Thermal stability of the Pt bearing sulfate-promoted zirconia in the presence of hydrogen

Raymond Le Van Mao [1], Shuyong Xiao and Tuan Si Le

Catalysis Laboratory and Laboratories for Inorganic Materials,
Department of Chemistry and Biochemistry, Concordia University, 1455 De Maisonneuve West,
Montreal, Quebec, Canada H3G 1M8

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Molecular hydrogen reduces the sulfate groups of the sulfate-promoted zirconia into volatile species, at a temperature much lower than the temperature of decomposition–oxidation of these groups in inert atmosphere or in air. This reduction effect is enhanced with the incorporation of Pt into the sulfate-promoted zirconia (the so-called "Pt-to-sulfate" effect), resulting in the loss of the sulfate groups at a significantly lower temperature. Such an enhanced reduction activity of hydrogen can be explained by the well known activation action of Pt on molecular hydrogen at relatively high temperatures. Moreover, this also results in the production of some surface zirconium sulfide.

Keywords: sulfate-promoted zirconia; thermal stability; effect of hydrogen; activation by Pt

1. Introduction

Sulfate-promoted zirconia is an inorganic solid superacid extensively studied in recent years [1–5]. The Lewis acid character of its surface and the (partial) conversion of these sites into Brønsted acid sites are well-known. More recently, several studies show that sulfate species may have some significant effect on the incorporated transition metal [6], specially Pt [7,8] (the so-called "*sulfate-to-Pt*" effect). However, to the best of our knowledge, there have been no investigations of the effect of hydrogen activated by Pt species on the thermal stability of the sulfate groups (the so-called "*Pt-to-sulfate*" effect in the presence of hydrogen). The study of this effect is of utmost importance since sulfate groups are key components for strong acid (usually assumed as superacid) sites. Therefore, the results of this investigation appear most useful for catalytic reactions requiring hydrogen in the feed and Pt species on the surface of sulfate-promoted zirconia, such as hydroisomeriza-

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[1] To whom correspondence should be addressed.

tion and hydrocracking of long chain *n*-paraffins [9–11]. This is in line with today's concern because, during a recent public discussion between Tanabe and Maxwell [12], reduction of sulfate groups of the promoted zirconia at relatively low temperature was specifically mentioned.

Results reported in this paper include characterization data using differential thermal–thermoanalysis gravimetry (DTA-TGA) and other techniques, and some data obtained in the catalytic conversion of *n*-octane. The Pt bearing Y zeolite (Pt/HY) was used as reference catalyst.

2. Experimental

2.1. PREPARATION OF THE SAMPLES

$Zr(OH)_x$ was prepared by hydrolysis of zirconyl nitrate (Aldrich) with aqueous ammonium hydroxide (28%, Anachemia) at ambient temperature. The solid was filtered and thoroughly washed with distilled water in order to remove nitrate ions, then dried in air at 120°C for 24 h.

ZrO_2, hereafter denoted ZrO, was obtained by calcining the $Zr(OH)_x$ material in air at 600°C for 2.5 h.

Sulfate-promoted zirconia, hereafter referred to as SO-ZrO, was obtained by immersing 4.5 g of the $Zr(OH)_x$ into 50 cm^3 of a 0.5 mol dm^{-3} solution of sulfuric acid. After 1 h of stirring at ambient temperature, the solid was filtered and dried at 120°C for 24 h, then calcined at 600°C for 2.5 h.

SO-ZrO powder (30 g) was immersed in an aqueous solution of tetraamine platinum(II) chloride (Aldrich, 0.293 g dissolved in 30 cm^3 of distilled water), and evaporated in a rotovapor system to dryness, dried again at 120°C for 24 h, and calcined at 400°C for 24 h. The Pt content of the material, called Pt/SO-ZrO, was equal to 0.5 wt%. This sample and the Pt/HY obtained by incorporation of Pt (0.5 wt%) in the similar way into the HY (LZY-82, Linde, powder form, activated in air at 550°C overnight) were used for characterization and DTA-TGA studies.

