5.0 CATALYST CHARACTERIZATION

5.1 Objectives

The physical and acidic properties of the catalysts in **Table 3** were characterized in order to investigate the effects of the catalyst preparation conditions on their physical and acidic properties. The catalyst conditions refer to the precipitation method, the nature and amount of added anion and/or hydrogenation metal, and calcination temperature. The physical properties included sulfate content, crystallography, specific surface area, pore volume and area distributions, thermal stability the number and nature of acid sites.

Sulfate contents were evaluated in terms of the sulfur content which was measured by a sulfur analyzer. The average particle size and crystallography of catalysts were characterized by X-Ray Diffraction (XRD). Their specific surface areas, and pore volume and area distributions were measured by liquid nitrogen adsorption. The nature of the acid sites of the catalysts was identified upon examining the infrared spectrum of adsorbed pyridine. The number of acid sites and acid strength were measured by the method of temperature-programmed desorption of pyridine (TPD).

5.2 Background

The acidity of zirconium oxide (ZrO_2) is weak. It was reported[10] that the highest acid strength (H_o) of the acid sites of ZrO_2 calcined in air at 773 K for three hours was 1.5 with the number of acid sites of 0.06 mmole g^{-1} for $H_o \leq 1.5$ and 0.280 mmole g^{-1} for $H_o \leq 4.0$. Its acidic properties can be improved greatly by addition of anions such as SO_4^{2-}, MoO_4^{2-} or WO_4^{2-}[41,103,104]. The acid strength of a sulfate promoted zirconium oxide can be greater than that of 100% sulfuric acid[41,76]; it is considered a strong solid superacid. Addition of the anion also affects the crystallographic phase transformation of ZrO_2, leading to formation of high surface area and a thermally stable crystalline phase (tetragonal form)[66,67]. Impregnation of the crystallized form

of ZrO_2 with a sulfate group does not create strong acid sites, calcination leading to the tetragonal form does for strong acid sites.[66]

5.3 Experimental

5.3.1 Characterization of the Physical Properties

5.3.1.1 Crystalline Structures and Average Particle Size.

These were deter...ined using a Philips X'Pert X-ray diffractometer. Cu-Kα radiation at 30 kV and 25 Ma was used. Sample preparation consisted of sprinkling and spreading the catalyst powder on a double sided adhesive tape on a microscopic slide. XRD scans were carried out between 20 and 60 degrees, 2θ at a rate of two degrees per minute.

The crystalline structure was identified by the wavelengths (λ) and the intensities of the XRD peaks. The average crystallite size was determined by line broadening, and calculated using the Scherrer equation[124]:

$$t=0.9\lambda/[B \cos\theta]$$

where t is the thickness of the crystal, and B is the angular width of the diffraction peak in terms of 2θ, measured at half its maximum intensity.

5.3.1.2 BET Surface Area, Pore Volume and Area Distributions.

The specific surface area of the catalysts was measured using the method of nitrogen physisorption. A small amount of sample (0.5 g) was preheated in a sample holder under vacuum for two hours, and cooled to room temperature. The sample holder was then quenched into liquid nitrogen (-198.5°C). Nitrogen adsorption was carried out by introducing nitrogen gas into the system over a range of pressures at less than one atmosphere to avoid nitrogen adsorption of multimolecular layers on the catalyst surface. The amount of nitrogen physically adsorbed on the catalyst surface was measured after the system reached equilibrium. The surface area was calculated using the BET equation. The measurement of the pore characteristics (distribution of incremental pore volume and incremental pore area) of sulfate promoted oxides was also based on the principle of liquid nitrogen physisorption at higher nitrogen pressures, where capillary

condensation occurs. The pore volume and pore area distributions were evaluated using a Micrometrics 2600 Surface Area Analyzer.

5.3.1.3 Sulfur Analysis.

The amount of sulfur in the sulfate-promoted metal oxides was determined using an SC-132 sulfur analyzer. The dried sample was weighed, placed in a high temperature furnace, and burned completely in a flow of oxygen. The sulfate group in the sample was dissociated into SO_2 during combustion. The SO_2 adsorbed IR energy at a specific wavelength of the IR spectrum, and its concentration was detected by an IR detector. Typically, prior to the beginning of an analysis, samples of known sulfur contents were used for calibrating the sulfur determinator.

5.3.1.4 Thermal Stability.

A Hi-Res 2950 thermogravimetric analyzer (TGA) was used to study the thermal stability of sulfate-promoted zirconium oxide. The temperature and amount of decomposition of the sulfate group during calcination were determined in this way.

In a TGA experiment, a small amount (0.04 g) of zirconium precipitates in the presence of sulfate and platinum ($Pt/Zr(OH)_4/SO_4$) was placed in a sample holder. The sample holder was then placed in a closed chamber over which nitrogen was continuously passed. The chamber was then heated from room temperature to 973 K at a rate of five degrees per minute. Results were presented in terms of the weight percentage of the remaining sample or the rate of the sample loss versus temperature, as shown later.

5.3.2 Characterization of Acidic Properties

5.3.2.1 Nature of Acid Sites by FTIR.

FTIR was employed to study the binding structure between the sulfate group and zirconium oxide. The nature of the acid sites of this catalyst was identified and its surface acidity and acid strength qualitatively evaluated by a Mattson Polaris FTIR spectrometer coupled with in-situ pyridine adsorption.

