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Platinum-Promoted and Unpromoted Sulfated Zirconia Catalysts Prepared by a One-Step Aerogel Procedure

2. Catalytic Activity in the Isomerization of *n*-Butane

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The catalytic activity in the isomerization of butane of a variety of zirconia sulfate catalysts, both unpromoted (AZS samples) and promoted with Pt (PZS samples), prepared by an aerogel technique, is reported. Catalysts have either different sulfate contents (AZS samples) or different Pt content and constant sulfate content (PZS samples). Catalysts are studied in a continuous flow system at 150 and 250°C, both in the absence and in the presence of hydrogen in the feed. AZS samples have identical specific activity at 150°C, while differences are observed at 250°C both in the absence and in the presence of H_2. PZS samples are more active and stable, particularly when activated in air only. No effect of Pt content on the catalytic activity is observed in the range explored (0.65–4.96%), while a negative effect of hydrogen can be evidenced under suitable conditions. An FTIR analysis performed on both AZS and PZS samples using a procedure that mimick the catalysis conditions suggest that contamination of the active sites on stream is mainly due to water and, in the absence of H_2 in the feed, to coke or oligomers deposition. A reaction mechanism is proposed involving an intermediate intermolecular butane dimerization where Zr^{4+} Lewis acid centers promote the initial C4 carbenium ion formation, followed by addition to *in situ* formed butene. The roles of Pt in the catalysis are also discussed. © 1997 Academic Press

INTRODUCTION

In the first part of this work (1), the characterization of a series of sulfated zirconia catalysts was reported. The catalysts were either promoted with platinum (PZS samples) or unpromoted (AZS samples) and were prepared by an aerogel technique. This was chosen with the aim of finding a more reliable process for the preparation of this class of catalysts, allowing a better definition of their analytical and morphological properties (2, 3).

After defining some surface characteristics of the catalytic materials, and namely, the nature and stability of sulfate groups, the state of Pt, and its chemisorption properties, the changes induced by thermal activation, in this contribution a thorough study of the catalytic activity of the same materials in the isomerization of *n*-butane will be reported. This reaction has long been used for testing the acidic properties of these catalysts and has a significant industrial importance *per se* (see, for instance, Refs. (4–7)). We will also try to establish the overall reaction mechanism and the roles played by platinum, along with a definition of the features that are necessary to develop an active catalyst.

EXPERIMENTAL

Both platinum-promoted PZS catalysts and unpromoted AZS catalysts were prepared as aerogels according to the one-step method described in detail in (3) and summarized in the first part of this work (1). To prepare PZS samples, a 70% $Zr(OPr)_4$ solution in *i*-PrOH was hydrolyzed in the presence of the proper amounts of *i*-PrOH, H_2SO_4 (96%), and $H_2PtCl_6 \cdot 6H_2O$ dissolved in *i*-PrOH (20 ml). While, when preparing the AZS samples, the addition of H_2PtCl_6 solution was obviously omitted.

Aerogels were obtained by slowly heating the wet gel (2.6°C/min) covered with *i*-PrOH (450 ml) in a 2-liter autoclave up to 250°C. After stabilizing the maximum temperature and pressure (60 bar) for 1 h, the solvent was slowly removed under supercritical conditions. All samples were calcined in dry air (30 ml/min) for 3 h at $T_{calc} = 600°C$, cooled to ambient temperature and stored in closed vessels.

Pt analysis was performed with AA spectroscopy. Quantitative determination of sulfates was performed by ion chromatography following a procedure reported elsewhere (8).

BET surface areas were determined with N_2 at −196°C on a Carlo Erba 1900 Sorptomatic apparatus.

A summary of the analytical properties of the catalysts, including the theoretical sulfate content (based on the amount of H_2SO_4 used) and the sulfate content found after the calcination step, the Pt content, and the sulfate surface density, are reported in Table 1.

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TABLE 1

Analytical Data of the Catalysts

Sample	Nominal SO_4 (wt%)	Found SO_4 (wt%)	Pt (wt%)	SO_4 groups/nm^2
AZS1	6.6	6.2		2.64
AZS2	12.5	5.5		2.92
AZS4	22.3	9.0		4.34
PZS-A	12.3	6.1	0.65	2.73
PZS-B	12.3	6.2	1.06	2.71
PZS-C	11.7	5.8	4.96	2.50

FTIR spectra were obtained at 2 cm^{-1} resolution with a Bruker IFS 113v spectrometer, equipped with MCT cryodetector adopting a strictly *in situ* configuration. All samples employed for IR measurements were in the form of thin-layer deposition, prepared following a procedure described elsewhere (1, 9, 10). Prior to IR measurements, the samples were activated either in an inert gas stream or *in vacuo* at $T_{act} = 400$ (the activation step).