2.2. CHARACTERIZATION AND DTA-TGA STUDIES OF THE SAMPLES

Atomic absorption, nitrogen adsorption/desorption, FT-IR, ammonia adsorption/temperature desorption (TPD) and DTA-TGA were used to determine, respectively, the chemical composition, the textural properties including the BET surface area and the pore size distribution, the surface acidity (density and strength), the thermal stability (weight loss and phase change). The Micromeritics ASAP 2000 instrument was also used for the determination of the mesopore size distribution using nitrogen adsorption/desorption (BJH method [13]). Measurements of acid density were carried out during the ammonia TPD experiments by using a 0.05 N HCl solution to determine the amount of NH_3 evolved, and backtitration of the HCl excess with a 0.05 NaOH solution. Combined TG-DT analyses were carried out using a PL Thermal Sc. Model STA 1500 apparatus (heating rate = 15°C/min). Reducing atmosphere used for TGA-DTA studies was obtained by flowing a mixture of nitrogen and hydrogen ($N_2/H_2 = 16/12$ mol/min).

In table 1 are reported the chemical and textural data for the samples studied.

2.3. PREPARATION OF THE CATALYSTS

The procedure for the preparation of the catalysts was reported in ref. [11]. In particular, Pt (0.5 wt%) was incorporated into the powder materials (HY, ZrO and SO-ZrO) during the extrusion phase with bentonite (used as binder) according to a technique known as "dry impregnation" [11,14–17]. The technique which is quite different from the conventional incipient wetness impregnation, ensures the highest activity in the conversion of *n*-octane [11,17].

The final catalysts were called Pt/HY, Pt/ZrO and Pt/SO-ZrO, respectively.

2.4. CATALYST TESTING

The experimental set-up for the catalytic conversion of *n*-octane was similar to that described elsewhere [18,19]. The procedure for catalyst testing (atmospheric pressure, carrier gas: $N_2/H_2 = 16/12$ ml/min, unless otherwise specified) and that for product analysis were similar to those described in ref. [14]. The weight hourly space velocity (WHSV, g of *n*-octane injected per hour and per g of catalyst) was equal to 0.1 h^{-1} for the Pt/SO-ZrO and 3.0 h^{-1} for the Pt/HY. The weight of catalyst was 0.625 g. The use of higher WHSV with Pt/HY was dictated by the need of having similar conversions for comparison purpose. The conversion and the product selectivities, expressed in C atom%, had the same definitions as in refs. [11,14–19].

Table 1
Results of the chemical and textural analyses on the samples studied

Sample	S (%)	BET [a]	Vol. N_2 [b]	Pore diam. [c]	Density of acid sites [d]
ZrO	–	66	0.113	5.6	1.0
SO-ZrO	5.0	116	0.154	4.8	1.8
Pt/SO-ZrO	5.1	105	0.137	4.9	na
Pt/SO-ZrO [e]	0.5	74	0.117	5.2	na
Pt/HY	–	610	0.393	0.74	1.5

[a] Surface area in m^2/g.

[b] Volume of nitrogen adsorbed, in cm^3/g.

[c] In nm (10^{-9} m).

[d] In µmol/m^2; na = not available.

[e] Activated under hydrogen atmosphere at 600°C.

3. Results and discussion

3.1. THERMAL STABILITY OF THE SULFATE GROUPS

As also reported in the previous work [11], sulfate-promoted zirconia when compared with parent zirconia (calcined zirconium hydroxide), exhibits a larger BET surface area and a higher volume of adsorbed nitrogen, owing to the new mesoporosity provided by these surface sulfate species (table 1).

TGA-DTA investigations in hydrogen flow of the "pure" zirconia (ZrO), the sulfate-promoted zirconia (SO-ZrO) and the Pt bearing sulfate-promoted zirconia (Pt/SO-ZrO), shows the following results:

(i) In the presence of hydrogen, while the ZrO sample does not show any weight change up to 950°C, the sulfate-promoted zirconia (SO-ZrO) starts losing its sulfate groups at ca. 520°C (figs. 1 and 2). This temperature is much lower than the corresponding temperature observed with the same sample (SO-ZrO) when heated in air (ca. 630°C [11]). Once the sulfate groups are eliminated, an additional run in the presence of hydrogen shows that the TGA-DTA behavior of the reduced SO-ZrO is similar to that of the pure zirconia. The similarity to the pure zirconia is also confirmed by surface are measurement (table 1) and FT-IR spectrometry in the region of the stretching bands of sulfate (absence of the characteristic sulfate bands within the 900–1400 cm^{-1} frequency range [11,20]).

