Table 10. Comparison of Activity Among the Various Pt/ZrO_2/SO_4 Catalysts Prepared from Different Precursors or under Different Precipitation Conditions

Run No.	Catalyst No.	Conversion (wt.%)	Selectivity (wt.%)		
			C5-C9	C10-C13	i-C16
R001	SZD1	68.0	58.8	17.6	23.6
R002	SZD3	66.0	56.1	21.2	22.7
R003	SZD4	67.9	57.2	18.6	24.2
R004	SZD22	30.0	57.1	23.3	19.6

(Reaction conditions: cat./feed: 1/6, 433 K, 300 psig H_2 (cold) and 50 min)

In sum, a highly active Pt/ZrO_2/SO_4 catalyst was successfully prepared by the heterogeneous precipitation method using $Zr(SO_4)_2 \cdot 4H_2O$ as a zirconia precursor to obtain zirconium hydroxide precipitates. This zirconia precursor reduces a considerable amount of water washing effort in the synthesis compared to the use of the conventional precursors ($ZrOCl_2$ and $ZrO(NO_3)_2$).

6.4.1.2 Effect of Calcination Temperature.

Five Pt/ZrO_2/SO_4 catalysts (SZD4-SZD8) obtained after calcination at different temperatures (773 - 973 K) were used for hydrocracking and hydroisomerization of n-hexadecane. The conversion of n-hexadecane with respect to the calcination temperature is shown in Figure 3. Clearly, the catalyst activity depends strongly on the calcination temperature. The conversion of n-hexadecane increased with the increase in calcination temperature when the latter was between 773 and 873 K. It reached its highest value when the catalyst was calcined at 873 K (SZD4). With a further increase in calcination temperature, however, the conversion decreased. The catalyst calcined at 973 K (SZD8) was almost inactive for the hydrocracking and hydroisomerization of n-hexadecane.

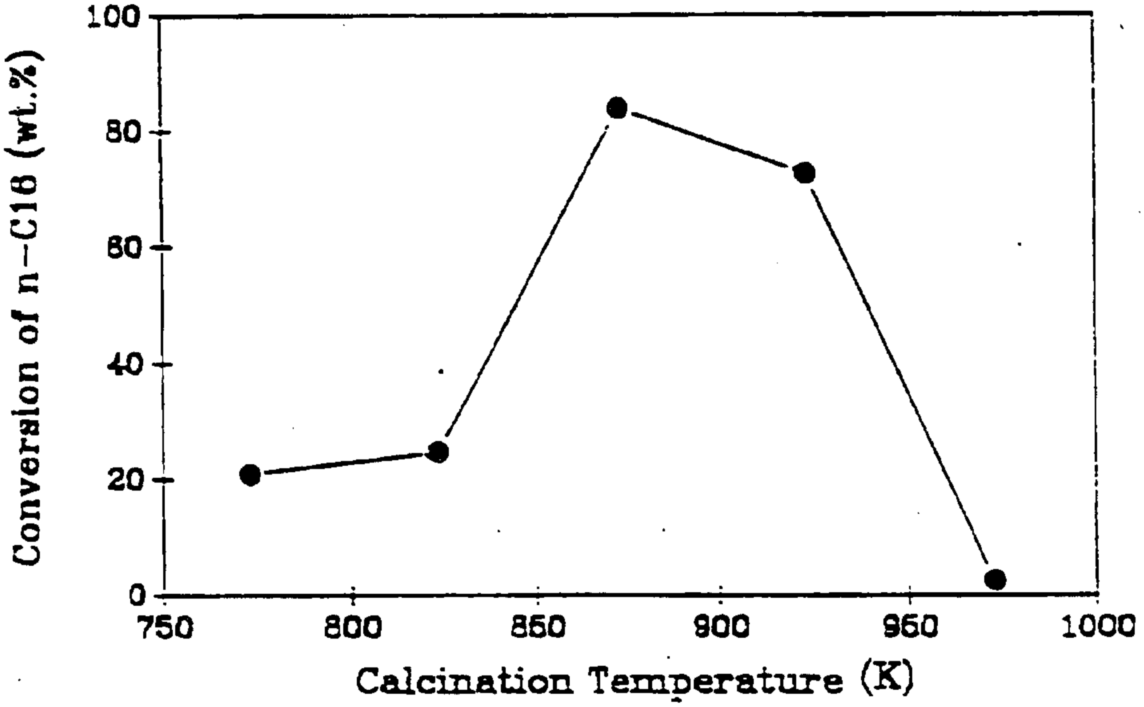

Figure 3. Effect of Calcination Temperature on the Conversion of n-C16 Using a $Pt/ZrO_2/SO_4$ Catalyst (433 K, 360 psig H_2 cold, 60 min).

The effect of calcination temperature on the catalytic activity of $Pt/ZrO_2/SO_4$ is connected to the phase transformation. The amorphous zirconium hydroxide crystallized above 823 K. At low calcination temperatures (< 823 K), the degree of crystallization of $Pt/ZrO_2/SO_4$ (**SZD5**) was low, consisting mainly of the amorphous form. It has been reported that highly acidic and catalytically active $Pt/ZrO_2/SO_4$ was completely in the tetragonal form(66). The low activity of the $Pt/ZrO_2/SO_4$ catalyst calcined at low temperatures was mainly attributed to the fact that the amount of tetragonal phase responsible for the formation of highly acidic sites was low. When $Pt/ZrO_2/SO_4$ was calcined at 873 K (**SZD4**), it consisted only of the tetragonal form, exhibiting the highest activity towards hydrocracking and hydroisomerization of n-hexadecane, although its sulfate content was much lower than that of the catalysts calcined at lower temperatures (see **Table 6 of Section 5.4.2.2**).

Similar findings has been reported by other researchers(105,126). This indicates that the total sulfur content does not necessarily reflect the amount of the surface sulfur complex responsible for formation of highly acidic sites. Although the $Pt/ZrO_2/SO_4$ catalyst calcined at a temperature above 873 K (**SZD7-8**) remained in the tetragonal form, its catalytic activity for conversion of n-hexadecane decreased. Calcination at high temperatures not only reduced the content of the surface sulfur species but the catalyst surface area as well(105,126). As the total number of the active sites is proportional to each of these two parameters, the calcination temperature is critical for obtaining $Pt/ZrO_2/SO_4$ catalyst with high activity. The catalyst (**SZD8**) calcined at 973 K lost about 28 wt.% of sulfur compared to that of **SZD4**,;however it gave a low conversion of n-C16.

6.4.1.3 Effect of the Nature of the Anion.

The catalytic properties of anion modified metal oxides are strongly related to the nature of anion. In this study, Pt/ZrO_2 was promoted with SO_4^{2-}, WO_4^{2-} and MoO_4^{2-}, respectively. The use of WO_4^{2-} and MoO_4^{2-} was motivated by the results reported in the literature that Pt/ZrO_2 promoted with WO_4^{2-} or MoO_4^{2-} was active for the isomerization of n-butane(114,115). The preparation conditions for these catalysts are specified in **Table 3 of Section 4.3.3** and their activity for the hydrocracking and hydroisomerization of n-hexadecane are shown in **Table 11.** Addition of a sulfate group to the Pt/ZrO_2 (**SZD4**) greatly enhanced its catalytic activity while the activities of Pt/ZrO_2 promoted by WO_3 (**TZD**) and MoO_3 (**MZD**) were much lower. This agrees with the fact that the number of the acid sites and acid strength of the SO_4^{2-} promoted Pt/ZrO_2 were much higher than those of WO_3 or MoO_3 promoted Pt/ZrO_2 (see **Table 9 of Section 5.4.3**). The weak capability for WO_3 and MoO_3 to improve the surface acidic properties of ZrO_2 compared to that of SO_4^{2-} may be related to their weak inductive effects. On the other hand, most of the WO_3 or MoO_3, which could be responsible for the formation of strong acid sites for the reaction of n-C16, may be in the bulk rather than on the ZrO_2 surface.