Catalytic activity tests in the isomerization of *n*-butane were performed in a glass tubular reactor (200 mm long, 8 mm i.d.) externally heated by an oven. The temperature was controlled with a thermocouple immersed in the catalytic bed. The reaction was carried out at atmospheric pressure at either 150 or 250°C. The feed was dependent on the reaction temperature and the type of catalyst, although the butane space velocity was kept constant at 100 h^{-1}. At 150°C (AZS samples) the feed (total flow 5.8 ml/min) was made of a mixture of *n*-butane and helium ($C_4H_{10}/He = 2.69$); at 250°C (AZS and PZS samples) it was made (total flow 31.2 ml/min) with *n*-butane, hydrogen, and helium: the butane flow was kept constant (4.23 ml/min), while the H_2 and He flows were made up to accomplish the required H_2/C_4H_{10} ratio. Prior to the reaction, all catalysts (1.5 g) were activated in dry air (30 ml/min) at 450°C for 2 h, but in some cases the PZS samples were also treated in a hydrogen stream (30 ml/min) at 300°C for 2 h. Isobutane was analyzed on line by gas chromatography. Reaction rates were defined as mole of *n*-butane converted per gram of catalyst per unit time, unless otherwise noted.

RESULTS AND DISCUSSION

AZS Catalysts: Reactivity Data

The reactivity of AZS samples in the isomerization of *n*-butane was initially checked at 150°C in the absence of hydrogen. The results obtained for the three catalysts AZS1, AZS2, and AZS4 are summarized in Fig. 1 where the activity (expressed al mol *i*-butane formed/h × g catalyst) vs time is reported. The type of profile shown is typical for most reactions and shows that quasi-steady state conditions can be reached after 120–150 min. It must be pointed out that in all cases the product mixture under quasi-steady state conditions consisted of >90% *i*-butane, with only minor amounts of propane (<6%) and pentanes (<4%). Under the analysis conditions used for the separation of products, traces (<1%) of methane could be detected, but not quantified.

As is clear from Fig. 1 (open symbol curves), AZS1 and AZS2, that have very close sulfate contents (∼6%) and sulfate surface densities (∼2.8 SO_4 groups/nm^2), behave very similarly (except at the beginning of the reaction), and after ∼150 min show the same conversion and a slow but constant decline in activity. The AZS4 sample, that contains a higher sulfate content (9.0%), is more active and more stable. In all cases the initial stage of the reaction, that shows a self-poisoning of the catalysts, is associated with larger amounts of propane and methane indicative of a cracking process. If the activity data reported in Fig. 1 are expressed as moles of product/hour × mole of sulfate, the three catalysts turn out to behave almost identically (see Fig. 1, solid symbol curves), indicating that, under these experimental conditions, the specific activity of the sulfate groups seems to be the same in all cases.

This result is rather surprising if it is considered that the crystal structure of AZS4 is 70% monoclinic (2) and that in previous studies carried out on catalysts made according to traditional synthetic methods (1), sulfates grafted on crystallized monoclinic zirconia compared to sulfates on crystallized tetragonal zirconia were found to have negligible activity in promoting the same reaction under the same conditions. This apparent discrepancy seems to suggest that, if sulfate is introduced on a zirconia gel before crystallization, the effect of the final crystal phase is null as long as surface sulfates of the same type are formed on the crystallized system. This is confirmed by the IR spectra of surface

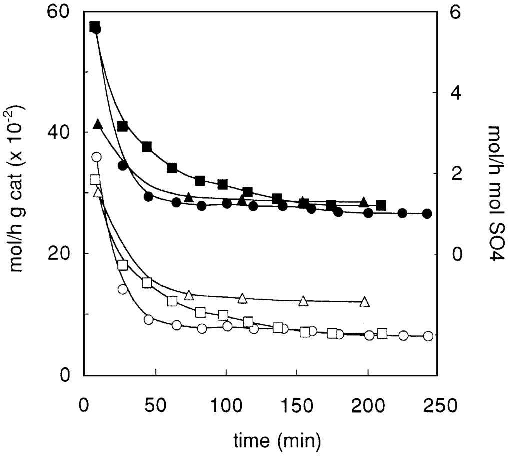


FIG. 1. Activity data for the isomerization of *n*-butane of AZS catalysts: circles, AZS1; squares, AZS2; triangles, AZS4. Open symbols, mol/h g cat; solid symbols, mol/h mol SO_4.