(ii) The incorporation of Pt to the sulfate-promoted zirconia decreases further the reduction temperature, which now starts at ca. 450°C (figs. 1 and 2). The similarity to the pure zirconia is confirmed by a subsequent TGA-TDA run in the presence of hydrogen (no TGA and DTA peak), the surface area measurement (table 1) and FT-IR spectrometry (no characteristic bands assigned to sulfate groups).

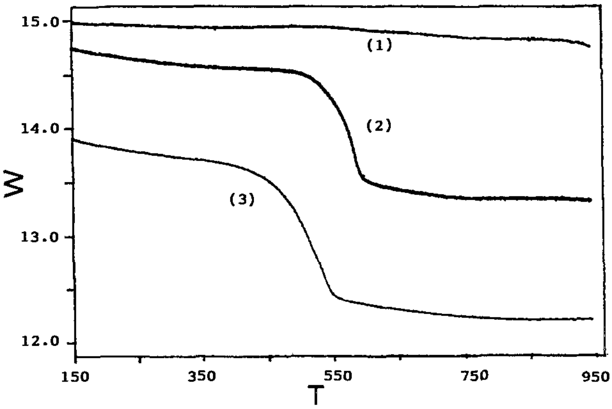

Fig. 1. TGA curves obtained under N_2/H_2 atmosphere with: (1) ZrO (IW or initial weight = 15.00 mg); (2) SO-ZrO (IW = 15.00 mg) and (3) Pt/SO-ZrO (IW = 15.00 mg). W and T are expressed in mg and °C, respectively.

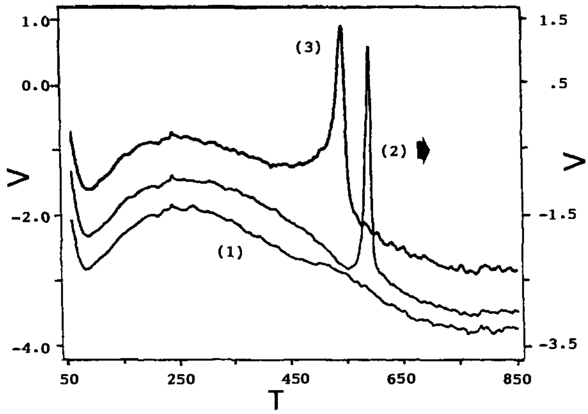

Fig. 2. DTA curves obtained under N_2/H_2 atmosphere with: (1) ZrO; (2) SO-ZrO and (3) Pt/SO-ZrO. V and T are expressed in microvolts and °C, respectively.

(iii) In the TGA-DTA study, the same Pt/SO-ZrO sample behaves differently with the nature of the flow gas (figs. 3 and 4). In inert (nitrogen) or oxidizing (air) atmosphere, we obtain a negative TDA peak while the presence of hydrogen induces the reduction with a positive TDA peak (fig. 4). Moreover, while the decomposition (in nitrogen) or decomposition–oxidation (in air) occurs at a temperature starting at ca. 630°C (fig. 3, same temperature as reported for the heating of SO-ZrO in nitrogen [11]), the reducing effect of hydrogen decreases this starting temperature down to 450°C (figs. 1 and 3).

