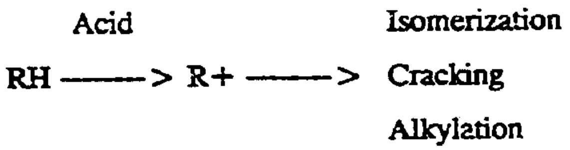
Several methods are available for characterizing acidic properties on a solid surface: titration, spectroscopic measurement by IR or UV (48), test reactions(49) and adsorption-desorption of bases(50). The most traditional method is titration of the solid acid with a base, using colored indicators. The color of suitable indicators adsorbed on a surface will give a measure of acid strength; the number of acid sites will be measured by base titration immediately after determination of acid strength. However, the major criticism of the titration method arises from the question of its reproducibility in view of the difficulty in reaching equilibrium(50). This technique is very difficult to apply to colored catalysts, as well as to catalysts deactivated and darkened by coke. Another technique widely practiced in characterization of acidic properties on a solid surface is gaseous base adsorption-desorption(50,51). The major advantages of this technique are its simplicity and reproducibility. The acidity can be quantitatively determined by the amount of adsorbed base from desorption measurements, and the desorption temperatures are related to acid strength distribution. A combined technique employing IR spectroscopy and temperature programmed desorption (TPD) has been successfully used to study the acidic properties of solid acid catalysts(52). It can give information about acidity, acid strength and nature of acid sites in a single experiment. More recently, several novel techniques such as ESR and NMR have been employed to characterize surface acidity of solid acid catalysts(53-56).

2.3.3 Hydrocarbon Transformation in Superacids

Protonation of exceedingly weak bases can occur with superacids. Not only can almost all π-electron donors such as olefins, acetylenes and aromatics be protonated, but even weak σ-electron donors such as saturated hydrocarbons can be protonated(42). Existence of the structures of alkylcarbenium ions, arylcarbenium ions, vinylcarbenium ions, acyl cations and so on has been spectrometrically identified by NMR in highly acidic media(42). A characteristic of protonation in superacidic media is that it takes place on C-H or C-C bonds to form two-electron-three center carbonium ions(41). Although direct evidence for the presence of carbocations on the surface of a solid catalyst has not been provided, it has been postulated that carbocations can be reaction intermediates in the conversion of hydrocarbons. Arguments in favor of the occurrence of carbocation intermediates have been that the reaction pathways of hydrocarbons can be predicted by considering the stability of the carbocations that may be formed and the rearrangement pathways these cations might follow(57).

Before the turn of the 20th century, saturated hydrocarbons (paraffins) played only a minor role in industrial chemistry because of their chemical inertness. After the first World War, the ever increasing demand for gasoline initiated study of isomerization and cracking reactions of petroleum fractions(21). In the early 1960s, the study of the behavior of saturated hydrocarbons in highly acidic media led to the discovery of hydrocarbon reactions, such as isomerization, Friedel-Crafts alkylation and cracking(58). The fundamental step in these acid-catalyzed hydrocarbon conversion processes is the formation of intermediate carbocations(41).



$$\mathrm{RH} \xrightarrow{\text{Acid}} \mathrm{R+} \longrightarrow \begin{array}{l} \text{Isomerization} \\ \text{Cracking} \\ \text{Alkylation} \end{array}$$

Carbenium intermediates may be formed from a feed paraffin in the following ways(59): (a) by abstraction of a hydride ion at a Lewis acid site, (b) by dehydrogenation of the hydrocarbon and proton addition to the olefinic molecule at a strong Brönsted acid site, and (c) by hydride transfer with a surface carbenium ion formed as in (a) or (b). The carbenium ion may undergo isomerization, cracking or alkylation, and hence strong acids are suitable reagents for chemical transformation, particularly of alkanes.

2.4 Sulfate Promoted Metal Oxides

Among solid superacids, sulfate promoted metal oxides, an interesting class of relatively new solid acids, have gained attention because of their high catalytic activity. The enhancement of acidities and catalytic activities by addition of small amounts of sulfate ions (0.5-3 wt.%) has been reported for certain metal oxides such as ZrO_2(60) TiO_2(61), Fe_2O_3(62), HfO_2(63) and SnO_2(64), oxides which themselves are neutral or very weakly acidic or basic. The high activities of these sulfate doped metal oxides for acid-catalyzed reactions are considered to be due to generation of strong acid sites on the metal oxides. These materials are being explored as catalysts for hydrocarbon conversions. Their activities are strongly affected by preparation methods and reaction conditions.

2.4.1 Synthesis of Sulfate Promoted Metal Oxides

Sulfate promoted metal oxides are usually prepared by adding $(NH_4)_2SO_4$ or H_2SO_4 to the precipitates of their corresponding hydroxides, followed by calcination at desired temperatures (773 - 923 K)(65). For example, ZrO_2/SO_4 is often prepared by hydrolyzing commercially available $ZrOCl_2$ or $ZrO(NO_3)_2$ with aqueous ammonia (28%), and the precipitated $Zr(OH)_4$ is then treated with $(NH_4)_2SO_4$ or H_2SO_4, followed by calcination in air or in vacuum at 773 - 923 K. This preparation method is applicable to other metal oxides. It was found that superacid sites were not created during impregnation of sulfate groups on the crystallized metal oxides, but on the amorphous forms of hydroxides, $M(OH)_x$ on calcination to convert them to the crystalline form(66).