sulfates reported in Fig. 4 of the first part of this work (1) where it was evident that, after a standard calcination in air at 600°C and a standard vacuum activation at 400°C, sulfates at the surface of AZS4 present strong IR spectral components at ∼1400 and ∼1010 cm^{-1}: the relevant sulfate species have been recognized as necessary for good catalytic activity (1, 11) and have been ascribed to (covalent) sulfates localized on the "top" terminations of ZrO_2 crystallites, i.e., on regular patches of low index crystal planes, surrounded by crystallographically defective "side" terminations free from sulfates (11). This type of sulfates is constantly present on active tetragonal catalysts, whereas they are virtually absent in the case of inactive monoclinic systems obtained by surface sulfation of precrystallized monoclinic ZrO_2 (12). It must be pointed out that the possibility to observe this equivalence of surface sulfates on monoclinic and tetragonal specimens is related to the specific one-step preparation method reported here. In fact, the crystal phase composition of the present catalysts is already determined after the solvent evaporation step (2) under supercritical conditions (250°C, 60 bar) at variance with traditional preparative procedures where crystallinity is attained after the calcination step, i.e., at much higher temperatures.

TABLE 2

Summary of the Catalytic Activity in *n*-Butane Isomerization

Entry	Sample	Temp. (°C)	H_2/butane	$10^2 \times$ activity (mol/h × g cat)		
				10 min	200 min	1500 min
1	AZS1	150	—	36	7.0	
2	AZS2	150	—	31	7.1	
3	AZS4	150	—	30	12.7	
4	AZS4	250	—	29	4.6	
5	AZS4	250	6/1	30	5.8	
6	AZS1	250	1/1	20	4.6	
7	AZS1	250	3/1	25	4.6	
8	AZS1	250	6/1	26	13.2	8.4
9	AZS2	250	6/1	33	16	15
10	AZS4	250	6/1	30	6.0	
11	PZS-B	250	3/1	30	31	31
12	PZS-B[a]	250	3/1	21	25	25
13	PZS-A	250	1/1	38	27	19
14	PZS-A	250	3/1	39	35	35
15	PZS-A	250	6/1	26	30	29
16	PZS-B	250	3/1	30	31	31
17	PZS-C	250	3/1	40	36	35
18	PZS-B[b]	220	3/1	21	23	
19	PZS-B[b]	250	3/1	39	55	
20	PZS-B[b]	280	3/1	83	57	

Note. Activity expressed as *i*-butane formed. Catalysts (1.5 g) activated in dry air at 450°C for 2 h prior to the reaction.

[a] Catalyst activated in dry air at 450°C (2 h) and hydrogen at 300°C (2 h).

[b] 0.5 g catalyst used.

To understand better the unexpected behavior of the AZS4 system, a test of the effect of temperature and of the presence of hydrogen in the feed was performed. The results are reported in Table 2 where a summary of all the catalytic tests considered in this work is reported. The data refer to the activity observed in the initial stage of the reaction (10 min), after reaching quasi-steady state conditions (200 min) and after long reaction times (1500 min) where appropriate. As it can be seen from Table 2, entries 3–5, an increase of the reaction temperature to 250°C decreases drastically the conversion curve (albeit with a relative stability), while the addition at 250°C of an excess of H_2 in the feed (H_2/*n*-butane 6/1) slows down the initial deactivation of the catalyst, although a condition of stability is never attained (at least for reaction times up to 250 min). This behavior is at variance with that of the other (tetragonal) AZS samples (vide infra) and of other catalysts previously reported in the literature (13, 14). Interestingly, the initial conversion is approximately the same for all AZS samples under the different conditions, and the effect of increasing the reaction temperature seems to be associated for all samples with an increase of cracking, as indicated by the initial increase of propane and methane found in the reaction mixture.