(iv) Chemical analysis of the sulfate-promoted zirconia samples reduced at high temperature shows that the reduced Pt/SO-Zr (at 600°C) still contains some S (table 1), while this species is almost absent in the reduced (at 650°C) SO-ZrO sam-

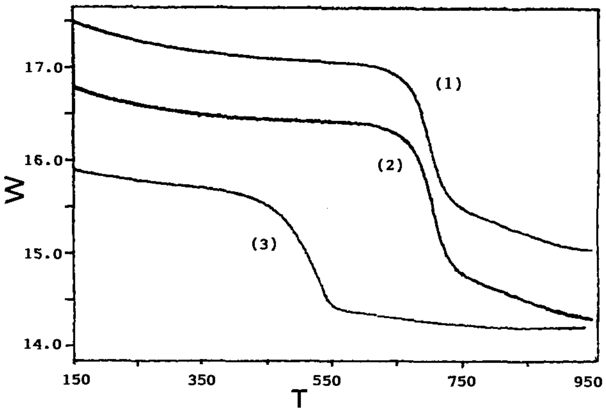

Fig. 3. TGA curves obtained under various atmospheres with the Pt/SO-ZrO sample: (1) nitrogen (IW = 17.80 mg); (2) air (IW = 16.90 mg) and (3) N_2/H_2 (IW = 15.00 mg). IW, W and T, as in fig. 1.

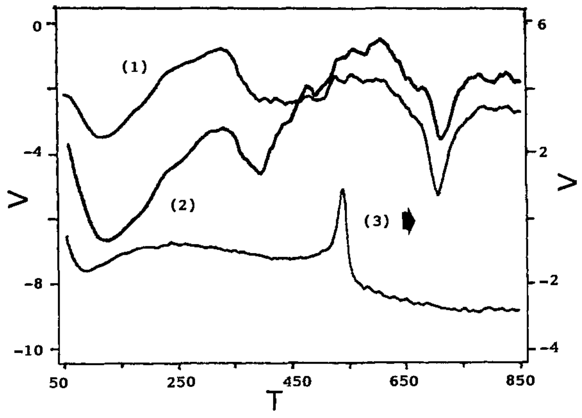

Fig. 4. DTA curves obtained under various atmospheres with the Pt/SO-ZrO sample: (1) nitrogen; (2) air and (3) N_2/H_2. V and T as in fig. 2.

ple. Moreover, the reduced Pt/SO-Zr provides a DTA curve in air which exhibits a double exothermic peak in the region of 450–480°C, respectively (fig. 5) whereas there is no such a DTA peak with the reduced SO-Zr sample. It is worth noting that: (i) this double DTA exothermic peak corresponds to a noticeable loss of weight (TGA curve, fig. 5); and (ii) the oxidation of the Pt species which occurs at a temperature higher than 550°C results in a gain in weight (TGA curve, fig. 5) and the formation of a broad DTA signal (fig. 5). Therefore, the double peak obtained at 450–480°C when the run is carried out in air on the reduced Pt/SO-Zr can be ascribed to the oxidation of some S species present on this sample.

These results lead to the following interpretations (in the following, all the equation are written in very simplified forms, with # designating the solid bulk).

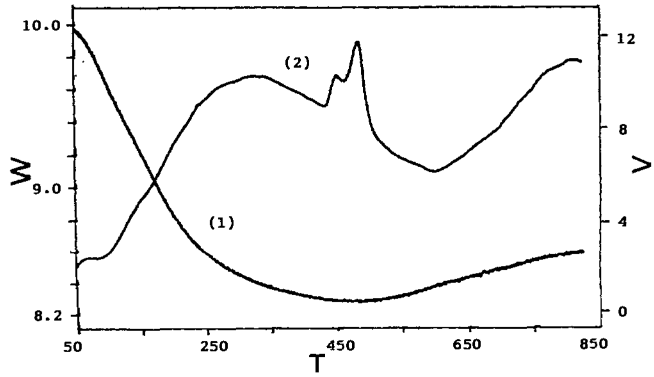

Fig. 5. Curves of TGA (1) and DTA (2) carried out in air on the Pt/SO-ZrO sample (IW = 10.00 mg) which was previously reduced by heating in situ, under N_2/H_2 atmosphere, from 25 to 600°C (15°C/min) and at 600°C for a further 30 min. T, IW, W and V as in figs. 1 and 2.