A self-supported thin wafer of the catalyst pressed from catalyst powder was placed into an in-situ IR cell with CaF_2 windows. The cell was then heated to a desired temperature (~433K)

in a continuous helium flow for two hours to remove moisture adsorbed on the catalyst surface. Pyridine adsorption was carried out at 433 K using helium as a carrier gas which was first passed through a saturator containing pyridine and then through the IR cell. All IR spectra were recorded at 433 K with a resolution of 4 cm^{-1} and 100 scans from 4000 to 400 cm^{-1}. They were represented either in absorbance or transmittance bands between 2400 and 1200 cm^{-1}. The nature of the acid sites (Lewis and Brönsted acid sites) was determined by wavelengths of the pyridine chemisorbed on the catalyst surface; the shift of the S=O band after pyridine adsorption was used to characterize the acid strength[69]. The effect of hydrogen on the Lewis acid sites, possibly converting them to protonic acid sites, was studied by introducing hydrogen into the IR cell after pyridine adsorption and then recording the IR spectra.

5.3.2.2 Temperature-Programmed Desorption.

The method of temperature programmed desorption (TPD) of basic molecules was used to quantitatively characterize the number of acid sites and acid strength of catalysts.

Pyridine was chosen as the base in the TPD experiments. In a typical run, a small amount of sample (~50 mg) was weighed and preheated in air in a furnace at 723 K for one hour and a half to remove the moisture. The sample was then transferred into a quartz tube, with a quartz wool inside to support the sample. A thermometer was inserted into the quartz tube to monitor the temperature in-situ of the sample. The latter was then preheated in a continuous helium flow at 623 K for twenty minutes to remove adsorbed moisture. Pyridine adsorption was carried out at 433 K using helium as a carrier gas which passed through a saturator containing pyridine and carried pyridine vapor to pass through the catalyst sample. After the catalyst surface was saturated with pyridine (determined by GC when the concentration of pyridine in the carrier gas was constant), the sample was purged with a helium flow for about 40 minutes to remove pyridine physically adsorbed on the catalyst surface. The temperature-programmed desorption of pyridine was carried out by increasing the temperature from 433 to 733 K within 20 minutes under flow rate of helium of 30 ml per minute. The desorbed pyridine was detected by an on-line Varian 3300 gas chromatograph (GC) with a thermal conductivity detector. The desorption peak area was

related to the number of acid sites, and the desorption temperature corresponding to the peak maximum (T_p) was used to characterize acid strength.

5.4 Results and Discussion

5.4.1 Effect of Addition of Sulfate Group on Properties of Zirconium Oxide

The effect of incorporation of a small amount of a sulfate group on the physical and structural properties of zirconium oxide (ZrO_2) was studied by the several techniques described earlier. Some properties of ZrO_2 with and without an added sulfate group are shown in **Table 4**.

Table 4. Effect of Addition of Sulfate Group on Some Properties of ZrO_2

Cat. No.	Catalyst	Sulfur content (wt. %)	Crystalline form	Specific surface area (m^2/g)	Average particle size (nm)
ZD	ZrO_2	0.0	Tetragonal (773 K)*	47.0	13.2
SZD2	ZrO_2/SO_4	2.71	Tetragonal (873 K)*	83.4	8.4

a: the temperatures given in the brackets are the calcination temperatures

Note that these two catalysts were calcined at different temperatures. These temperatures were so chosen that ZD and SZD2 had the same crystalline structure, the tetragonal form, making comparison between them more meaningful. A large increase in surface area with a decrease in particle size was observed when a small amount of the sulfate group was added to ZrO_2; this agrees qualitatively with experimental findings in the literature[71,77]. The XRD patterns of ZD and SZD2 after calcination at 773 and 873 K, respectively showed that they were in the tetragonal form. The monoclinic form was not found in the case of ZD. Results reported in the literature[66] claimed that ZrO_2 calcined at 773 K consisted of a mixture of tetragonal and monoclinic forms; a higher calcination temperature (973 K) was required to convert the tetragonal form into the

monoclinic one. Also noteworthy is that the calcination temperature necessary for a complete transformation of the amorphous form to the tetragonal crystalline one was at about 100 K higher for the sulfate-treated ZrO_2 than for the sulfate-free ZrO_2. This indicates that the phase transformation of the sulfated zirconium oxide from the amorphous form to the tetragonal one requires a higher thermal activation, as observed also by other researchers[64]. The distribution of the pore volume is very broad, as indicated by the diameter of the pores which range from 21 to 1083 Å, and a large portion of the pore volume is in the mesopore region (20 - 500 Å). In terms of the pore area distribution, most of the BET surface area of this catalyst is located in a narrow range of the mesopore region, 21 - 60 Å, with a very small portion being located in the larger pore area region.