Table 11. Comparison of the Catalytic Activity of Pt/ZrO_2 Promoted by Various Anions (Reaction conditions: feed/cat.: 6/1, 433 K, 360 psig H_2 (cold) and 60 min)

Run No.	Catalyst No.	Catalyst formula	Anion	Conversion (wt.%)
R005	SZD4	$Pt/ZrO_2/SO_4$	SO_4^{2-}	83.9
R006	TZD	$Pt/ZrO_2/WO_3$	WO_4^{2-}	1
R007	MZD	$Pt/ZrO_2/MoO_3$	MoO_4^{2-}	0

6.4.1.4 Effect of H_2SO_4 Concentration.

Addition of a sulfate group to ZrO_2 greatly enhances its surface acidity. The most common way to introduce a sulfate group is to impregnate zirconium hydroxide precipitates ($Zr(OH)_4$) with an H_2SO_4 solution. While the effect of the concentration of H_2SO_4 solution on sulfate adsorption and surface area of catalysts has been reported in the literature,(129) its effect on the activity of the resulting catalysts has received little attention. The effect of the concentration of H_2SO_4 solution on the physical and acidic properties of the $Pt/ZrO_2/SO_4$ catalyst was discussed earlier. To that end, zirconium hydroxide precipitates were impregnated with H_2SO_4 solutions of various concentrations ranging from 0.2 to 6.0 N. They were then calcined at 873 K for three hours.

The activity and product selectivity of these catalysts were compared using the hydrocracking and hydroisomerization of n-hexadecane as the reacting system. The conversion of n-hexadecane obtained with a particular $Pt/ZrO_2/SO_4$ catalyst and the number of acid sites for this catalyst as a function of H_2SO_4 concentration are shown in **Figure 4**.

Conversion first increased with increasing H_2SO_4 concentration, reaching the highest conversion at a concentration of H_2SO_4 of about 1N. It then decreased slightly with a further

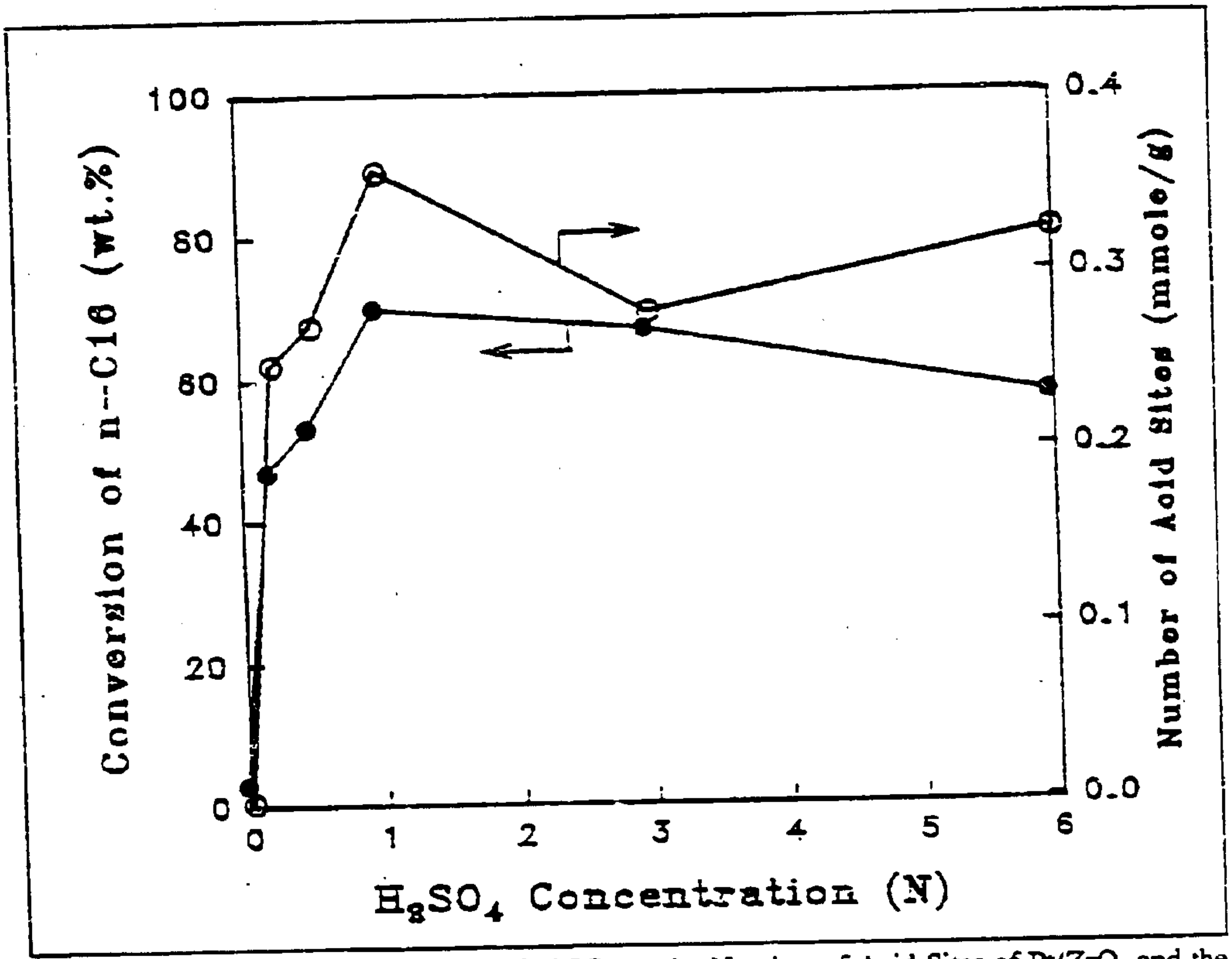

Figure 4. Effect of the Concentration of H_2SO_4 on the Number of Acid Sites of Pt/ZrO_2 and the Conversion of n-16, 433K, 360 psig H_2 cold, 40 min.

increase in the concentration of H_2SO_4. An important finding was that there was a similarity between the dependency of the conversion of n-hexadecane and that of the number of acid sites of the Pt/ZrO_2/SO_4 catalyst on the H_2SO_4 concentration used for sulfation of these catalysts (**Figure 4**) when the H_2SO_4 concentration is less than 1N. However, when the H_2SO_4 concentration was higher than 1N, the dependency of the conversion of n-hexadecane and that of the number of the acid sites of the Pt/ZrO_2/SO_4 catalyst on the H_2SO_4 concentration was different. The number of acid sites of Pt/ZrO_2/SO_4 at 3N was lower than that of Pt/ZrO_2/SO_4 at 1N or 6N, which was unexpected, because the sulfur content of the former one was similar to that of the latter one. This might be due to the error of TPD measurements. The use of these catalysts led to a similar product selectivity (Figure 5).

In sum, the activity of Pt/ZrO_2/SO_4, which depended on its surface acidity, was affected by the concentration of the H_2SO_4 solution used in the preparation of the catalysts. A Pt/ZrO_2/SO_4 sample prepared from 1 N sulfation gave the highest activity for conversion of n-C16.