2.4.2 Structure and Properties of Sulfate Promoted Metal Oxides

The oxides of metals such as Zr, Ti, Hf, Fe and Sn, whose metal cations have high coordination numbers and high electronegativities, can be effectively promoted by the sulfate group to become superacids(67). X-ray photoelectron spectroscopy of Fe_2O_3/SO_4 and Fe_2O_3/H_2S treated under oxidizing and reducing conditions, respectively, revealed that the oxidation state of sulfur is S^{6+} and S^{2-}, respectively. No intermediate oxidation states were found during in-situ oxidation and reduction(68). Since high acidic properties as well as high catalytic activity were observed for Fe_2O_3/SO_4 and oxidized Fe_2O_3/H_2S but not for Fe_2O_3/H_2S and reduced Fe_2O_3/SO_4, it was concluded that generation of strong acidity on metal oxides was independent of the sulfur source provided that the oxidation state of sulfur is +6(69). The existence of covalent S=O bonds on a metal oxide probably accounts for the enhanced acidic properties(70). The IR spectra of strong solid acids (ZrO_2/SO_4(71), TiO_2/SO_4(71), Fe_2O_3/SO_4(69) and SnO_2/SO_4(64)) show a strong adsorption band at about 1375 cm^{-1} and broad bands located between 1200 and 900 cm^{-1} in the S=O stretching frequency region, which were different from the corresponding metal sulfates. The structure of a chelating bidentate sulfate coordinated to metal elements(70,72), was proposed to be responsible for the generation of strong acidity; the central metal served as a Lewis acid site, and the acid strength was strongly enhanced by the inductive effect of $S=O$(73). Traces of moisture in such a formulation convert Lewis acid sites to Brönsted acid sites.

The appearance of oxide catalysts treated with the sulfate group differs greatly from that without treatment. It was found(66) that the former were finely powdered solids which coated the wall of glass ampules obscuring vision, whereas the latter did not. The highest acid strengths of TiO_2/SO_4 and ZrO_2/SO_4, measured by the Hammett indicator method using sulfuryl chloride as a solvent, were $H_o \le -14.5$(74) and $H_o \le -16.04$(75), respectively. The acid strength of the ZrO_2/SO_4 was 10,000 times higher than that of 100% H_2SO_4 ($H_o=-11.9$). The acid strength of Fe_2O_3/SO_4 and HfO_2/SO_4 could not be measured by the Hammett indicator method because of their colors; their relative acid strength could be estimated by model reactions. The surface areas of these sulfate-promoted metal oxides were much larger than their corresponding counterparts without sulfate treatment (the specific surface area of TiO_2 increased from 55 to 100 m^2/g when treated with sulfate group). Analysis by scanning electron microscope showed that, after the sulfate treatment, the ZrO_2 catalyst disintegrated into fine particles(66). XPS analysis showed that the surface of the ZrO_2/SO_4 was composed of ZrO_2 and SO_4, not $Zr(SO_4)_2$(67). The same finding was also observed in the XPS spectra of TiO_2/SO_4(67). They showed that crystallization of metal oxides during calcination was retarded upon addition of a sulfate group; the most active TiO_2/SO_4 was in the anatase form(66), and ZrO_2/SO_4, whose acidity was higher, was in the tetragonal form(76).

2.4.3 Hydrocarbon Reactions Catalyzed by Sulfate Promoted Metal Oxides

Sulfate-promoted metal oxides have been used extensively in hydrocarbon reactions. Skeletal isomerization of n-butane, n-pentane and other n-paraffins did not occur at room temperature, even in the presence of H_2SO_4 (100%) as a catalyst. But n-butane was isomerized in the presence of Fe_2O_3/SO_4, TiO_2/SO_4 or ZrO_2/SO_4 at temperatures between 293 and 323

K(74,77), the main product being 2-methylpropane. A ZrO_2/SO_4 catalyst exhibited high activity for acylation of chlorobenzene with o-chlorobenzoyl chloride at about 407 K, and the conversion was 100% after ten hours of reaction(78). Disproportionation of alkylsilanes(79) and dehydrocyclization of hexane to benzene(80) could also be effectively catalyzed by ZrO_2/SO_4 under mild reaction conditions. Fe_2O_3/SO_4 containing 2 wt.% of SO_4^{2-} was highly active for dehydration of alcohols (2-propanol, ethanol(81), etc.), double bond isomerization of 1-butene(70) and isomerization of cyclopropane to propylene(62). TiO_2/SO_4 calcined at 773 K was much more active than SiO_2-Al_2O_3 for esterification of terephthalic acid with ethylene glycol at 473 K(66). The catalytic activity of SnO_2/SO_4 for the isomerization of cyclopropane at 373 K was found to be 100 times greater than SnO_2 alone for the same reaction at 573 K(82). The SnO_2/SO_4 was also found to be highly effective for the dehydrogenation of cyclohexanol to cyclohexanone in the presence of water, with a selectivity of as high as 99% for a conversion of 90%(83).