Formation of acid sites of SZD2 upon addition of a sulfate group was investigated using FTIR. Before calcination, the absorption bands of the sulfate group could not be identified. The peak at 1610 cm^{-1} was attributed to adsorbed molecular water. After calcination, besides a bending vibration of adsorbed molecular water at 1610 cm^{-1}, four additional strong vibration peaks were observed at 1240, 1140, 1020 and 924 cm^{-1}. These four peaks are assigned to the asymmetric and symmetric stretching frequencies of the S=O and S-O groups of the chelating bidentate sulfate ions coordinated to zirconium cations (Zr^{4+}) in zirconium oxide[67]. The sulfate groups bound to the zirconium cations were formed during calcination which converted the amorphous zirconia to the crystalline one, ZrO_2.

The nature of acid sites was examined using platinum doped and sulfate-promoted zirconium oxide (SZD1). The catalyst was heated in-situ under a helium flow at 423 K while IR spectra were recorded after various heating times. These IR spectra showed that the intensity of the band corresponding to molecular water decreased substantially and a new band at 1378 cm^{-1} appeared, which was characteristic of the asymmetric stretching frequency of the S=O covalent bond[67]. This change of the IR spectrum is due to the removal of molecular water absorbed on the catalyst surface during heating, which transformed the catalyst from one with a chelating inorganic complex to one with an organic sulfate.

After SZD1 was heated in-situ under a helium flow at 423 K for 60 minutes, pyridine was introduced using helium as a carrier. The presence of pyridine in this catalyst resulted in a shift in the asymmetric stretching frequency of the $S=O$ bond from 1378 cm^{-1} to 1338 cm^{-1}, with three new adsorption bands appearing at 1537, 1491 and 1444 cm^{-1}. This shift is believed to be due to the fact that when pyridine was adsorbed on the central zirconium cation, it changed the nature of the $S=O$ bond from a highly covalent double bond to one with less double bond character. In fact, the magnitude of this shift was used by other researchers for evaluating the acid strength of sulfate-promoted metal oxides[69].

The nature of the acid sites on SZD1 can be identified from the three pyridine adsorption bands appearing at 1444, 1491 and 1537 cm^{-1}, respectively. They are assigned to the pyridine chemisorbed on the Lewis acid sites (L-Py), both the Lewis and Brönsted acid sites (L+B-Py), and the Brönsted acid sites (B-Py)[111,112], respectively.

5.4.2 Effect of the Preparation Procedures on Properties of Pt/ZrO$_2$/SO$_4$

5.4.2.1 Precipitation Methods.

Two Pt/ZrO$_2$/SO$_4$ catalyst samples, SZD1 and SZD22, were prepared from Zr(SO$_4$)$_2$·H$_2$O using heterogeneous and homogeneous methods, respectively. Some selected physical and acidic properties of these catalysts are shown in **Table 5**.

Table 5. Comparison of Selected Physical and Acidic Properties Between SZD1 and SZD22 Prepared by the Heterogeneous and Homogeneous Precipitation Methods

Cat. No.	Physical Properties				Acidic Properties	
	sulfur (wt. %)	surface area (m^2·g^{-1})	crystalline form	average particle size (nm)	T_p (K)	acidity (mmole/g)
SZD1	2.71	83.4	tetragonal	8.4	563	0.358
SZD22	1.34	90.0	tetragonal	8.2	530	0.150

The nature of crystalline phases, specific surface area and average particle size of these two

catalysts were close with a notable difference in sulfur content. On the other hand, their acidic properties were strongly affected by the precipitation method, as revealed by TPD measurements. The peak desorption temperature (T_p) of SZD1, which is related to acid strength, was about 30 K higher than that of SZD22. This indicates that the acid strength of $Pt/ZrO_2/SO_4$ synthesized by the heterogeneous precipitation method (SZD1) was higher than the one obtained by the homogeneous method (SZD22). The number of acid sites of SZD1 was also larger than that of SZD22, which was probably attributed to the fact that the sulfur content of SZD22 was lower than that of SZD1. The experimental results indicate that the heterogeneous precipitation method is better than the homogeneous one to synthesize the $Pt/ZrO_2/SO_4$ catalyst with higher acid strength and acidity.

Additional TPD runs for SZD1 and SZD22 were carried out under similar conditions to check the reproducibility of measurements for the acidity and acid strength of these two catalysts.

5.4.2.2 Effect of Calcination Temperature.

Calcination temperature is important as it dictates the degree to which the amorphous phase of such catalysts is converted to crystalline forms. It also affects the sulfur content. The effect of calcination temperature was examined by calcining platinum doped and sulfate-promoted zirconium hydroxide at various temperatures. The results are shown in **Table 6.**

Table 6. Effect of Calcination Temperature on the Physical Properties of $Pt/ZrO_2/SO_4$

Catalyst No.	Calcination Temperature (K)	Sulfur content (wt. %)	Crystalline form	Average particle size (nm)
SZD5	773	4.32	A	not applicable
SZD6	823	4.07	A + T	8.4
SZD4	873	1.58	T	7.0
SZD7	923	1.51	T	7.6
SZD8	973	1.16	T	8.4

A: the amorphous form; T: the tetragonal form

Sulfur is evidently lost upon calcination. The loss was negligibly small when the calcination temperature was below 823 K but it became severe when the calcination temperature was above 873 K. In this later case, more than 70% of the sulfur contained in the catalyst was lost. On the other hand, the TGA profile of the amorphous $Pt/Zr(OH)_4/SO_4$ recorded from room temperature to 973 K indicated that the weight loss of the catalyst started in the temperature range between 373 and 473 K, which is related to the amount of the physically adsorbed water and that of the water generated by the decomposition of $Zr(OH)_4$ into ZrO_2 and H_2O. The weight loss from 573 to 823 K was insignificant; it became important (6.85% of the weight of the initial sample was lost) when temperature was between 873 and 973 K. This later was revealed by a peak which appeared in that temperature range in the TGA profile. This observation indicated that when the calcination temperature exceeded 873K, a significant amount of sulfur was lost due to thermal decomposition of the sulfate group.