The effect of the partial pressure of H_2 in the feed is reported for AZS1 in Table 2, entries 6–8, and is typical. The reaction was tested at 250°C and, as can be seen, a 6/1 H_2/*n*-butane ratio is necessary to observe acceptable conversions and a relative stability of the catalyst, while for lower H_2/*n*-butane ratios (1/1 or 3/1) a slow deactivation is noticed. Here again, a decrease in activity is observed under the latter conditions with respect to the reactions carried out at 150°C without H_2 in the feed (see Fig. 1 and Table 2, entry 1). An increase in activity at 250°C of about two to three times can be achieved only by increasing the hydrogen pressure (6/1 H_2/*n*-butane ratio). However, even under these conditions, some deactivation of the catalyst occurs for reaction times longer than 1200 min.

Finally, a comparison of the reactivity of the three catalysts (AZS1, AZS2, and AZS4) at 250°C in the presence of H_2 (H_2/*n*-butane 6/1) is reported in Fig. 2 and Table 2, entries 8–10. A clear inversion of reactivity is evident with respect to the data reported in Fig. 1. The slowest catalyst is now AZS4, with a sharp decrease in reactivity with respect to Fig. 1. The effect is even more evident if the specific activity expressed per sulfur site is considered. Conversely, the two low sulfur tetragonal catalysts (AZS1 and AZS2) increase significantly their reactivity in the presence of H_2 and, in particular, AZS2 displays a relatively constant conversion even after long reaction times.

The data here reported seem to suggest the following considerations.

In the absence of hydrogen in the feed, the nature of the active sites responsible for the catalysis seems to be similar in all systems, as is indicated in Fig. 1 by the practical equivalence of the activity data expressed per sulfate site. Indeed,

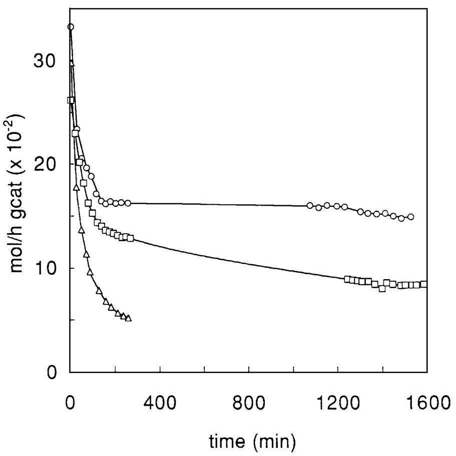


FIG. 2. Comparison of the activity of the AZS catalysts at 250°C in the presence of H_2 (H_2/*n*-butane 6/1): squares, AZS1; circles, AZS2; triangles, AZS4.

specific activity expressed per sulfate site may be misleading; in particular, in the case of AZS4, we know from the previous work (1) that, although its sulfate surface density is higher than a statistical monolayer, it still contains a significant amount of Lewis acid sites, i.e., coordinatively unsaturated Zr^{4+} centers, whose presence indicates that appreciable fractions of the surface are not covered by sulfates. In other words, there will be a fair amount of sulfate groups, as is also indicated by the IR data reported in the previous paper (1) and concerning the nature of the sulfate groups, that will not be directly involved in the catalytic reaction.

When hydrogen is added to the reaction feed, the apparent equivalence among different AZS catalysts is broken. This could be the result of different effects, among which: (i) a change in the nature of the active sites. For example, there might be a different Lewis/Brønsted acid sites ratio, as suggested by other authors (15), depending on the different sulfur contents and/or the different crystal structure (AZS1 and AZS2 are completely tetragonal (2), whereas AZS4 is over 70% monoclinic); (ii) a different behavior with respect to poisoning and/or a different stability of the surface sulfate layer.

To put the last considerations in more general terms, the two following questions should preliminarily be answered: (i) what modifications are induced at the surface of a working catalyst during the isomerization reaction, and what are the differences under the various reaction conditions? (ii) on a surface chemical ground, what is the difference between the AZS4 catalyst and all other catalysts of the AZS series, when brought to reaction conditions?

AZS Catalysts: IR Data

Looking for an answer to the questions above, we have resorted to *in situ* IR spectroscopy. Needless to say, the best solution would be to run *in situ* spectra of the working catalysts, but so far it has been impossible to obtain reliable and meaningful spectra of catalyst samples still in contact with reactants and products at the reaction temperature. Consequently, in order to test how the surface features of a catalyst are affected by the reactants flow, we have studied the surface spectral features of catalyst samples before and after the exposure for a certain time to the same conditions experienced in the reactor during the catalytic reaction.