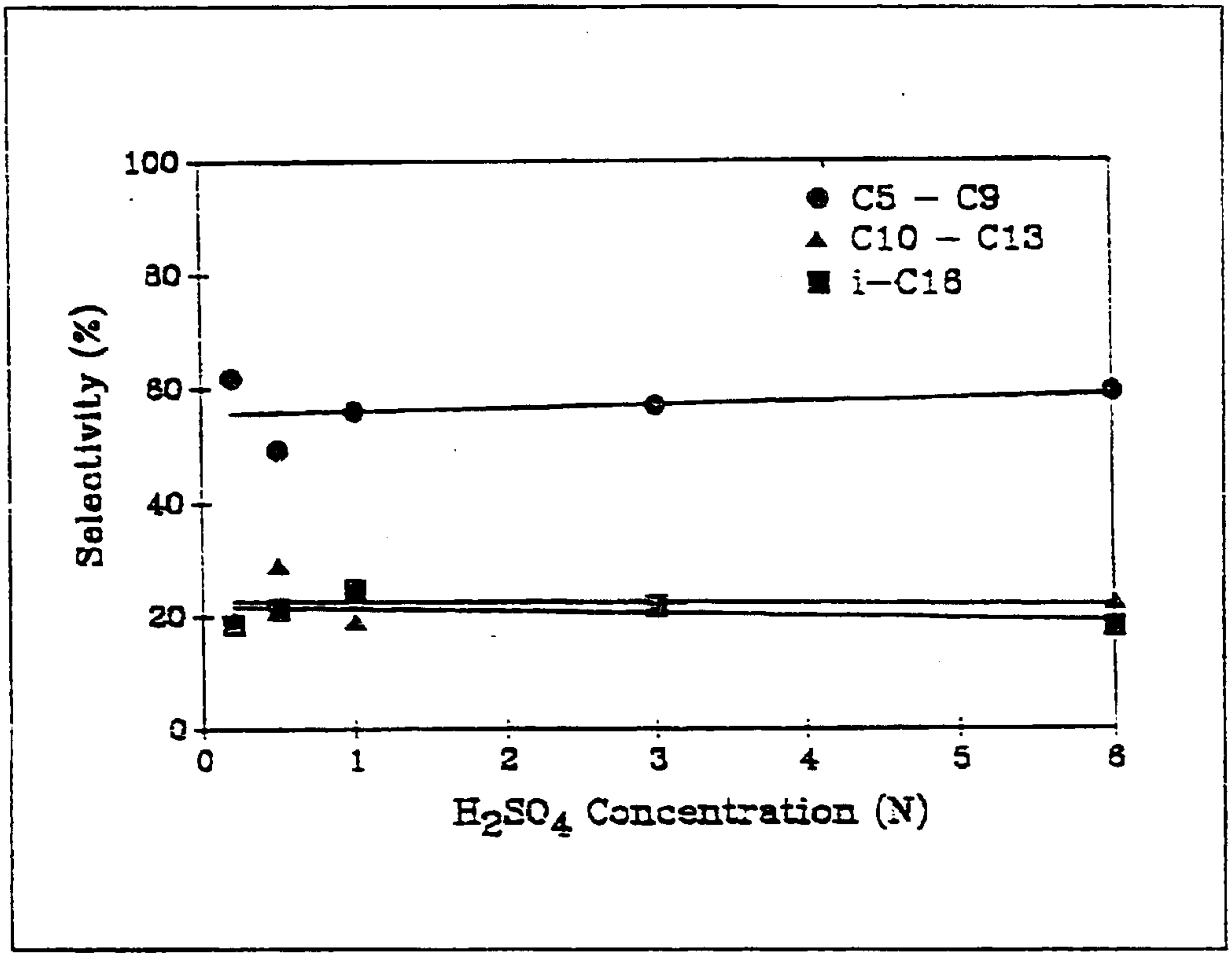

Figure 5. Effect of the Concentration of H_2SO_4 on the Product Selectivity from the Reaction of n-C16 and H_2.

6.4.2 Effect of Addition of Hydrogenation Metals on the Catalytic Activity of ZrO_2/SO_4

6.4.2.1 Hydrogenation Metal.

Bifunctional catalysts, consisting of both a hydrogenation metal and an acidic support, are widely used in the hydrocracking and hydroisomerization of hydrocarbons; the balance between the hydrogenation capacity and the acidic function strongly affects catalytic activity and product selectivity. In order to investigate the role of addition of a hydrogenation metal during the reaction, and its effect on catalytic activity, ZrO_2/SO_4 doped with various hydrogenation metals was used in experiments on hydrocracking and hydroisomerization of n-hexadecane. The preparation conditions of these catalysts have been specified in **Table 6** of **Section 4.3.3**. The catalytic activities of these catalysts are shown in **Table 12**.

The conversion of n-C16 using the ZrO_2/SO_4 catalyst (SZD2) was low, likely due to rapid formation of coke. Addition of a hydrogenation metal such as Pt is known to the effective in reducing coke formation(106,107). In this study, platinum was introduced to the ZrO_2/SO_4 catalyst in three different ways: (a) the classic way: impregnation of $Zr(OH)_4/SO_4$ precipitates with H_2PtCl_6 using the method of incipient wetness followed by calcination at 873 K (SZD1), (b) PtO_2 powder suspended in distilled water was impregnated with $Zr(OH)_4/SO_4$ precipitates and then calcined together at 873 K (SZD17), and (c) PtO_2 powder was mechanically mixed with the ZrO_2/SO_4 catalyst (SZD2) which was already calcined at 873 K (SZD18).

There was an increase in the conversion of n-hexadecane with all three Pt doped ZrO_2/SO_4 catalysts (SZD1, SZD17 and SZD18) compared to that of the untreated ZrO_2/SO_4 catalyst (SZD2). Specifically, the use of the $Pt/ZrO_2/SO_4$ or $PtO_2/ZrO_2/SO_4$ as the catalyst gave high conversions (about 72 wt.%). A conversion of only 11.0 wt.% was obtained upon using the mechanically mixed PtO_2+ZrO_2/SO_4 as the catalyst. Deactivation was not found in the case of $Pt/ZrO_2/SO_4$ and $PtO_2/ZrO_2/SO_4$ during reaction, as suggested by the fact that their colors did not change after reaction. For the PtO_2+ZrO_2/SO_4 catalyst, deactivation seemed to occur during reaction.

The presence of platinum as a hydrogenation metal component was indeed effective in reducing coke formation of the ZrO_2/SO_4. Perhaps more important, the activity of the platinum doped ZrO_2/SO_4 catalyst after calcination apparently did not depend on the nature of starting platinum material used for impregnation. The difference in activity between the calcined $PtO_2/ZrO_2/SO_4$ (**SZD17**) and mechanically mixed PtO_2+ZrO_2/SO_4 (**SZD18**) catalysts suggests that there was modification of the PtO_2 after calcination which favored the catalytic activity.