The XRD profiles of platinum doped and sulfate-promoted zirconium hydroxide before and after calcination at different temperatures were obtained. Before calcination, the precipitates were amorphous. When they were calcined at 773 K (SZD5), XRD pattern did not eventually change, indicating that they did not crystallize at that temperature. On the other hand, ZrO_2 without a sulfate treatment was found to be only in tetragonal crystalline form when calcined at the 773K for the same period of time. The presence of the sulfate group in the zirconia precipitates evidently retards crystallization of ZrO_2/SO_4. The XRD spectra also show that the phase transformation of the $Pt/ZrO_2/SO_4$ from the amorphous form to the tetragonal one occurred when the calcination temperature reached 823 K. The tetragonal crystalline structure developed further with increasing calcination temperature. When temperature was above 873 K, it was completely converted into the tetragonal form. It was also in the tetragonal form after calcination at 973 K. By contrast, ZrO_2 without sulfate treatment was converted from the tetragonal into the monoclinic form at 973 K[66].

The average particle size of the $Pt/ZrO_2/SO_4$ catalysts increased visibly with increasing calcination temperature when the latter was above 873 K. This finding agrees reasonably well

with the experimental fact that the surface area of such a catalyst decreased when it was calcined at a temperature above 873 K[116,126].

5.4.2.3 Effect of the Nature of the Anion.

It is known that when an anion (e.g. SO_4^{2-}, WO_3 or MoO_3) is introduced to certain metal oxides, their surface acidities are strongly enhanced[103,104]. Their effect on the acidic properties of Pt/ZrO_2 was determined by TPD. The experimental results are shown in Table 7.

Among the various anions, the sulfate group gave the best performance in terms of the increase in acidic properties of the Pt/ZrO_2. This may be due to a stronger inductive effect of SO_4^{2-} in the formation of the sulfur surface complex compared to WO_3 and MoO_3. The XRD profiles of the Pt/ZrO_2 promoted by SO_4^{2-}, WO_3 and MoO_3 were obtained. The Pt/ZrO_2 promoted with WO_3 was in the tetragonal form, and so was the Pt/ZrO_2 promoted with MoO_3. The Pt/ZrO_2 without anion treatment was in the monoclinic form when it was calcined at 973 K[66]. This leads to the conclusion that during calcination at high temperatures, the presence of WO_3 or MoO_3 stabilizes the tetragonal phase of the Pt/ZrO_2, as does SO_4^{2-}. A similar conclusion has been drawn by other researchers[103,104].

Table 7. Effect of Addition of Anions on the Acidic Properties of the Pt/ZrO_2 Catalysts

Catalyst No.	Catalyst formula	Anion	Acidic properties	
			Acidity (mmole/g)	T_n (K)
SZD4	$Pt/ZrO_2/SO_4$	SO_4^{2-}	0.358	563
TZD	$Pt/ZrO_2/WO_4$	WO_3	0.144	556
MZD	$Pt/ZrO_2/MoO_4$	MoO_3	0.085	520

5.4.2.4 Effect of the Concentration of Sulfuric Acid.

The effect of the concentration of sulfuric acid used for sulfation on the physical and acidic properties of sulfate-promoted and Pt doped zirconium oxide metal oxides was investigated. To that end, zirconium hydroxide precipitates were impregnated with sulfuric acid of various

concentrations. The sulfur content and acidity of these catalysts are shown in **Table 8**. Interestingly, the weight percentage of the sulfate adsorbed on the Pt/ZrO_2 after calcination at 873 K differed only slightly for a relatively wide range of the sulfuric acid concentration (0.2 - 6.0N). Although this finding was unexpected, it should be pointed out that in addition to the concentration of sulfuric acid used for sulfation, the sulfur content also depends, possibly to a great extent, on the calcination temperature. This latter statement is supported by the results in **Table 6**. It was also reported[105,126] that, at calcination temperatures below 873 K, the sulfur contents increased with increasing concentration of sulfuric acid; at a calcination temperature above 873 K, the sulfur contents became relatively insensitive to the concentration of sulfuric acid. The surface area of the $Pt/ZrO_2/SO_4$ impregnated with 1 N H_2SO_4 (SZD3) was 107 m^2/g, close to the result reported in the literature[105,112]; the calculated surface sulfur is $14.5 \cdot 10^{-5}$ g/m^2. This calculation was done by dividing the amount of sulfur in the catalyst by its surface area. If it is assumed that each sulfur species occupies 25 $Å^2$ (corresponding to $21 \cdot 10^{-5}$ g/m^2)[105], the sulfur adsorbed on the surface of the $Pt/ZrO_2/SO_4$ catalyst would be close to a monolayer.