(i) Sulfate-promoted zirconia, with or without Pt incorporated, undergoes a decomposition (in nitrogen or in air), producing SO_2:

$$\#Zr{-}O{-}SO_3 \rightarrow \#ZrO_2 + SO_2 \tag{1}$$

(ii) Sulfate-promoted zirconia (SO-ZrO) undergoes a complete reduction according to the following equation [21,22]:

$$\#Zr{-}O{-}SO_3 + 4.5H_2 \rightarrow \#Zr{-}OH + H_2S + 3H_2O \tag{2}$$

This temperature of reduction is much lower than that of the decomposition or oxidation of the sulfate groups.

(iii) Pt bearing sulfate-promoted zirconia (Pt/SO-ZrO) may undergo the same reduction mentioned previously, however at a much lower temperature than with the SO-Zr sample. Moreover, chemical analysis shows the presence of a noticeable amount of S species in the pre-reduced Pt/SO-ZrO sample (table 1) and an additional TGA-DTA run in the presence of hydrogen does not show any further reduction. Thus, it is believed that, in addition to the reduction reaction (2), there is another reduction reaction which occurs in the presence of hydrogen activated by Pt at a slightly lower temperature than that required for reaction (2). Such a reaction may be written as follows [21]:

$$Pt/\#Zr{-}O{-}SO_3 + 2H_2 \rightarrow PtS/\#ZrO_2 + 2H_2O \tag{3}$$

A subsequent TGA-DTA run in air over this Pt/SO-ZrO sample pre-reduced at 600°C, shows a double peak previously mentioned, which is missing in a similar run with the SO-ZrO pre-reduced at 650°C (fig. 5). Thus, this supports the fact that the S species is present on the pre-reduced Pt/SO-ZrO surface and may be associated with Pt itself [23]. Nevertheless, this S species undergoes an oxidation according to the following reaction [21]:

$$PtS/\#ZrO_2 + O_2 \rightarrow Pt/\#ZrO_2 + SO_2 \tag{4}$$

The difference between eq. (1) and eq. (4) is that the former is the decomposition of sulfate groups while the latter is the oxidation of S species (surface S or/and sulfide). At a higher temperature, there is also a slow oxidation of the Pt species according to the following equation:

$$Pt/\#ZrO_2 + O_2 \rightarrow PtO_2/\#ZrO_2 \tag{5}$$

Therefore, we can report the sequence of the thermal stability of the samples studied as follows: Pt/SO-ZrO (hydrogen atmosphere) < SO-ZrO (hydrogen atmosphere) < SO-ZrO (inert or oxidative atmosphere).

3.2. CATALYTIC RESULTS

As mentioned in the introduction, we did not consider the change experienced by the Pt species. However, there would be some influence of the sulfate groups on the size and state of the Pt particles of the Pt/SO-ZrO material during the heating at high temperature. Such "sulfate-to-Pt" effects were already investigated by Sayari et al. [7,8]. It was also said that there was an auto-reduction of the Pt species by the sulfate–zirconia surface upon heating in air [7,8]. However, to achieve the maximum catalytic performance, the Pt/SO-ZrO catalyst had to be pre-reduced with hydrogen [19] and/or activated with co-fed hydrogen. In fact, if the catalyst was not pre-reduced and if hydrogen was absent in the feed, there was only a very low conversion of *n*-octane (table 2), mostly to mono-branched isomers of *n*-octane. It is also believed that hydrogen activated by Pt is capable of converting Lewis acid sites of the Pt/SO-ZrO catalyst to Brønsted acid sites [2]. In passing, the weakly acidic Pt/ZrO catalyst was not at all active under our experimental conditions. It is also worth noting that, in the absence of hydrogen in the feed, the conversion over the Pt/SO-ZrO was extremely low (table 2) and the catalyst experienced a rapid decay with the time-on-stream. In addition, mono-branched octane isomers were formed as primary products in accordance with the widely accepted isomerization mechanism via formation of CPCP (substituted corner protonated cyclopropane) intermediate [24]. Subsequent reaction steps involve further isomerization and β-scission, resulting majorily in isobutane. The temperature used was relatively low so that no aromatics and olefins were formed by hydrogen transfer, as usually observed with catalytic cracking. On the other hand, the *n*-octane conversion over the same Pt/SO-ZrO was much higher in the presence of hydrogen. The selectivity to branched hydrocarbons decreased with increasing formation of cracked products, owing to the rapid conversion of the former to the latter products. The same