Table 12. Conversion of n-C16 Using ZrO_2/SO_4 Doped with Various Hydrogenation Metals with 0.5 wt. % of Metal
(Reaction conditions: feed/cat.: 1/6, 433 K, 360 psig H_2 (cold) and 60 min)

Run No.	Catalyst No.	Catalyst formula	Conversion (wt. %)	Selectivity (wt. %)	
				C5 - C13	i-C16
R008	SZD2	ZrO_2/SO_4	0	0	0
R009	SZD1	$Pt/ZrO_2/SO_4$	71.7	82.5	17.5
R010	SZD17	$PtO_2/ZrO_2/SO_4$	72.5	88.4	11.6
R011	SZD18	PtO_2+ZrO_2/SO_4	11	10	90
R012	SZD19	$Pd/ZrO_2/SO_4$	50	76.4	23.6
R013	SZD20	$Ni/ZrO_2/SO_4$	0	0	0

Recently, Ebitani et al.(113) investigated the state of platinum in the $Pt/ZrO_2/SO_4$ catalyst by means of XPS technique. They found that platinum was essentially in an oxidized state, even after hydrogen reduction at 673 K for one hour. On the contrary, Sayari et al.(116) found that it was in the metallic state (Pt^0) in $Pt/ZrO_2/SO_4$, as also revealed by XPS; however, it was in an oxidized form in a non-sulfated Pt/ZrO_2 catalyst. They further suggested that platinum in $Pt/ZrO_2/SO_4$ was reduced to the metallic state by SO_2 generated from the decomposition of the sulfate group during calcination at high temperatures (873 K). In our opinion, the evidence provided by Sayari et al. appears to be more convincing. The effect of calcination observed in this study on the activity of the Pt doped ZrO_2/SO_4 catalysts can thus be explained: platinum was reduced to its metallic state after calcination regardless of the nature of starting platinum material used for impregnation. The low conversion of n-C16 using the mechanically mixed PtO_2 + ZrO_2/SO_4 catalyst without calcination may be due to the fact that the hydrogenation ability of PtO_2 is poorer than that of platinum in the metallic state.

The activities of the ZrO_2/SO_4 doped, respectively, with Pt, Pd and Ni which are in the same group in the periodic table, were investigated for the hydrocracking and hydroisomerization of n-hexadecane (see **Table 12**). The conversion of n-hexadecane using the ZrO_2/SO_4 catalyst doped with Pt (SZD1) was higher than that doped with Pd (SZD19); the ZrO_2/SO_4 catalyst doped with Ni (SZD20) had virtually no activity. The striking difference in activity between the Pt and Ni doped ZrO_2/SO_4 catalysts can be explained by the fact that protonic acid sites were generated on the former catalyst, but not on the latter one, as supported by the IR spectra of the pyridine adsorbed on these two catalysts in the presence of hydrogen. The generation of the active protonic acid sites was thought to be via dissociative adsorption of hydrogen molecules on Pt, followed by spillover of hydrogen atoms onto the ZrO_2/SO_4 and electron transfer from hydrogen atoms to give protonic acid sites.(111,112) Electrons released from the hydrogen atoms to Lewis acid sites reduced their acid strength. As a result, such weakened Lewis acid sites generated less coke, increasing the lifetime of the catalyst. We may conclude that the high catalytic activity of the ZrO_2/SO_4 catalyst doped with Pt or Pd compared to that doped with Ni was due to generation of highly active protonic acid sites and reduced coke formation. Nickel may not be reduced to its metallic state after calcination, and it could not play the same role as Pt in generation of highly protonic acid sites on $Ni/ZrO_2/SO_4$ under given reaction conditions.

The Pt and Pd doped ZrO_2/SO_4 catalysts gave similar selectivities to cracked products (C5-C13) and isomerized hexadecanes (i-C16). The carbon number distributions of the products with these two catalysts are shown in **Figure 6.** Methane (C1), ethane (C2), tetradecane (C14), pentadecane (C15) or compounds greater then C16 were not detected in the cracked products using either of these two catalysts. The carbon number distributions obtained were asymmetrical. Similar experimental findings have been reported by others.(9,128) The conversion of n-C16 as a function of reaction time using the Pt and Pd doped ZrO_2/SO_4 catalysts is shown in Figure 7. The conversion of n-C16 by $Pt/ZrO_2/SO_4$ (SZD1) was higher than that by $Pd/ZrO_2/SO_4$ (SZD19), probably due to the higher hydrogenation capability of Pt.

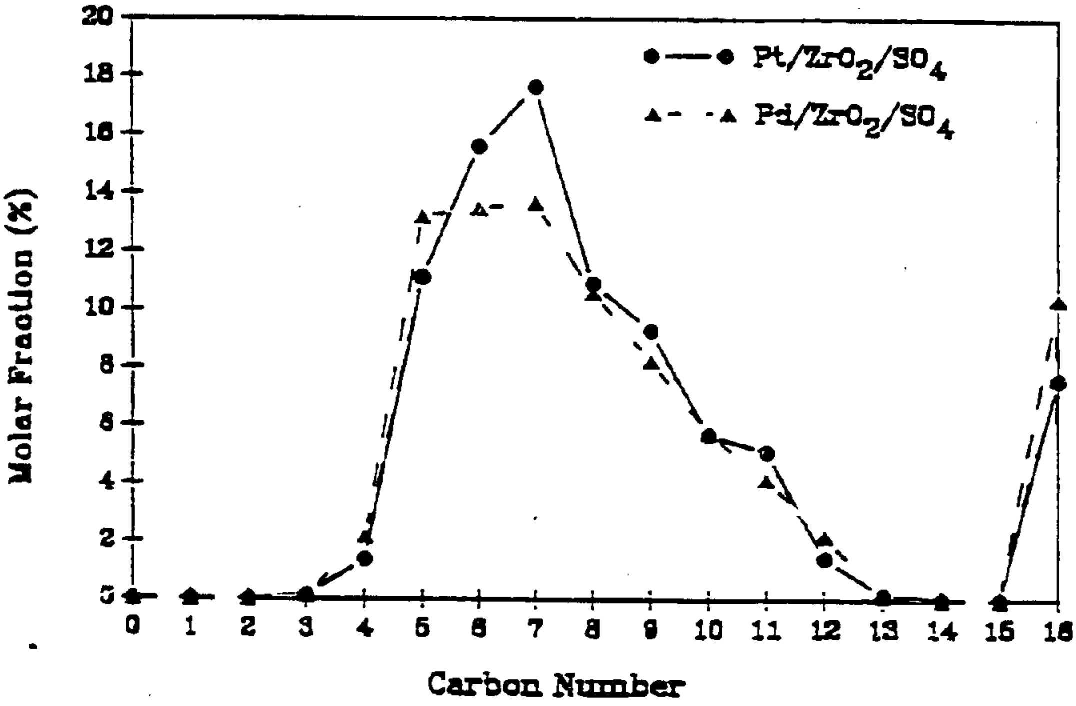

Figure 6. Comparison of Product Distributions Obtained Using Pd and Pt Dopants on the Reaction of n-C16 and H_2.

6.4.2.2 Platinum Loading.

The effect of Pt loading on catalytic activity was studied by varying the weight percent of Pt (0.2 - 5.0 wt.%) on the catalyst. The conversion of n-hexadecane as a function of reaction time using different amounts of Pt loaded on the ZrO_2/SO_4 catalyst is shown in **Figure 8**. The conversion was 74.4 wt.% in the case of the 5.0 wt.% Pt doped catalyst (SZD16) after 10 minutes of reaction, much higher than that for the 0.5 wt.% Pt doped catalyst (SZD1) with a conversion