The "health status" of a sulfated zirconia catalyst to be used for the isomerization of *n*-butane can be guessed spectroscopically by checking the following aspects: (i) the dehydration level, which must be as high as possible (9); this guarantees that surface sulfates are in the highest covalent configuration, the Brønsted acidity is at a minimum, and the Lewis acidity is at a maximum; (ii) the amount of (covalent) sulfates of the family absorbing at ~1400 and ~1010 cm^{-1} must be as high as possible (11); (iii) the ambient temperature adsorption of carbon monoxide must yield a ν_{CO} band at (2200 cm^{-1} as strong as possible, as a measure of the strong surface Lewis acidity available). In fact, strong Lewis acidity has been shown to be necessary for a good catalytic performance (10, 11).

The bottom half of Fig. 3 reports schematically the (normalized) intensity of the ν_{CO} band at ~2200 cm^{-1} observed on a AZS2 catalyst in various steps of a catalytic cycle carried out with *n*-butane at 150°C (A), with *n*-butane at 250°C (B), and with *n*-butane plus H_2 at 250°C (C).

Figure 3A shows that, after 2 h reaction at 150°C, the strong Lewis acidity content of the AZS2 system (used as a monitor of the catalytic efficiency) has declined of some 25% (step 2) and after 6 h of some 40%. This decline of the strong Lewis acidity corresponds, on a catalytic ground, to reaching the quasi-steady-state plateau, typical of *n*-butane isomerization at 150°C on active tetragonal sulfated zirconia catalysts. Step 3 of Fig. 3A shows that, after outgassing the catalyst at 400°C (vacuum activation), the strong Lewis acidity of the AZS2 system has recovered the starting level, and step 4 indicates that, upon a further oxidation at 400°C (oxidative activation), no appreciable changes of Lewis acidity are produced. This trend suggests that, under the conditions explored, the decline of Lewis acidity (that parallels the decline of catalytic activity) is mainly due to a partial rehydration of the catalyst and, in fact, section of Fig. 4A (showing segments of the ν_{OH} and the $\nu_{S=O}$ spectral regions of the AZS2 catalyst) confirms that a moderate rehydration of the catalyst occurred during the catalytic reaction (step 2), and that the reactivation at 400°C (step 3) restores the strength and shape of the bands due to surface hydroxyls and surface sulfates.

Figure 3B shows that, when the reaction is carried out in the absence of H_2 at a higher temperature, the deactivation of the catalyst discussed above is paralleled by a drastic decrease of the strong Lewis acidity (as dosed by CO uptake at the temperature of the sample in the IR beam

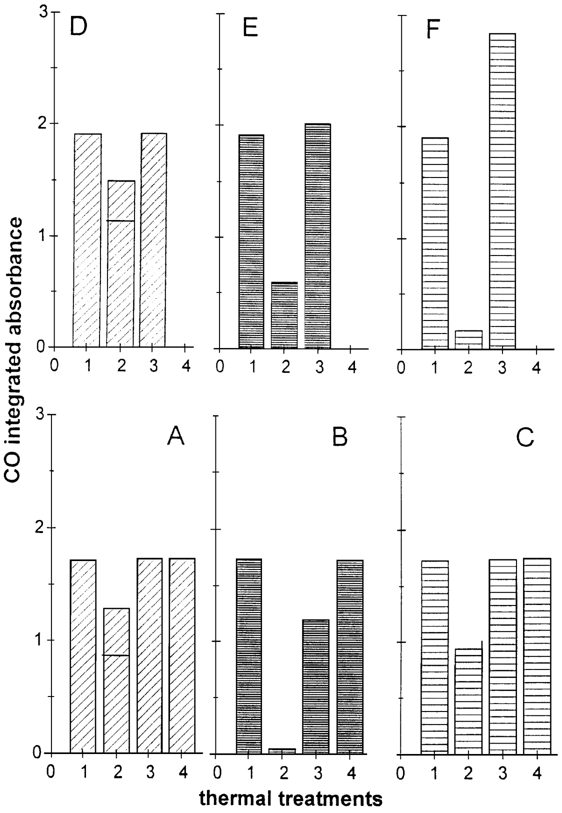


FIG. 3. Schematic diagrams showing the weight-normalized integrated absorbance of the band of 100 Torr CO adsorbed at beam-temperature on a AZS2 catalyst (A–C) and on a AZS4 catalyst (D–E). (A and D) Catalysts contacted at 150°C with pure *n*-butane. (B and E) Catalysts contacted at 250°C with pure *n*-butane. (C and F) Catalysts contacted at 250°C with a 1/6 mixture of *n*-butane/H_2. The catalytic cycles are made up of four steps, designated in the diagrams as 1–4. 1, (adsorption of CO on) the catalyst vacuum activated at 400°C; 2, (adsorption of CO on) the catalyst after 2 h reaction (6 h in the case of the horizontal bars) and evacuation at the reaction temperature; 3, (adsorption of CO on) the catalyst after vacuum activation at 400°C; 4, (adsorption of CO on) the catalyst after oxidation/evacuation at 400°C.