2.4.4 Sulfate Promoted Zirconium Oxide

Among the sulfate-promoted metal oxides, ZrO_2/SO_4 is probably the highest in terms of its acid strength and reactivity in isomerization, cracking and alkylation of hydrocarbons. Tanabe and Yamaguchi(76) found that changing the mode of preparation of zirconium hydroxide and the source of the sulfate gave slightly different ZrO_2/SO_4 products. They also demonstrated that the stability of sulfate-promoted zirconium oxide was strengthened when it existed in the tetragonal phase.

Hino and Arata(75) found that ZrO_2/SO_4 could isomerize and crack n-butane at room temperature. Addition of the sulfate group to ZrO_2 caused a significant increase in its surface area. More recently, it was claimed that ZrO_2/SO_4 containing Fe and Mn prepared by the heterogeneous co-precipitation method(94,95) exhibited higher activity for isomerization of n-butane at 301 K than that of ZrO_2/SO_4 alone. It was also claimed that the acid sites generated in the Fe or Mn doped ZrO_2/SO_4 were probably much stronger than those in ZrO_2/SO_4(96).

Recently, other efforts have been made to disperse ZrO_2/SO_4 on carriers of high surface area, such as SiO_2(97,98,99), Al_2O_3(100) or active carbon(101), with the aim of increasing the number of acid sites. Such supported catalysts could be important for use in industry from the viewpoint of increased mechanical strength and low cost of solid acid catalysts. Mixed metal oxides treated with the sulfate group, $(ZrO_2.SnO_2)/SO_4$, were reported to exhibit higher activity for isomerization of cyclopropane than that of ZrO_2/SnO_2 and even higher than that of ZrO_2 or SnO_2 containing a similar amount of sulfate group(102). Zirconium oxide promoted with other metal oxides (WO_3(103) and MoO_3(104)) has also been prepared. The ZrO_2/WO_3 catalyst was active for acylation of toluene with benzoic anhydride at 303 K and the skeletal isomerization of n-butane and n-pentane at 373 K. The ZrO_2/MoO_3 was effective for acylation of toluene with benzoic anhydride at 373 K.

Vedrine et al.(105) employed infrared spectroscopy to study the nature of acid sites of the ZrO_2/SO_4 catalyst that might be responsible for isomerization of n-butane. They claimed that the activity of ZrO_2/SO_4 catalyst correlated with the intrinsic sulfur content despite the finding that part of the sulfur was in the bulk. The maximum activity happened to be the case where the intrinsic sulfur content corresponded roughly to a full coverage of the catalyst surface with a monolayer of sulfur. The maximum catalytic activity for isomerization of n-butane to isobutane was related to the presence of both Brönsted and Lewis acid sites with a ratio of Brönsted to Lewis infrared band intensities close to one. It was concluded that both Brönsted and Lewis acid sites must be present in the catalyst for it to have a high catalytic activity.

Hosoi et al.(106) reported that introduction of a small amount of a transition metal such as Pt or Pd on ZrO_2/SO_4 could effectively avoid catalyst deactivation when the reaction was carried out in the presence of hydrogen. The presence of hydrogen seemingly prevented coke formation during the reaction. Among the eight transition metals (Pt, Pd, Ni, Ru, Rh, Fe, W and Mo), Pt doped ZrO_2/SO_4 exhibited the highest activity and selectivity for the skeletal isomerization of n-pentane in the presence of hydrogen, without catalyst deactivation. Its activity remained unchanged after 1000 hours of use in the isomerization of light straight-run naphtha composed of mainly C5 and C6 hydrocarbons(106,107). This was considered to be due to reduced coke formation in the presence of Pt(108,109). Recent studies by Hattori and coworkers(110,111,112) have provided evidence that Pt added to ZrO_2/SO_4 not only prolongs its lifetime due to reduced coke formation, but also preserves its acidity. IR studies of pyridine adsorption have showed that, upon heat treatment of $Pt/ZrO_2/SO_4$ in the presence of hydrogen in the temperature range between 373 and 623 K, protonic acid sites were formed with a concomitant decrease in the number and strength of Lewis acid sites(111).

The oxidative state of Pt on the ZrO_2/SO_4 surface in the presence of hydrogen remains controversial. Ebitani.et al.(113) using in-situ XPS analysis claimed that platinum particles consisted mainly of platinum cations, a mixture of platinum oxide and platinum sulfate, dispersed on the ZrO_2/SO_4 surface in the presence of hydrogen. However, Para et al.(114,115) suggested that platinum was mostly in the metallic state. More recently, Sayari et al.(116) claimed that Pt was reduced to the metallic state upon calcination of the sulfate zirconium oxide at 873 K, whereas Pt in the zirconium oxide without sulfate treatment remained in an oxidized form after calcination at the same temperature.