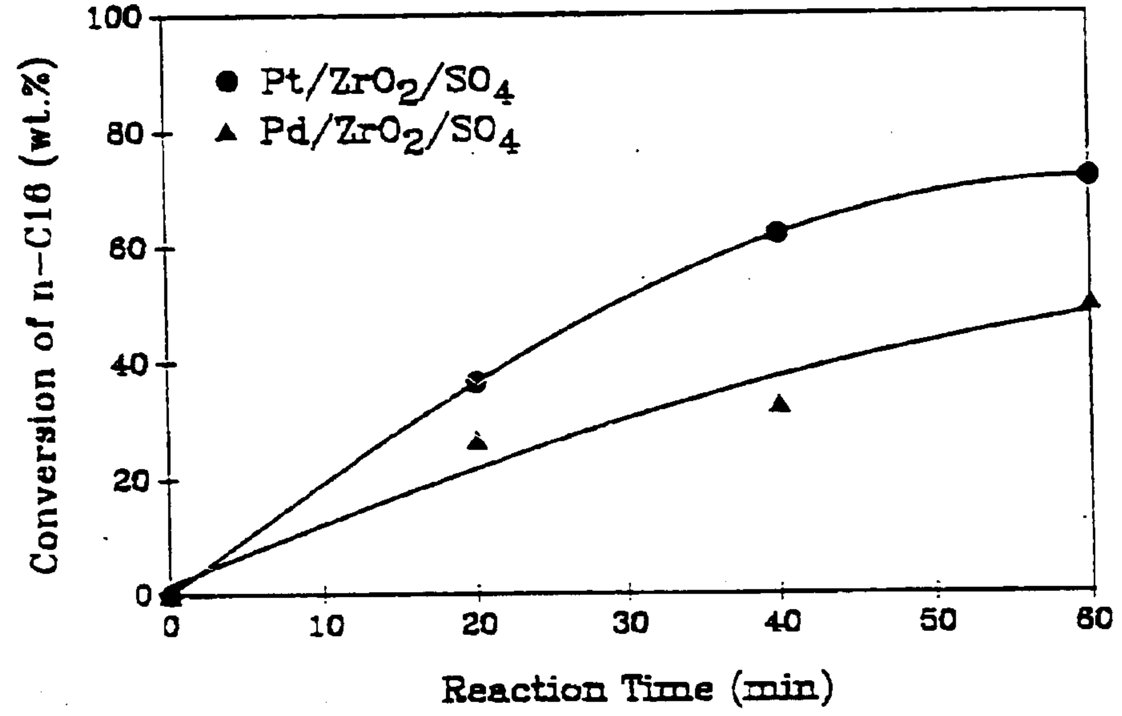

Figure 7. Comparison of Conversion of n-C16 Using Pd and Pt Dopants on ZrO_2/SO_4 Catalyst at 433K and 360 psig H_2cold.

of 36.5 wt. % after 20 minutes of reaction. It can be concluded that the catalytic activity of $Pt/ZrO_2/SO_4$ increases with increasing Pt loading.

Our results have shown that addition of platinum to the ZrO_2/SO_4 not only prolongs catalyst life by preventing coke formation, but also modifies its acidic properties. The role of Pt in an acid catalyzed reaction was investigated by examining the IR spectrum of pyridine absorbed on the $Pt/ZrO_2/SO_4$ catalyst in the presence of hydrogen. The amount of the pyridine adsorbed on the Lewis acid sites (L-Py) decreased upon introduction of hydrogen with a concomitant

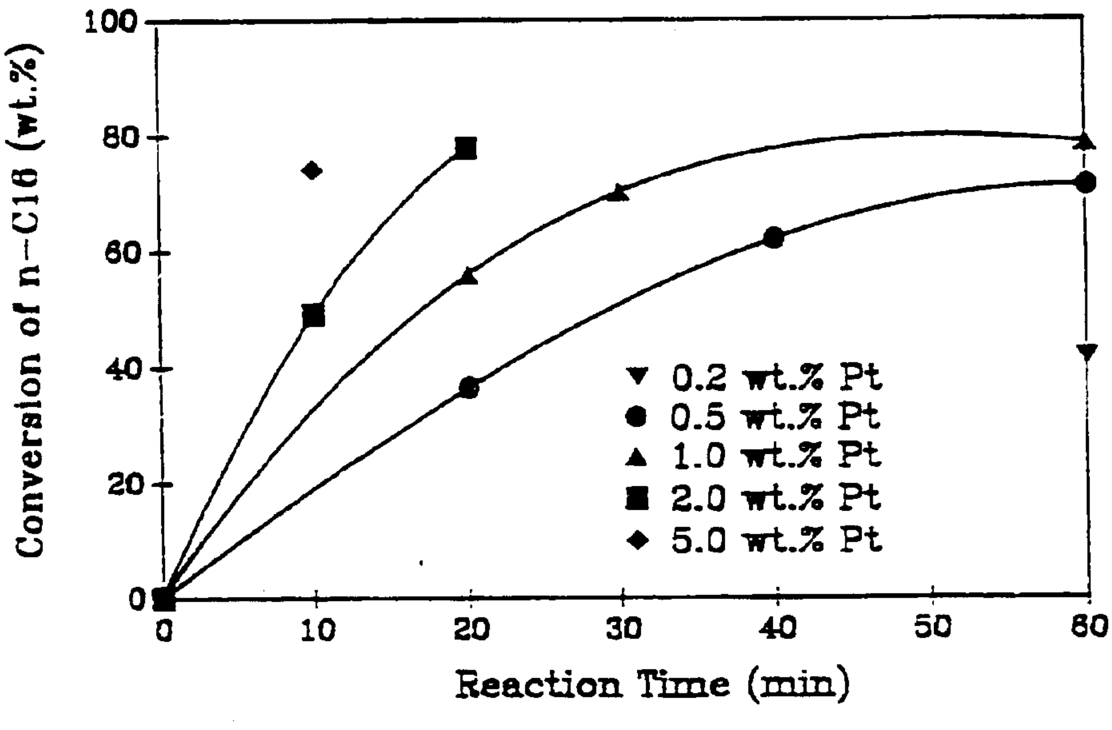

Figure 8. Effect of Pt loading on the Conversion of n-C16 Using a $Pt/ZrO_2/SO_4$ Catalyst at 433K and 360 psig cold.

increase in that of the pyridine adsorbed on the Brönsted acid sites (B-Py). Similar findings have been reported by others(111,112). Ebitani et al.(112) proposed a mechanism for the generation of the protonic acid sites which involved: (a) dissociation of hydrogen molecules on Pt into hydrogen atoms; (b) spillover of hydrogen atoms onto the ZrO_2/SO_4 surface; and (c) electron transfer from hydrogen atoms to the Lewis acid sites forming protonic acid sites. According to this mechanism, the role played by a Pt doped ZrO_2/SO_4 catalyst in a hydrocracking and hydroisomerization reaction differs from that of a hydrogenation metal in the conventional bifunctional mechanism. In the latter, the proposed role of the metal in a bifunctional catalyst system was to dehydrogenate