Table 8. Effect of the Concentration of Sulfuric Acid on the Properties of the $Pt/ZrO_2/SO_4$ Catalysts (calcined at 873 K in air for three hours)

Catalyst No.	H_2SO_4 (N)	Sulfur (wt. %)	Acidity (mmole/g)	
			Calculated[a]	Experimental
SZD9	0.2	1.48	0.463	0.249
SZD10	0.5	1.51	0.472	0.271
SZD3	1.0	1.56	0.488	0.358
SZD11	3.0	1.58	0.494	0.263
SZD12	6.0	1.56	0.488	0.323

a: the calculation was based on the assumption that each sulfate group incorporated in the catalyst forms an acid site.

The number of acid sites of the $Pt/ZrO_2/SO_4$ catalyst increased with increasing H_2SO_4

concentration in the range of 0.2 - 1 N. With further increase in the H_2SO_4 concentration, the number of acid sites decreased first and then increased. The $Pt/ZrO_2/SO_4$ catalyst prepared by impregnation of zirconium precipitates with 1 N H_2SO_4 concentration gave the highest number of acid sites. The calculated number of acid sites of the $Pt/ZrO_2/SO_4$ catalysts were higher than the experimental ones determined by TPD. This may be understood by stating that the acid sites distributed on the catalyst surface may possess different acid strengths with some weak acid sites being unable to adsorb pyridine. On the other hand, not all of the adsorbed sulfate species would form a bidentate complex with the zirconium cations responsible for generation of highly acidic sites.

5.4.3 Properties of Pt and Sulfate-Promoted Mixed Zirconium and Hafnium Oxides

Platinum and sulfate-promoted mixtures of zirconium and hafnium oxides, $Pt/ZrO_2 \cdot HfO_2/SO_4$, were prepared by the heterogeneous coprecipitation method. Their acidic properties were compared with platinum and sulfate promoted zirconium oxide and hafnium oxide, respectively (Table 9).

Table 9. Acidic Properties of Pt and Sulfate-Promoted ZrO_2, HfO_2 and Their Mixtures
(calcined at 873 K for three hours)

Catalyst No.	Catalyst formula	$Zr/(Hf+Zr)$ molar fraction	Acidic properties	
			Acidity (mmole/g)	T_p (K)
SZD3	$Pt/ZrO_2/SO_4$	1	0.358	553
SZHD1	$Pt/ZrO_2 \cdot HfO_2/SO_4$	0.8	0.228	543
SZHD2	$Pt/ZrO_2 \cdot HfO_2/SO_4$	0.5	0.215	533
SZHD3	$Pt/ZrO_2 \cdot HfO_2/SO_4$	0.2	0.198	533
SHD	$Pt/HfO_2/SO_4$	0	0.186	533

The number of acid sites of the $Pt/ZrO_2/SO_4$ catalyst (SZD3) was much higher than that of the $Pt/HfO_2/SO_4$ catalyst (SHD). Its number of acid sites was reduced when HfO_2 was present.

The acid strength, characterized by the peak desorption temperature (T_p) of the $Pt/ZrO_2/SO_4$ was also higher than that of the $Pt/HfO_2/SO_4$ and the mixtures, $Pt/ZrO_2 \cdot HfO_2/SO_4$.

The metal oxide that can be effectively promoted by a sulfate group to form strong acid sites should have a metal atom with high electronegativity and high coordination number[67]. Zirconium and hafnium cations of the same group in the periodic table have the same charge, same size and same electronegativity[127]. The difference in acidic properties between sulfate-promoted and platinum-doped zirconium oxide and hafnium oxide may be related to the different structures of these two catalysts. The XRD pattern of the $Pt/ZrO_2/SO_4$ calcined at 873 K showed a completely tetragonal form . The XRD pattern of $Pt/ZrO_2 \cdot HfO_2/SO_4$ consisted of a mixture of the tetragonal and monoclinic forms. However, the XRD pattern of the $Pt/HfO_2/SO_4$ catalyst calcined at the 873 K was in the mixture of monoclinic form and amorphous. It has been reported[66] that the ZrO_2/SO_4 catalyst in the tetragonal form was more active than that in the monoclinic form or amorphous. This suggests that the $Pt/HfO_2/SO_4$ catalyst in the mixture of monoclinic form and amorphous might account for its low number of acid sites and weak acid strength compared to those of the $Pt/ZrO_2/SO_4$ catalyst in the tetragonal form.

5.4.4 Effect of Addition of Hydrogenation Metals on the Acidic Properties of ZrO_2/SO_4

Addition of a hydrogenation metal to the ZrO_2/SO_4 catalyst not only prolongs its catalytic life but also affects its acidic properties. FTIR technique was mainly employed for this study.