$Pt/ZrO_2/SO_4$ showed high activity not only for isomerization of short paraffins at room temperature but also for hydrocracking and hydroisomerization of long chain paraffins such as n-hexadecane under mild reaction conditions(9) ($T < 473$ K, $P < 400$ psig of hydrogen). Typical features of a useful acid catalyst in hydrocracking of long chain alkanes should be that (a) its activity and selectivity for isomerization are high at low reaction temperatures, (b) primary cracking predominates over secondary and further cracking(15), and (c) its environmental effects can be tolerated. Compared with conventional amorphous hydrocracking catalysts or platinum-doped zeolite catalysts, $Pt/ZrO_2/SO_4$ (**Table 1**) exhibited high activity in hydrocracking and hydroisomerization of n-hexadecane at mild temperatures; moderate conversion levels of 60%-80% were achieved in the temperature range of 413 - 443 K. Gasoline and kerosene fractions predominated in the hydrocracked products. A small amount of gaseous products (-3%) was also produced, consisting of butanes and propane; no methane and ethane were obtained. With n-hexadecane, this catalyst showed a high selectivity to isoparaffins (> 90%), of which more than 50% of the isohexadecane and C10-C13 isoparaffins were multibranched. In terms of reactivity and product quality for hydrocracking and hydroisomerization of long chain paraffins, the

$Pt/ZrO_2/SO_4$ catalyst showed some advantages over industrial commercial catalysts.

Table 1. Reactivity Comparison of Various Catalysts for the Hydrocracking and Hydroisomerization of Hydrocarbons

Feed	Catalyst	Temp (K)	H_2 Press (psig)	Products	Conv.	Ref.
n-C16	$Pt/ZrO_2/SO_4$	403-443	300	C3-C13 & Iso-C16	56-73	9
n-C16	$Pt/SiO_2\text{-}Al_2O_3$	643-667	1000	C1-C15 & Iso-C16	>53	30
n-C20	$Pt/Cl\text{-}F\text{-}Al_2O_3$	643	500	12.5% Gas 14.6% Liq. 70.8% Iso-C20	48	25
C11-C15	$Pt/F\text{-}Al_2O_3$	643	50-1000	Fractions	5-70	24
n-C12	Pt/Ca/Y-Zeolite	538-623	600	C3-C9 & Iso-C12	39-100	31
n-C12	Pt/USY-Zeolite	403-523	87-1465	C3-C9 & Iso-C12	0-100	32
n-C15	Pt/Ca/Y-Zeolite	513	540	Cracked Prod. & Iso-C15	95	26
n-C15	Pt/HZSM-5	483-533	300	C3-C12 & Iso-C15	9-99	33
n-C16	Pt/USY-Zeolite	415-436	30-300	C3-C13 & Iso-C16	20-49	34
n-C10	Pt/USY-Zeolite	434	30	C3-C7 & Iso-C10	27	117
n-C7	Pt/HY-Zeolite	523	30	C3-C6 & Iso-C7	0-80	118
n-C7	Pt/H-OFF-Zeolite	523	30	C3-C6 & Iso-C7	0-90	119

2.5 Mechanism of Bifunctional Catalysis in Hydrocracking and Hydroisomerization

The generally accepted mechanism of hydrocracking and hydroisomerization of long chain hydrocarbons catalyzed by a bifunctional catalyst was proposed by Weisz(120) and by Goonradt (30), as shown in Figure 1.

$$\text{n-Alkane} \xrightleftharpoons[+H_2]{-H_2} \text{n-Alkenes} \xrightleftharpoons[-H^+]{+H^+} \text{sec.n-Alkyl cations} \xrightarrow{\beta\text{-scission}} \text{Cracked products}$$

$$\downarrow\uparrow$$

$$\text{i-Alkanes} \xrightleftharpoons[+H_2]{-H_2} \text{i-Alkenes} \xrightleftharpoons[-H^+]{+H^+} \text{tert. Alkyl cations} \xrightarrow{\beta\text{-scission}} \text{Cracked products}$$

Figure 1. Proposed Mechanism of Bifunctional Catalysis in Hydrocracking and Hydroisomerization of Alkanes

An equilibrium between alkanes and alkenes as a result of dehydrogenation and hydrogenation is established on the metal of the catalyst. Alkylcarbenium ions are formed upon protonation of the alkenes on the Brönsted acid sites. The alkylcarbenium ions can either undergo β-scission to form carbenium ions of lower carbon number and olefins as cracked fragments or isomerized to produce branched hydrocarbons. Carbenium ions play a role as key intermediates in hydrocracking and hydroisomerization, and the overall reaction rate is limited by their rate of formation. There are five modes of β-scission reactions.(33) Starting from a secondary carbenium ion derived from a normal paraffin, primary carbenium ions, which are energetically unfavorable, are formed. The only way to avoid this problem by β-scission is to isomerize the normal paraffins into multibranched ones, which are cracked to form olefins and tertiary or secondary carbenium ions. Unfortunately, many experimental observations cannot be reasonably explained on the basis of this requirement. Sie(121,122,123) has proposed a somewhat different reaction mechanism to account for acid catalyzed hydrocracking of n-paraffins. The only new feature of this mechanism is a postulation of 1,3-hydrogen shifts, which are known to be unfavorable relative to consecutive 1,2-shifts.