Table 2
Conversion of *n*-octane over the Pt/SO-ZrO catalyst under different reaction atmospheres (temperature = 210°C; averaged data for time on stream of 4 h)

	Carrier gas (H_2/N_2) (ml/min)	
	0/28	12/16
conversion	2.8	47.8
product selectivities		
$C_1 + C_2$	0.3	0.0
propane	1.2	11.4
n-butane	7.3	11.5
isobutane	31.9	58.9
butenes	1.0	0.0
n-pentane	0.0	3.7
isopentane	3.8	8.0
mono-branched C_8	54.7	3.5
multi-branched C_8	0.0	3.0

holds true at higher reaction temperatures where higher conversions were obtained (tables 2 and 3).

Table 4 reports the catalytic results obtained with the Pt/HY zeolite catalyst. In terms of selectivity to cracked products as a function of conversion, a normal figure was obtained, e.g. "the higher the degree of conversion, the higher the selectivity to cracked products [24], and also the higher the selectivity to isobutane". However, if the catalytic results of the Pt/SO-ZrO catalyst (table 3) are compared to those of the Pt/HY zeolite (table 4), there are several differences as follows:

(i) The selectivities to cracked products and to isobutane obtained with the Pt/SO-ZrO reaches high values (close to 100%), much faster than those of the Pt/HY, at comparable conversion levels. Undoubtedly, this is due to the stronger acidic properties of the Pt/SO-ZrO.

(ii) With the Pt/SO-ZrO catalyst, the selectivity to isobutane goes to a maximum at a conversion of 47.8% (obtained at 220°C, table 3). The decrease in the selectivity to isobutane at temperatures higher than 220°C and the catalyst behavior which is getting closer to that of the Pt/HY (table 4), suggest that the strong acid sites of Pt/SO-ZrO are gradually losing their efficiency at higher reaction temperatures. This may be ascribed to the gradual thermal degradation of the sulfate groups under the action of the fed hydrogen which is strongly activated by the catalyst Pt species. This instability starts having an effect even at 250°C under our catalytic testing conditions (table 3) or at ca. 300°C under our TGA running conditions (fig. 1). This is essentially in agreement with the Tanabe's comment [12], although the pressure used in this work is much lower than that normally used for the conver-

Table 3
Conversion of *n*-octane over Pt/SO-ZrO catalyst at various temperatures under N_2/H_2 atmosphere

	Temperature (°C)						
	160	190	220	230	250	270	290
conversion	2.3	26.6	47.8	47.2	53.8	59.5	59.6
product selectivities							
$C_1 + C_2$	0.0	0.0	0.0	0.0	0.0	0.1	0.2
propane	3.7	9.3	11.4	12.9	14.1	15.2	15.3
n-butane	2.7	8.0	11.5	16.3	20.8	24.8	28.3
isobutane	26.3	54.5	58.9	56.1	49.8	44.2	39.9
n-pentane	0.0	1.7	3.7	5.6	6.3	6.8	7.2
isopentane	2.1	7.6	8.0	7.8	7.9	8.1	8.2
mono-branched C_8	65.3	9.7	3.5	1.4	1.1	0.8	1.0
multi-branched C_8	0.0	9.2	3.0	0.0	0.0	0.0	0.0
selectivity to cracked products							
total	34.7	81.1	93.5	98.6	98.9	99.2	99.0
iso/*n*	4.44	3.27	2.51	1.84	1.40	1.12	0.95

Table 4
Conversion of *n*-octane over Pt/HY zeolite catalyst at various temperatures (N_2/H_2 atmosphere; WHSV = 3.0 h^{-1}; and 0.1 h^{-1} for 222(*))