The IR spectra of pyridine adsorbed on the ZrO_2/SO_4 doped with 1.0 wt.% of Pt (SZD14) and 2.0 wt.% of Ni (SZD21) and the IR spectrum of the ZrO_2/SO_4 catalyst (SZD2) were obtained. After 60 minutes of in-situ preheating of these samples in the presence of helium, the band at 1616 cm^{-1}, corresponding to physically adsorbed molecular water, decreased substantially, and a new band at 1398 cm^{-1} in the case of SZD2, and 1385 cm^{-1} in the case of SZD21, due to S=O appeared. Upon introducing pyridine carried by helium, three new bands appeared in the wavelength region between 1440 and 1550 cm^{-1}; the ones at 1444, 1491 and 1537 cm^{-1} were attributed to pyridine chemisorbed on Lewis acid sites (L-Py), on both the Lewis and Brönsted acid sites (L+B-Py) and the Brönsted acid sites (B-Py), respectively. The band at 1398 cm^{-1}

corresponded to the S=O in the ZrO_2/SO_4; it shifted to 1378 cm^{-1} when 0.5 wt.% of Pt was added to the ZrO_2/SO_4. After adsorption with pyridine, this band shifted to 1330 cm^{-1} in the case of ZrO_2/SO_4, and to 1338 cm^{-1} in the case of Pt doped ZrO_2/SO_4. The amount of the shift in the wavelength of the S=O was lower in the case of the Pt doped ZrO_2/SO_4, indicating that the acid strength of the ZrO_2/SO_4 catalyst decreased upon addition of Pt. The amount of shift of the S=O was used to quantify the acid strength of sulfated metal oxides[69].

The effect of the presence of hydrogen on the acidic properties of the ZrO_2/SO_4 with or without an added hydrogenation metal was also studied by FTIR. The IR spectrum showed that when hydrogen was introduced to the $Pt/ZrO_2/SO_4$ (SZD14), the band at 1491 cm^{-1} due to the L+B-Py increased significantly with a concomitant decrease in that at 1444 cm^{-1} due to the L-Py. This experimental finding agrees with published work[111,112]. The conversion between the Lewis and Brönsted acid sites in the $Pt/ZrO_2/SO_4$ in the presence of hydrogen was explained by the dissociation of the hydrogen molecules adsorbed on Pt into hydrogen atoms, their spillover onto the ZrO_2/SO_4 surface and electron transfer from hydrogen atoms to the Lewis acid sites producing protonic acid sites[112]. Interestingly, the presence of hydrogen with ZrO_2/SO_4 in the absence of a hydrogenation metal did not have any effect on the bands of the L-Py and L+B-Py mentioned above (Figure 20a). This was also observed with $Ni/ZrO_2/SO_4$. The fact that platinum and nickel did not play the same role with ZrO_2/SO_4 may be understood as follows: nickel is not as good a hydrogenation metal as is platinum, so that there is little hydrogen spillover from nickel.

5.5 Summary

We have demonstrated that addition of SO_4^{2-}, WO_3 and MoO_3, to platinum promoted zirconium oxide is instrumental in changing both physical and acidic properties. Small amounts of these materials (~2%) on the zirconium oxide significantly increased its surface area and improved the thermal stability of its tetragonal phase. As a result, its surface acidic properties increased greatly. Among these anions, the sulfate gave the best promotional effect on acidic properties of zirconium oxide. It was found that the method of preparation of catalyst, the nature

of the anion and that of hydrogenation metal were also important for modifying the physical and acidic properties of the catalyst. A $Pt/ZrO_2/SO_4$ sample prepared by heterogeneous precipitation with 1 N sulfuric acid for sulfation and calcination for three hours at 873 K gave better acidic properties. We have found that, in the presence of hydrogen, protonic acid sites could be formed on platinum doped ZrO_2/SO_4 but not on nickel doped ZrO_2/SO_4.

6.0 ACTIVITY OF ANION-MODIFIED METAL OXIDES FOR HYDROCRACKING AND HYDROISOMERIZATION OF ALKANES

6.1 Objectives

The activity of anion-modified metal oxides for hydrocracking and hydroisomerization of long chain hydrocarbons was measured experimentally. Normal hexadecane was chosen as a model compound to represent the behavior of F-T waxes. A batch reactor was used to carry out the reactions. The main objectives of this study were:

(1) to investigate the effect of catalyst preparation conditions on the catalytic activity for the hydrocracking and hydroisomerization of n-hexadecane. These catalyst preparation conditions included the nature of the starting zirconia precursor, the precipitation method, the nature and amount of anion, and the calcination temperature. It was also hoped to gain an insight into the relationship between catalytic activity and acidic properties of $Pt/ZrO_2/SO_4$.

(2) to study the effect of addition of various hydrogenation metals on the catalytic activity and product selectivity of ZrO_2/SO_4 toward hydrocracking and hydroisomerization of n-hexadecane.

(3) to determine the activity of sulfate promoted bimetallic oxides ($Pt/ZrO_2·HfO_2/SO_4$) for hydrocracking and hydroisomerization of n-hexadecane.