Starting from a straight-chain paraffin, the classic carbenium ion is generated by hydride abstraction or protonation of an olefin derived from dehydrogenation of a paraffin. Through cyclization of the alkylcarbenium ion, a non-classical carbonium ion is formed. The cracking step is completed by a hydride shift from a carbon atom in the β-position of the cyclopropyl ring to the nearest ring carbon atom, followed by a hydride shift between two carbon atoms of the cyclopropane ring and bond scission, which leads to a tertiary carbenium ion and a linear olefin. The main difference between Sie's mechanism and the classical β-scission one is that in the former mechanism, a non-classical carbonium ion is formed at the cracking step instead of a classical carbenium ion. Sie claimed that this mechanism not only avoided formation of an energetically unfavorable primary carbenium ion but also logically explained the features of acid catalyzed cracking and hydrocracking.

3.0 RESEARCH OBJECTIVES

The main objective of this project was to study the use of anion promoted metal oxides for converting long chain hydrocarbons such as F-T waxes into liquid fuels by hydrocracking and hydroisomerization processes under relatively mild reaction conditions. Specific goals were as follows:

(1) To investigate the effect of the method of synthesis of anion-modified metal oxides (especially zirconium oxide) and mixed metal oxides on the activity of the resulting catalysts for the hydrocracking and hydroisomerization of long chain hydrocarbons. The method of synthesis includes the nature of the starting zirconia precursor, the precipitation route, the concentrations of H_2SO_4 and calcination temperatures.

(2) To establish the relationship between the acidic properties of anion-promoted metal oxides and their activities for hydrocracking and hydroisomerization of Fischer -Tropsch waxes.

(3) To determine the variation in the acidic properties, catalytic activity and product selectivity of sulfate promoted zirconium oxide (ZrO_2/SO_4) with catalyst parameters such as the amount of sulfate group and the nature and amount of dopant metal.

(4) To compare the effect of anions such as SO_4^{2-}, MoO_4^{2-} and WO_4^{2-} on the acidic properties and catalytic activity of platinum doped on ZrO_2.

(5) To study the effects of hydrogen pressure, reaction time, the presence of a hydride transfer agent or an olefin, on the catalytic activities and product selectivities of $Pt/ZrO_2/SO_4$.

(6) To gain an insight into the reaction mechanism of hydrocracking and hydroisomerization of long chain hydrocarbons and F-T waxes catalyzed by $Pt/ZrO_2/SO_4$.

4.0 SYNTHESIS OF ANION-MODIFIED METAL OXIDES

4.1 Objectives

(1) To synthesize Pt-promoted zirconium oxide products starting from various zirconia precursors, by different precipitation procedures. These products were then modified by SO_4^{2-}, MoO_4^{2-} or WO_4^{2-}.

(2) To prepare $Pt/ZrO_2/SO_4$ catalysts containing various amounts of sulfate and Pt loadings.

(3) To synthesize Pt doped sulfate promoted mixed metal oxides.

(4) To develop better routes for obtaining sulfate-modified metal oxide catalysts and $Pt/ZrO_2/SO_4$ in particular.

4.2 Background

Considering the role of superacids in hydrocarbon chemistry and the advantages of solid catalysts in industry, it is not surprising that research activities on catalysis by solid acids have been increasing. It was found that when a few percent of some anions such as a sulfate group was introduced to certain metal oxides and then subjected to heat treatment, their surface acidity and catalytic activity increased greatly(10,41,45). The most common method for synthesizing sulfate-modified metal oxides is based on aqueous precipitation of the hydroxides of metals followed by drying, treatment with an appropriate sulfate containing material like aqueous sulfuric acid or aqueous ammonium sulfate, and calcination at appropriate temperatures. Calcination allows the products to form stable crystalline phases. A procedure of precipitation-sulfation-calcination has been patented and used by several researchers(63-65,71). Our catalyst preparation follows this general route with a modification in the synthesis of sulfate-promoted zirconium catalysts: instead of $ZrOCl_2$ or $ZrO(NO_3)_3$ which have been used frequently by many researchers, $Zr(SO_4)_2 \cdot 4H_2O$ is employed as a starting material for catalyst preparation. The main advantage of this modification lies in that, unlike $ZrOCl_2$ or $ZrO(NO_3)_3$ which contain unwanted anions requiring thorough water washing of precipitates, the use of $Zr(SO_4)_2 \cdot 4H_2O$ as the starting material simplifies water washing greatly. Zirconium oxides modified by other anions such as WO_4^{2-} and MoO_4^{2-} were prepared by heterogeneous coprecipitation of the hydroxide of zirconium with the hydroxide of tungsten or molybdate followed by calcination. Hydrogenation metals were usually introduced into the precipitates by the method of incipient wetness before calcination. Both homogeneous and heterogeneous precipitation methods were used for the synthesis of anion-modified metal oxides. The heterogeneous precipitation method consisted of dropwise addition of aqueous ammonium hydroxide as the precipitating agent to a solution of starting metal salts. In this case, the concentration of ammonium hydroxide was not uniform locally during the formation of precipitates. The homogeneous precipitation method used an excess of urea (NH_2CONH_2) instead of ammonia. The precipitates were formed from the homogeneous solution of hydroxide ion as urea decomposed to ammonium hydroxide at temperatures above 343 K.