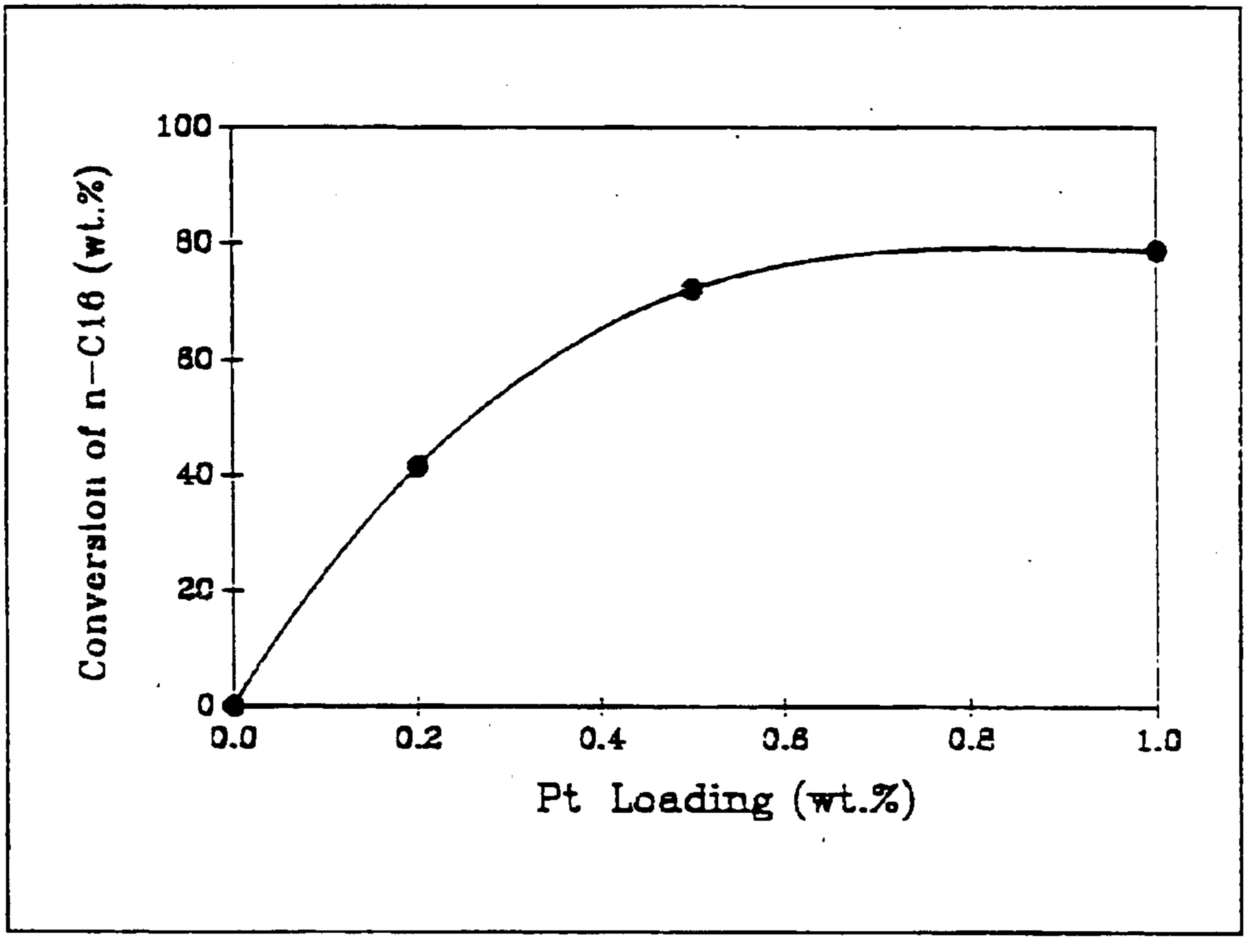

Figure 9. Conversion of n-C16 as a Function of Platinum Loading over a $Pt/ZrO_2/SO_4$ Catalyst at 433K, 360 psig H_2 cold and 60 min.

hydrocarbons to the corresponding olefins and to hydrogenate cracked olefins.(30,120)It was reported(112) that a $Pt/ZrO_2/SO_4$ catalyst with a higher platinum loading accelerated hydrogen spillover, which favored generation of more active protonic acid sites. This agrees with our experimental finding that an increase in Pt loading on the $Pt/ZrO_2/SO_4$ catalyst enhanced its catalytic activity for conversion of n-C16 significantly. The conversion of n-hexadecane (after 60 minutes of reaction) as a function of Pt loading is shown in **Figure 9**. The conversion increased significantly with increasing amount of Pt in the $Pt/ZrO_2/SO_4$ catalyst when Pt loading

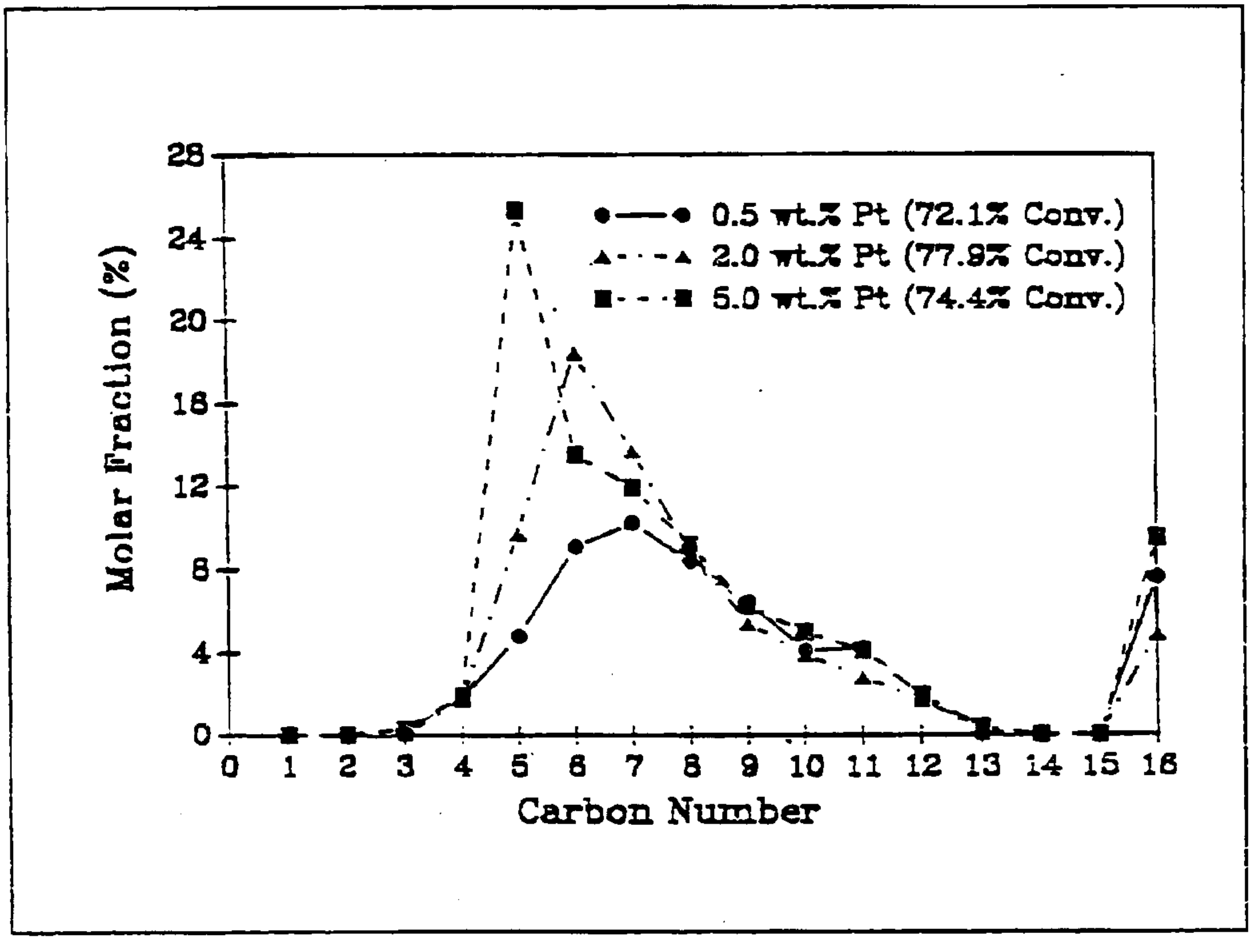

Figure 10. Effect of Pt Loading on the Product Distribution from Hydrocracking of nC-16 over a $Pt/ZrO_2/SO_4$ catalyst at 433K and 360 psig H_2 cold.

was between 0 and 0.5 wt.%. It then leveled off when Pt loading exceeded 0.5 wt.%. The product distributions at similar conversion levels of n-hexadecane, obtained from three different Pt loadings, 0.5 wt.%, 1.0 wt.%, and 5.0 wt.%, on ZrO_2/SO_4 catalysts (**SZD1**, **SZD14** and **SZD16**), are shown in **Figure 10**. All of the carbon number distributions appeared to be asymmetric. No C1, C2, C14, C15 and products higher than C16 were detected. A high Pt loading favored cracking activity, shifting products to shorter chain compounds.

