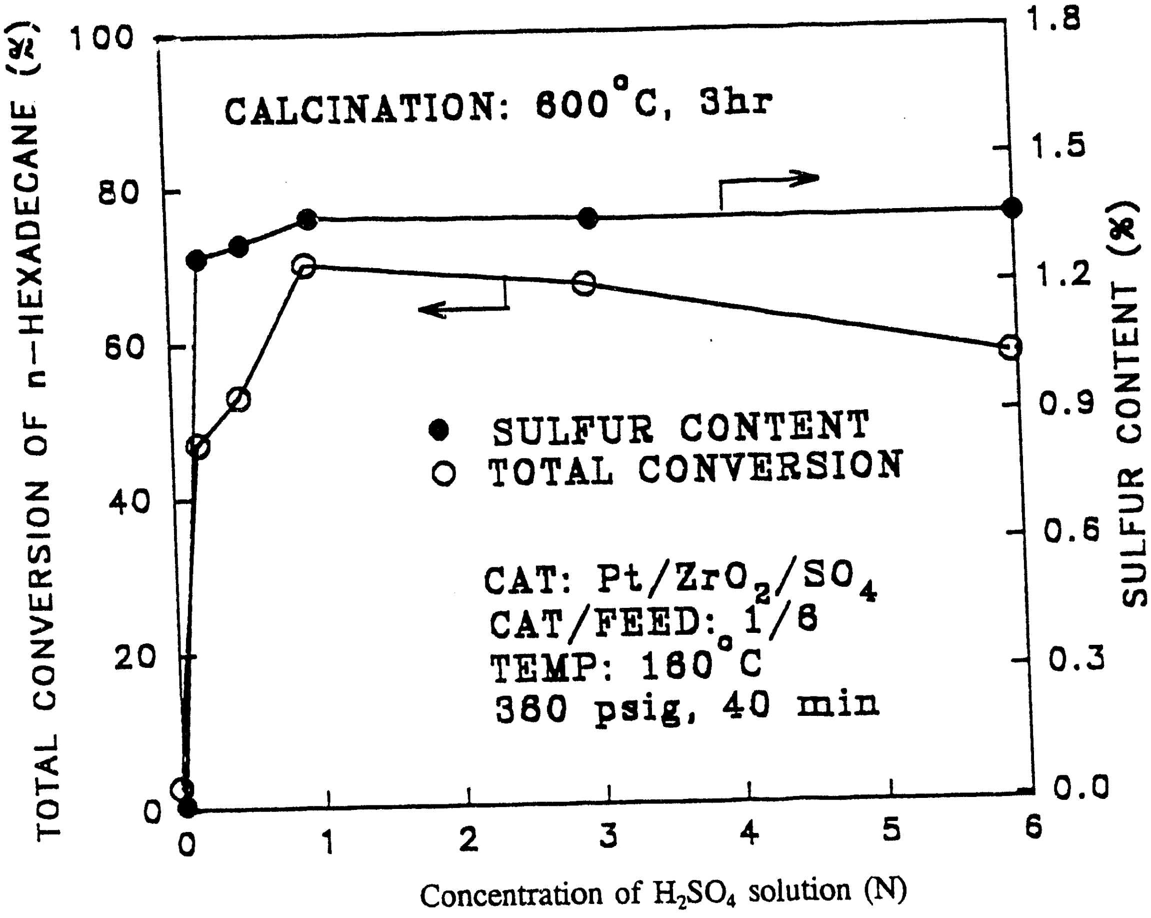

Figure 3. Effect of the concentration of sulfation solution on catalytic activity of $Pt/ZrO_2/SO_4$ catalyst

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