6.2 Background

Addition of a sulfate group to certain metal oxides such as ZrO_2, HfO_2 and TiO_2 enhances their surface acidity significantly[63,74,75]. Consequently, their catalytic activity for acid-catalyzed reactions increases to a great extent. Hino and Arata[75] found that sulfated zirconium oxide catalyst could be used to isomerize light alkanes at low temperatures (~423 K). Formation of multibranched isomers was favored at these low temperatures. Hosoi et al.[106,107,110] reported that incorporation of certain transition metals such as Pt, Pd and Ni on ZrO_2/SO_4 enhanced catalytic performance for isomerization of n-pentane in the presence of hydrogen; a major purpose of the

metal was to prevent deactivation of the catalyst due to coke formation. Wen et al.[9,125] found that Pt/ZrO$_2$/SO$_4$ was highly active in hydrocracking and hydroisomerization of n-heptane and n-hexadecane under relatively mild reaction conditions (383 - 443 K; 200 - 300 psig of hydrogen pressure) obtaining a high selectivity (> 90%) to hydrocracked isoparaffins. In terms of catalytic activity and product selectivity, the Pt/ZrO$_2$/SO$_4$ catalyst seemed to be promising for upgrading F-T waxes to obtain liquid fuels.

It is believed that the catalytic activity of Pt/ZrO$_2$/SO$_4$ for acid catalyzed hydrocracking and hydroisomerization of hydrocarbons is related to its acidic properties. The latter can be affected by several parameters, such as the preparation procedure, the amount and nature of the anion and the hydrogenation metal. A main objective of our work was to explore the effects of these parameters on the catalytic activity and product selectivity of the Pt/ZrO$_2$/SO$_4$ catalyst for hydrocracking and hydroisomerization, and to gain insights into the relationship between the catalyst activity and acidic properties of this metal oxide.

6.3 Experimental

n-Hexadecane (99%) was purchased from Aldrich Chemical Company, and used as received.

6.3.1 Experimental Setup

A horizontal shaking microreactor system (**Figure 2**), providing good catalyst-reactant mixing and gas-liquid mass transfer, was used to carry out hydrocracking and hydroisomerization experiments with n-hexadecane. The microreactor consisted of three portions: a horizontal reactor tube (1 in.o.d. x 4.625 in.), a vertical reactor stem (1/2 in.o.d. x 10 in.), and a multiport valve connected on top of the reactor stem. The horizontal tube was sealed at one end, and the other end was fitted with a cap to allow charging of the catalyst and discharging of the products. The reactor stem isolated the multiport valve from the heating source (a fluidized sandbath), and accommodated a pressure transducer, a thermocouple and a quick connector to allow for monitoring of the reaction variables and charging and discharging of gases.

6.3.2 Reaction Procedure

In a typical experiment, one gram of catalyst was activated in a furnace at 723K for one hour and a half, then quickly transferred to a predried hot tubing bomb microreactor. After the catalyst was placed in the horizontal reactor, the open end was immediately closed and the top of the reactor stem plugged. The horizontal portion of the reactor was cooled to room temperature with water. Upon removal of the plug, six grams of n-hexadecane was charged into the reactor through the reactor stem. After connecting the multiport valve to the reactor stem, the reactor was
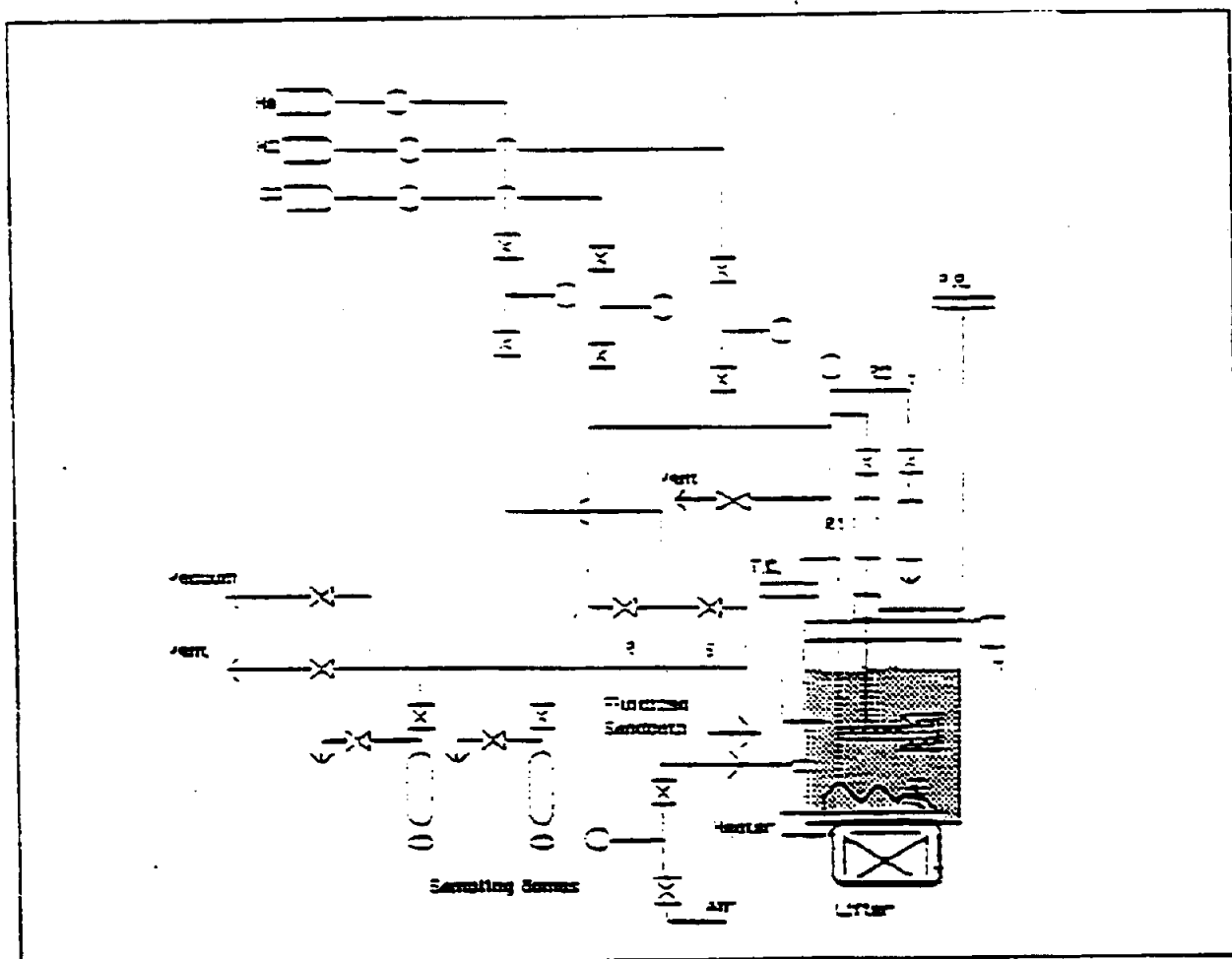