4.3 Experimental

4.3.1 Chemicals and Materials Used

The starting materials used for the synthesis of bifunctional anion-modified metal oxides and mixed oxides are shown in **Table 2.**

4.3.2 Heterogeneous Precipitation Method

4.3.2.1 Synthesis of ZrO_2/SO_4 and $Pt/ZrO_2/SO_4$ Using $Zr(SO_4)_2 \cdot 4H_2O$.

(i) *Dissolution*: 50 g of $Zr(SO_4)_2 \cdot 4H_2O$, a water-soluble salt, was added to 564 ml of distilled water. The resulting solution was stirred using a magnetic bar for one hour at room temperature.

(ii) *Hydrolysis*: Aqueous ammonia (28%) was added dropwise through a burette (10 -15 drops/min) to the solution with constant stirring while monitoring the pH of the hydrolyzing solution. A white gel was formed immediately after several drops of the aqueous base were added. The addition rate of the base was raised to 20 drops/min after the pH of the solution reached 5.0. This continued to the point where the final pH reached 10.0. Thereafter the solution was stirred continuously for an additional five minutes before it was allowed to age overnight. About 90 ml of the aqueous ammonia was used in the precipitation process. The final product obtained consisted of fine particles of zirconium hydroxide ($Zr(OH)_4$).

(iii) *Water washing of precipitates*: The precipitates after hydrolysis were washed twice with 600 ml of distilled water under constant stirring for about 10 minutes at room temperature in order to remove impurities and unreacted aqueous ammonia.

Table 2. Chemicals for the Preparation of Bifunctional Anion-modified Metal Oxides

Description	Chemical	Purity (%)	Supplier
Starting salt	Zirconium sulfate	99.0	Pfaltz & Bauer
	Zirconium dichloride oxide octahydrate	99.998	Strem Chemical
	Zirconium dinitrate oxide hydrate	unavailable	Strem Chemical
	Hafnium dichloride oxide octahydrate	> 98	Stream Chemical
Precipitating agent	Aqueous ammonium hydroxide (28%)	not given	Fisher Scientific
	Urea	99.99	EM industries
Anion	Sulfuric Acid	95.9	Mallinckrodt
	Ammonium metatungstate	>99.9	Strem Chemical
	Ammonium molybdate tetrahydrate	99.999	Strem Chemical
Hydrogenation Metal	Chloroplatinic acid hexahydrate	99.9	Strem chemical
	Palladium (II) chloride	99.9	Strem Chemical
	Nickel (II) nitrate hexahydrate	99.999	Aldrich Chemical

(iv) *Filtration and collection of precipitates*: The washed precipitates were then filtered under vacuum using a Whatman No.1 filter paper. Some very fine particles of the precipitates were lost during filtration as they passed through the filter. The final precipitates were collected from the filter and placed in a glass beaker.

(v) *Drying*: The precipitates of zirconium hydroxide after filtration were dried in an oven at 383 K for 24 hours in order to remove water and other volatile impurities such as ammonia.

(vi) *Grinding*: The dried precipitates were ground into powder, which could pass through a -100 mesh sieve (149 microns).

(vii) *Sulfation and Drying*: The dried and ground precipitates were weighed to determine the yield of the hydrolysis reaction (18.2 g of $Zr(OH)_4$ was obtained). The precipitates were slurried and digested for one hour with 180 ml of sulfuric acid (1 N) (10 ml of the sulfuric acid solution per gram of precipitates). The slurry was then filtered to remove excess water, dried in an oven at 383 K for 24 hours in order to remove physically adsorbed water. The product thus dried was then powdered to -100 mesh.

(viii) *Impregnation*: The dried sulfated precipitates ($Zr(OH)_4/SO_4$) were impregnated with an aqueous solution containing $H_2PtCl_6 \cdot 3H_2O$ (0.5 wt.% Pt per gram of ZrO_2) using the method of incipient wetness. The amount of distilled water used in the aqueous solution was 0.9 ml per gram of the sulfated precipitate.

(ix) *Drying and Calcination*: The precipitates after impregnation were dried in an oven at 383 K for 12 hours to remove excess water, and then powdered to -100 mesh. The powdery product was then calcined at 873 K in air for three hours to convert the amorphous zirconium hydroxide to zirconium oxide to a stable crystalline state. The final product (denoted as **SZD1**) was stored in desiccator. The dried precipitates before impregnation with platinum were also calcined following the same procedure. This catalyst will be denoted as SZD2.

4.3.2.2 Synthesis of $Pt/ZrO_2/SO_4$ Using Zirconium Oxide Dichloride and Zirconium Oxide Dinitrate.

This was done under the same conditions as those used for the preparation of **SZD1** with modifications concerning the starting zirconia material and the water washing step. $Zr(SO_4)_2{\cdot}4H_2O$ was replaced either by zirconium oxide dichloride ($ZrOCl_2$) or zirconium oxide dinitrate ($ZrO(NO_3)_2$). These two zirconia salts are widely used in the literature. As mentioned in the **Background** section of this chapter, the main disadvantage of using $ZrOCl_2$ or $ZrO(NO_3)_2$ lies in that, unlike $Zr(SO_4)_2{\cdot}4H_2O$, $ZrOCl_2$ and $ZrO(NO_3)_3$ contain unwanted ions (Cl^- and NO_3^-), thus requiring a considerable amount of water washing effort in order to remove them. The final catalysts obtained using $ZrOCl_2$) and $ZrO(NO_3)_2$ will be denoted as **SZD3** and **SZD4**, respectively. The catalyst, ZrO_2 denoted as **ZD**, was prepared by calcining the precipitates obtained from $ZrOCl_2$ without sulfation in air at 773 K for three hours.