6.4.3 Catalytic Activity of Sulfate-Promoted Bimetallic Oxides ($Pt/ZrO_2 \cdot HfO_2/SO_4$)

Sulfate promoted-bimetallic oxides, $Pt/ZrO_2 \cdot HfO_2/SO_4$, with various molar ratios of Zr to Hf were prepared and their activities tested for hydrocracking and hydroisomerization of n-hexadecane. The amount of reacted n-hexadecane per millimole of acid sites of the catalyst versus molar fraction of ZrO_2 in the bimetallic oxides is shown in **Figure 11**, and it increased significantly with an increase in molar fraction of ZrO_2, reaching a maximum when the mole fraction of ZrO_2 equaled 0.5 and then decreased slightly when the molar fraction of ZrO_2 exceeded 0.5.

The results can be explained as follows: catalyst activity is dictated by acidic properties, i.e., acidity and acid strength. A decrease in the number of acid sites results in a decrease in catalytic activity. On the other hand, a decrease in the acid strength reduces coke formation and favors product desorption. As both the total number of acid sites and the acid strength of these bimetallic oxides decreased with a decrease in the mole fraction of ZrO_2 (see **Table 9 of Section 5.4.3**), it is thought that the high activity of $Pt/ZrO_2 \cdot HfO_2/SO_4$ with a molar ratio of ZrO_2/HfO_2

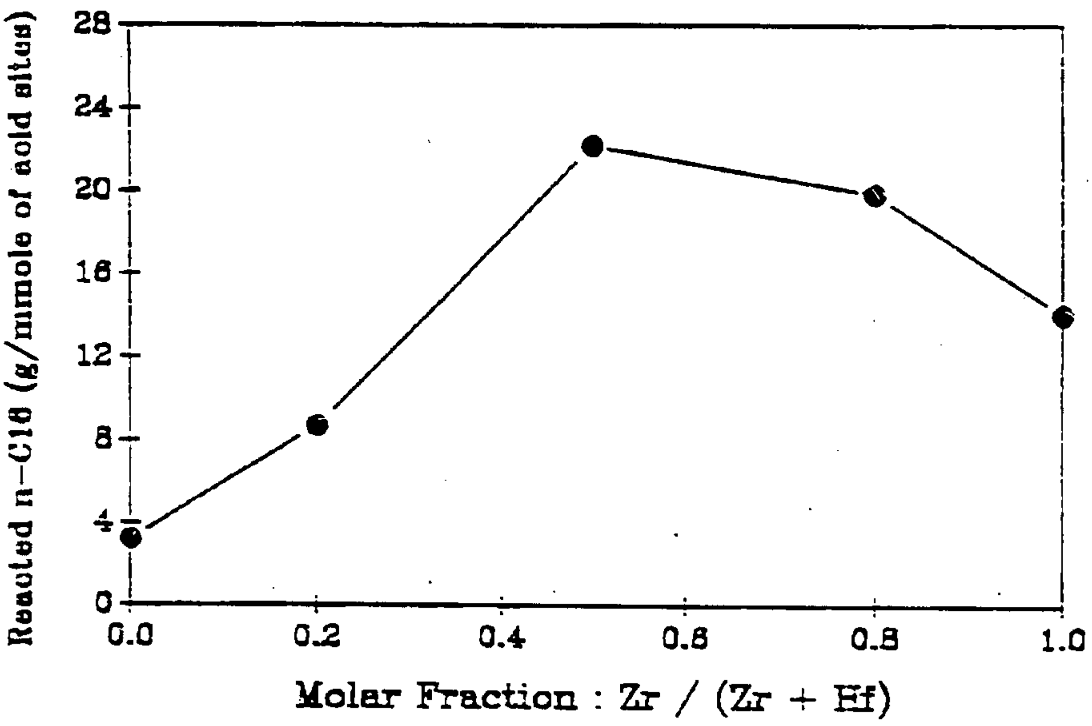

Figure 11. Effect of Molar Fraction of ZrO_2 in a Mixture of ZrO_2 and HfO_2 on the Conversion of n-C16 Using a $Pt/ZrO_2 \cdot HfO_2/SO_4$ at 433K and 360 psig H_2 cold.

being 1:1 (SZHD2), was due to a good balance between the number of acid sites and acid strength. The XRD profiles of these bimetallic oxides showed that the crystalline phase of the sulfate promoted mixtures of zirconium and hafnium oxides consisted of a mixture of tetragonal and monoclinic forms, while the $Pt/HfO_2/SO_4$ alone (SHD) had a mixture of monoclinic form and amorphous, which was reported to be less superacidic.(66) This may explain the low catalytic activity and poor acidic properties of the $Pt/HfO_2/SO_4$ compared with those of the $Pt/ZrO_2/SO_4$ (SZD3).

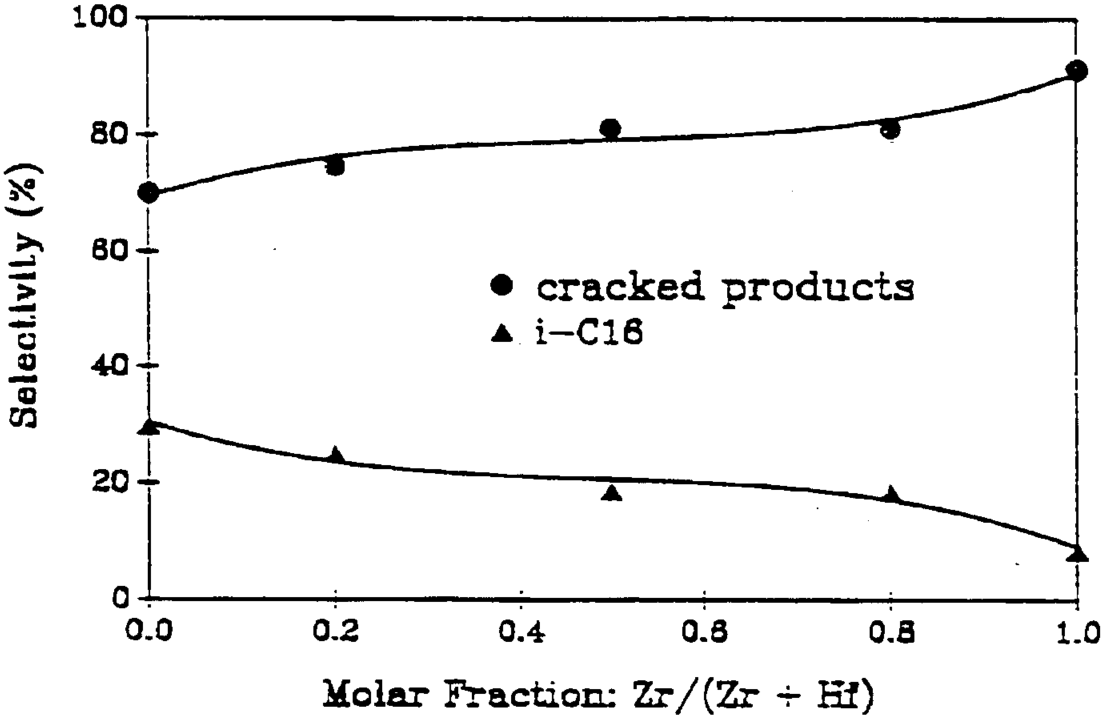

Figure 12. Effect of the Molar Fraction of ZrO_2 on the Product Selectivity on Hydrocracking of n-C16 Using $Pt/ZrO_2{\cdot}HfO_2/SO_4$.