Figure 2. Schematic Drawing of Microautoclave Reactor.

mounted on the stand, purged with hydrogen (99.99%) three times, and then pressurized to a desired pressure (360 psig). The reactor was shaken for about three minutes at room temperature at 160 cycles per minute to allow for pre-reaction feed mixing and hydrogen dissolution in the slurry. At time zero, the reactor was immersed in the sandbath which was preheated to the reaction temperature (433 K). Typically, the reactor reached the reaction temperature in three minutes while being shaken at 160 cycles per minute during which the initial pressure increased to about 440 psig at the reaction temperature of 433 K. After reaction, the reactor was removed from the sandbath and quenched to a cooling water bath for about ten minutes. Because the yield of gas products obtained in our reactions was less than 3 wt.%, they were considered negligible and were vented after cooling. The liquid products were filtered to remove suspended catalyst powder and analyzed using an HP-5890 gas chromatograph through a 30 m x 0.25 mm i.d. DB-1 capillary column with an injection split ratio of 50 to 1. A flame ionization detector was used for product analysis. The hydrocarbon components were identified upon comparing their retention times with those known standards calibrated in the same GC. The conversion was defined as the disappearance of n-C16 in the liquid phase, isomerization as the mass of isohexadecanes (i-C16) and cracking as the mass of compounds with carbon numbers less than 16. The selectivity of cracking was the mass of cracked products (C5-C13) divided by the mass of n-C16 converted, and correspondingly the selectivity of isomerization was the mass of i-C16 divided by the mass of n-C16 converted.

6.4 Results and Discussion

6.4.1 Effect of Preparation Procedure on Catalytic Activity

6.4.1.1 Effect of the Precipitation Method and Nature of Zirconia Precursor.

Four Pt-doped sulfated zirconium oxide samples were prepared from different precursors and under different precipitation conditions, as described in **Table 3** of **Section 4.3.3**. Their activity was tested using the hydrocracking and hydroisomerization of n-hexadecane as the reaction model. The experimental results are given in **Table 10**.

Under the same reaction conditions, the $Pt/ZrO_2/SO_4$ catalysts (**SZD1, SZD2** and **SZD4**) prepared by the heterogeneous method using $Zr(SO_4)_2 \cdot 4H_2O$, $ZrOCl_2$ and $ZrO(NO_3)_2$ as zirconia precursors showed similar activities and product selectivities towards hydrocracking and hydroisomerization of n-hexadecane. This indicates that the activity and product selectivity of the $Pt/ZrO_2/SO_4$ catalyst evidently does not depend on the particular starting zirconia precursor. As mentioned earlier, the use of $Zr(SO_4)_2 \cdot 4H_2O$ as a zirconia precursor greatly reduced the washing effort involved in the synthesis procedure. Thus, $Zr(SO_4)_2 \cdot 4H_2O$ was a good replacement for the conventional zirconia precursors: $ZrOCl_2$ and $ZrO(NO_3)_2$. Duplicate runs for hydrocracking and hydroisomerization of n-hexadecane were carried out under similar reaction conditions in the presence of the $Pt/ZrO_2/SO_4$ catalysts; these catalysts were prepared from the same or different batch reactions, using $Zr(SO_4)_2 \cdot 4H_2O$ as the zirconia precursor. The experimental data obtained were reproducible, within 4% of experimental error.

The catalyst **SZD22** prepared by the homogeneous precipitation method showed a lower activity than that of the catalyst **SZD1** obtained by the heterogeneous precipitation method; both **SZD22** and **SZD1** used $Zr(SO_4)_2 \cdot 4H_2O$ as the zirconia precursor. The lower activity of **SZD22** agrees with the finding that the number of acid sites and acid strength of **SZD22** were much lower than those of **SZD1** (see **Table 5** of **Section 5.4.2.1**).