The precipitates obtained using $ZrO(NO_3)_2$ as the starting material after sulfation and impregnation with $H_2PtCl_6{\cdot}3H_2O$ solution were also calcined in air at 773, 823, 923 and 973 K, respectively. The resulting catalysts will be denoted as **SZD5**, **SZD6**, **SZD7** and **SZD8**, respectively.

In order to obtain the $Pt/ZrO_2/SO_4$ catalysts containing different amounts of sulfate anion, the precipitates obtained using $ZrOCl_2$ as the starting material were also impregnated with sulfuric acid solutions of different concentrations (0.2, 0.5, 3.0 and 6.0 N). The catalysts obtained after impregnation with $H_2PtCl_6{\cdot}3H_2O$ solution and calcination under the same conditions as for **SZD3** will be denoted as **SZD9**, **SZD10**, **SZD11** and **SZD12**, respectively.

4.3.2.3 Synthesis of $Pt/ZrO_2/SO_4$ With Various Pt Loadings, $PtO_2/ZrO_2/SO_4$ and PtO_2 + ZrO_2/SO_4.

The $Pt/ZrO_2/SO_4$ catalysts containing various platinum loadings (0.2, 1.0, 2.0 and 5.0 wt.% per gram of ZrO_2) were prepared as follows: the precipitates obtained using $Zr(SO_4)_2{\cdot}4H_2O$ as the starting salt after sulfation were impregnated with $H_2PtCl_6{\cdot}3H_2O$ solutions of desired concentrations in platinum; they were then calcined under the same conditions as **SZD1**. These catalysts will be denoted as **SZD13**, **SZD14**, **SZD15** and **SZD16**, respectively.

The same precipitates after sulfation were also impregnated with platinum oxide (PtO_2) dispersed in distilled water. The catalyst containing 0.5 wt.% Pt per gram of ZrO_2

($PtO_2/ZrO_2/SO_4$) obtained after calcination under the same conditions as **SZD1** will be denoted as **SZD17**. A mechanical mixture of **SZD2** with PtO_2 powder (PtO_2 + ZrO_2/SO_4) will be denoted as **SZD18**.

4.3.2.4 Synthesis of $Pd/ZrO_2/SO_4$ and $Ni/ZrO_2/SO_4$.

The precipitates obtained using $Zr(SO_4)_2 \cdot 4H_2O$ as the starting material were impregnated after sulfation with an aqueous solution of palladium (II) chloride or nickel (II) nitrate hexahydrate. Palladium (0.5 wt.% per gram of ZrO_2) or nickel (0.5 and 2.0 wt.% per gram of ZrO_2) was added. The products after impregnation were dried and then calcined in air at 873 K for three hours. These catalysts will be denoted as **SZD19**, **SZD20** and **SZD21**, respectively.

4.3.2.5 Synthesis of $Pt/ZrO_2/WO_3$ and $Pt/ZrO_2/MoO_3$.

Zirconium oxide promoted either by WO_3 or MoO_3 was prepared by the heterogeneous coprecipitation method. The hydrolysis step was modified and the sulfation step eliminated. The amount of ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$) or ammonium molybdate tetrahydrate ($(NH_4)_6H_2Mo_7O_{24} \cdot 4H_2O$) (13 wt.% of either W or Mo per gram of ZrO_2) and the calcination conditions followed the literature(103,104). An aqueous solution of $ZrO(NO_3)_2$ mixed with $(NH_4)_6H_2W_{12}O_{40}$ or $(NH_4)_6H_2Mo_7O_{24} \cdot 4H_2O$ was hydrolyzed by aqueous ammonia (28%) to a final pH of 10. After impregnation with $H_2PtCl_6 \cdot 3H_2O$ solution, the precipitates containing WO_4^{2-} were calcined in air at 973 K for three hours, and those containing MoO_4^{2-} at 1073 K for three hours. These catalysts will be denoted as **TZD** and **MZD**, respectively.

4.3.2.6 Synthesis of $Pt/HfO_2/SO_4$ and $Pt/ZrO_2 \cdot HfO_2/SO_4$.

The $Pt/HfO_2/SO_4$ catalyst (denoted as **SHD**) was prepared from hafnium oxide dichloride ($HfOCl_2$) upon following the same procedure as that for **SZD3**. The $Pt/ZrO_2 \cdot HfO_2/SO_4$ catalysts with three different ZrO_2 to HfO_2 molar ratios (0.2, 0.5 and 0.8) were prepared by the heterogeneous coprecipitation method followed by sulfation, impregnation and calcination under the same conditions as those for **SZD3**. They will be denoted as **SZHD1**, **SZHD2** and **SZHD3**, respectively.