	Temperature (°C)					
	172	197	222	247	272	222(*)
conversion	5.5	7.5	30.1	49.1	67.4	99.1
product selectivities						
$C_1 + C_2$	0.0	0.0	0.0	0.0	0.0	0.1
propane	4.7	6.4	10.3	14.7	15.8	15.5
n-butane	4.3	4.9	8.3	13.1	15.4	12.6
isobutane	23.8	24.8	35.3	45.5	43.9	53.8
n-pentane	0.0	0.0	0.0	1.9	2.9	1.9
isopentane	6.6	6.5	10.2	13.5	13.6	13.2
C_6–C_7	0.0	1.8	0.5	0.7	0.6	1.8
mono-branched C_8	51.6	29.0	17.4	5.6	4.4	0.6
multi-branched C_8	9.0	26.3	18.1	5.0	3.4	1.8
selectivity to cracked products						
total	39.4	44.7	64.5	89.4	92.2	97.6
iso/*n*	3.38	2.92	2.47	2.01	1.69	2.25

sion of hydrocarbons under hydrogen atmosphere. Therefore, when the Pt/SO-ZrO catalyst is used in the presence of hydrogen (mostly, high-pressure hydrogen such as in the hydroisomerization of long chain *n*-paraffins), the thermal instability of the superacid sites (which would become worse under high hydrogen pressure) has to be taken into account. Finally, it is worth noting that the Pt/HY catalyst although having an acid density lower than that of the Pt/SO-ZrO, has a much higher surface area (table 1). This results in a higher conversion of *n*-octane for the Pt/HY carried out at the same WHSV (0.1 h^{-1}, tables 3 and 4). However, the higher density and strength of the acidic sites of the Pt/SO-ZrO catalyst are manifested by extremely high selectivities to isobutane and other cracked products even at relatively low conversions. Thus, with a conversion level of 30.1%, the Pt/HY catalyst provided a selectivity to cracked products of 64.5% (table 4) while with a conversion of 26.6%, the Pt/SO-ZrO exhibited a cracking selectivity of 81.1% (table 3). These results combined with an on-stream stability of the Pt/SO-ZrO catalyst quite acceptable when compared with the Pt/HY which shows high hydrogen activation properties under our experimental conditions [11,19], do not fully agree with the suggestion of Iglesia et al. [10] that the low metal activity of the platinized sulfated zirconia catalyst decreases the hydrogen transfer ability, increasing carbocation lifetimes, and thereby encourages cracking relative to isomerization. It is probable that such "insufficient" results for the isomerization of *n*-heptane are due to a too high density of strong acid sites ("cluster" configuration) of the sulfated zirconia based catalyst whose Pt component is not capable of transferring hydrogen with sufficiently rapid rate to desorb the adsorbed/readsorbed carbocation intermediates, favoring finally the cracking. Thus, it appears necessary to develop catalysts based on sulfate-promoted zirconia homogeneously dispersed on a very large surface area matrix [25]. These new catalysts seem to be very promising in several acido-catalysed reactions.

4. Conclusion

Molecular hydrogen reduces the sulfate groups of the sulfate-promoted zirconia into volatile species at a temperature much lower than the temperature of decomposition–oxidation of these groups in an inert atmosphere or in air. This reduction effect is enhanced by the incorporation of Pt into the sulfate-promoted zirconia, resulting in the loss of the sulfate groups at a significantly lower temperature. Such an enhanced reduction can be explained by the well known activation action of Pt on molecular hydrogen at high temperature. Moreover, some surface zirconium sulfide is produced by such an enhanced reduction.

The implication of this work is that if Pt bearing sulfate-promoted zirconia is used in a reaction such as the hydroisomerization of long chain *n*-paraffins where hydrogen is cofed with the hydrocarbons, the loss of the sulfate groups from the surface of the solid superacid occurs at a temperature much lower than that of the normal thermal decomposition of these groups. The situation would become worse if a high (partial) pressure of hydrogen were used (300 psi [9]). This requires further detailed investigations. Nevertheless, it is reasonable to predict that "the higher the hydrogen partial pressure, the lower the temperature limit for the stability of the Pt/SO-ZrO material". This is probably what was observed by Tanabe (instability at 200°C) [12].

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