In terms of product selectivity as a function of the molar fraction of ZrO_2 in these bimetallic oxides, (**Figure 12**), selectivity to cracked products increased while that to isomerized hexadecanes decreased when the molar fraction of ZrO_2 increased. An increase in the acid strength with increasing molar fraction of ZrO_2 was responsible for the increased cracking activity. The product distributions obtained using the $Pt/ZrO_2/SO_4$ (SZD3) and the $Pt/ZrO_2{\cdot}HfO_2/SO_4$ (ZrO_2/HfO_2 = 1/1) catalysts are shown in **Figure 13**. No methane or ethane was found in the cracked products using either of these two catalysts. The $Pt/ZrO_2/SO_4$ catalyst had a higher selectivity to shorter chain products (C5-C9), but a lower selectivity to isohexadecanes.

Incorporation of HfO_2 resulted in a wider product distribution spectrum and a higher selectivity to isohexadecanes.

6.5 Summary

We have found that the catalytic activity of an anion-modified metal oxide was determined by its number of acid sites as well as its acid strength, both of which depended on catalyst preparation conditions, the nature of the anion and sulfuric acid concentrations, and calcination temperatures. A $Pt/ZrO_2/SO_4$ sample prepared by heterogeneous precipitation with addition of 1N of sulfuric acid for sulfation and calcination of three hours at 873 K gave the highest number of acid sites and conversion of n-hexadecane. Incorporation of hydrogenation metals such as Pt and Pd on ZrO_2/SO_4 greatly improved its catalytic activity in the presence of hydrogen due

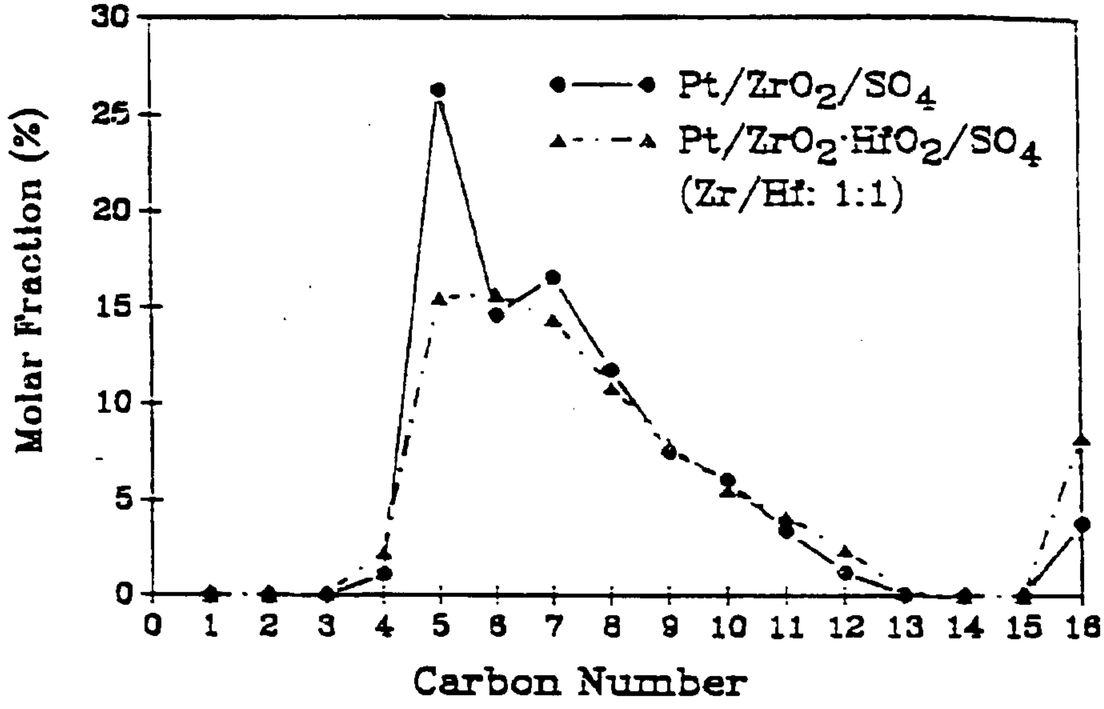

Figure 13. A Comparison of the Product Distribution from the Reaction of n-C16 and H_2 Using the $Pt/ZrO_2/SO_4$ and $Pt/ZrO_2 \cdot HfO_2/SO_4$ (Zr/Hf = 1) Catalysts

to prevention of coke formation as well as modification of its surface acidic properties. We have found that the nature and amount of a particular hydrogenation metal doped on ZrO_2/SO_4 also strongly affected its catalytic activity and product selectivity. Among Pt, Pd and Ni, Pt doped ZrO_2/SO_4 gave the highest conversion of n-hexadecane. The activity of $Pt/ZrO_2/SO_4$ for conversion of n-hexadecane increased greatly with increase in Pt loading. The sulfated promoted bimetallic oxides ($Pt/ZrO_2{\cdot}HfO_2/SO_4$) with a molar ratio of ZrO_2/HfO_2 of one exhibited higher catalytic activity and selectivity to isohexadecanes than those of the platinum doped and sulfate-promoted zirconium oxide.

7.0 EFFECT OF REACTION CONDITIONS ON CATALYTIC ACTIVITY IN HYDROCRACKING AND HYDROISOMERIZATION OF ALKANES

7.1 Objectives

The main objective of this study was to evaluate the catalytic activity of a particular $Pt/ZrO_2/SO_4$ catalyst (SZD1) for isomerization and hydrocracking of n-hexadecane and FT waxes under various reactions conditions. Emphasis was placed on the effects of operating parameters such as reaction temperature, time, operating hydrogen pressure, and the effect of addition of a hydride transfer agent or olefins on the catalytic activity and product selectivity of SZD1.

7.2 Background

$Pt/ZrO_2/SO_4$ is an active catalyst for the isomerization of n-butane and n-pentane(75,106,107) and for the hydrocracking and hydroisomerization of long chain hydrocarbons.(9,128) We have seen earlier that the catalytic activity and product selectivity of this catalyst were strongly affected by the preparation conditions as well as by its composition. In order to better understand the mechanism of the hydrocracking and hydroisomerization of long chain hydrocarbons, the effects of operating parameters, such as reaction temperature, time, operating hydrogen pressure as well as addition of a hydride transfer agents or olefins, on the catalytic activity and product distribution were investigated. The long-term performance of the $Pt/ZrO_2/SO_4$ catalyst towards the hydrocracking and hydroisomerization of n-hexadecane was carried out in a continuous fixed-bed reactor constructed by Dr. Jianli Hu in our laboratory.

7.3 Experimental

The chemicals used in this study were purchased from the Aldrich Chemical company except for the FT waxes which were provided by Sasol (Table 13). They were used as received.

All hydrocracking and hydroisomerization reactions of long chain hydrocarbons were performed in a horizontal shaken tube-microreactor ($45cm^3$) described earlier. Hydrogen pressure