4.3.3 Homogeneous Precipitation Method

In addition to the heterogeneous method, the homogeneous precipitation method was also used for the purpose of the preparation of a $Pt/ZrO_2/SO_4$ catalyst. The latter differs from the former method only in the following steps:

(i) *Dissolution*: 25 g of $Zr(SO_4)_2 \cdot 4H_2O$ and 75 g of urea were added to 1000 ml of distilled water with constant stirring at room temperature to a complete dissolution of the whole system. The initial pH of the system was about 2.5.

(ii) *Hydrolysis*: The solution was stirred and heated to 368 K. At that temperature urea decomposed into ammonia and carbon dioxide. Ammonia then reacted with water forming NH_4OH. After reaction with NH_4OH for two and a half hours, $Zr(SO_4)_2 \cdot 4H_2O$ was converted to $Zr(OH)_4$ in the form of fine particles. At the end of the reaction, the pH of the solution was about 7.5. The whole system was then cooled to room temperature without stirring.

(iii) *Washing*: The precipitates were washed with 500 ml of hot distilled water (343 K) three times to remove impurity ions and excess ammonium hydroxide.

The catalyst obtained by this method will be denoted as **SZD22**.

The synthesis procedures for all metal oxide catalysts used in this study are summarized in **Table 3**.

4.4 Final Remarks

The method employing the new starting zirconia salt, $Zr(SO_4)_2 \cdot 4H_2O$, is novel and very useful in the synthesis of sulfate-promoted zirconium oxides because it does not contain undesirable ions such as Cl^- and NO_3^- as in the conventional zirconia salts ($ZrOCl_2$ and $ZrO(NO_3)_2$); this reduces significantly the water washing effort. Additionally, the sulfate group already present in the starting material would be beneficial for formation of superacid sites on zirconium oxide. The price of $Zr(SO_4)_2 \cdot 4H_2O$ is cheaper than that of $ZrOCl_2$ or $ZrO(NO_3)_2$, and this may be considered another advantage.

Table 3. Summary of the Catalysts Obtained by the Heterogeneous and Homogeneous Methods

Catalyst No.	Catalyst formula	Preparation			
		starting salt	H_2SO_4 (N)	metal loading (wt.%)	calcination temperature (K)
ZD	ZrO_2	$ZrOCl_2$	0	0	773
SZD2	ZrO_2/SO_4	$Zr(SO_4)_2 \cdot 4H_2O$	1	0	873
SZD1	$Pt/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	0.5	873
SZD3	$Pt/ZrO_2/SO_4$	$ZrOCl_2$	1	0.5	873
SZD4	$Pt/ZrO_2/SO_4$	$ZrO(NO_3)_2$	1	0.5	873
SZD5	$Pt/ZrO_2/SO_4$	$ZrO(NO_3)_2$	1	0.5	773
SZD6	$Pt/ZrO_2/SO_4$	$ZrO(NO_3)_2$	1	0.5	823
SZD7	$Pt/ZrO_2/SO_4$	$ZrO(NO_3)_2$	1	0.5	923
SZD8	$Pt/ZrO_2/SO_4$	$ZrO(NO_3)_2$	1	0.5	973
SZD9	$Pt/ZrO_2/SO_4$	$ZrOCl_2$	0.2	0.5	873
SZD10	$Pt/ZrO_2/SO_4$	$ZrOCl_2$	0.5	0.5	873
SZD11	$Pt/ZrO_2/SO_4$	$ZrOCl_2$	3	0.5	873
SZD12	$Pt/ZrO_2/SO_4$	$ZrOCl_2$	6	0.5	873
SZD13	$Pt/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	0.2	873
SZD14	$Pt/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	1	873
SZD15	$Pt/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	2	873
SZD16	$Pt/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	5	873

Table 3 (continued)

Catalyst No.	Catalyst formula	Preparation			
		starting salt	H_2SO_4 (N)	metal loading (wt.%)	calcination temperature (K)
SZD17	$PtO_2/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	0.5	873
SZD18	$PtO_2 + ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	0.5	873
SZD19	$Pd/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	0.5	873
SZD20	$Ni/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	0.5	873
SZD21	$Ni/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	2	873
TZD	$Pt/ZrO_2/WO_4$	$ZrO(NO_3)_2$	NA	0.5	973
MZD	$Pt/ZrO_2/MoO_4$	$ZrO(NO_3)_2$	NA	0.5	1073
SHD	$Pt/HfO_2/SO_4$	$HfOCl_2$	1	0.5	873
SZHD1	$Pt/ZrO_2 \cdot HfO_2/SO_4$	$ZrOCl_2 + HfOCl_2$ (4:1 by mole)	1	0.5	873
SZHD2	$Pt/ZrO_2 \cdot HfO_2/SO_4$	$ZrOCl_2 + HfOCl_2$ (1:1 by mole)	1	0.5	873
SZHD3	$Pt/ZrO_2 \cdot HfO_2/SO_4$	$ZrOCl_2 + HfOCl_2$ (1:4 by mole)	1	0.5	873
SZD22[a]	$Pt/ZrO_2/SO_4$	$Zr(SO_4)_2 \cdot 4H_2O$	1	0.5	873

a: obtained by the homogeneous precipitation method