(BT)). Figure 4B (curve 2) indicates that the severe decline of surface Lewis acidity is mainly brought about by a much more pronounced rehydration of the catalyst surface (step 2). Curves 3 and 4 of Fig. 4B also show that both the intensity and the profile of the ν_{OH} and $\nu_{S=O}$ bands of the catalyst are recovered (at least up to a spectroscopically detectable level) upon a plain vacuum activation at 400°C (step 3), whereas Fig. 3B indicates that only some 70% of the strong Lewis acidity is recovered after vacuum activation at 400°C (step 3). Only a further oxidative activation at 400°C (step 4) yields back the original activity toward CO at BT. This datum is consistent with the indication reported in the previous section that the reaction, when carried out without H_2 at relatively high temperatures (250°C), leads to a much more abundant incidence of cracking reactions. It also tells us that coke (or oligomers) deposition interferes with the strong Lewis acidity of the catalyst as it does with the catalytic activity.

Finally, Fig. 3C shows that, when the reaction is carried out on AZS2 at 250°C in the presence of H_2 in the feed, the decline of strong Lewis acidity is more limited than in the absence of H_2 and, more important, the strong Lewis acidity is fully recovered upon a plain evacuation (activation) at 400°C (step 3). In fact, the further oxidation/evacuation at 400°C (step 4) does not modify any further the amount of CO adsorbable at BT, meaning that, whatever process was responsible for the difference observed between steps 3 and 4 in Fig. 3B, it is no longer active in the presence of H_2.

The top half of Fig. 3 reports similar schematic CO uptake data for the system AZS4, and from these plots some aspects of the anomalous behavior of the (mainly monoclinic) AZS4 catalyst can be understood. Figure 3D confirms that, at 150°C, the catalytic behavior of AZS4 and of AZS2 are very similar: also for AZS4 the decline of strong Lewis acidity is quite moderate (step 2), and the activity toward CO can be completely recovered by a mere vacuum activation at 400°C (step 3). But Fig. 3E and, more than that, Fig. 3F indicate that at a higher temperature and especially in the presence of H_2 the decline of Lewis acidity is large (step 2) and, more important, after a vacuum activation at 400°C (step 3) more CO can be adsorbed than on the starting activated catalyst (step 1). This unexpected result suggests that, during the reaction step, some portions of the surface were

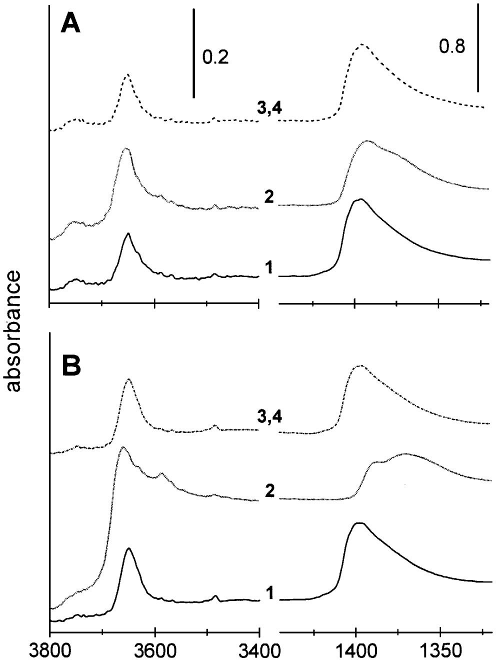


FIG. 4. Segments of the IR spectrum (in the ν_{OH} region; 3800–3300 cm^{-1}, and in the $\nu_{S=O}$ region; 1450–1300 cm^{-1}) of a AZS2 catalyst after the four steps of a catalytic cycle, as described in the legend to Fig. 5. (A) Reaction carried out at 150°C in pure *n*-butane. (B) Reaction carried out at 250°C in pure *n*-butane.

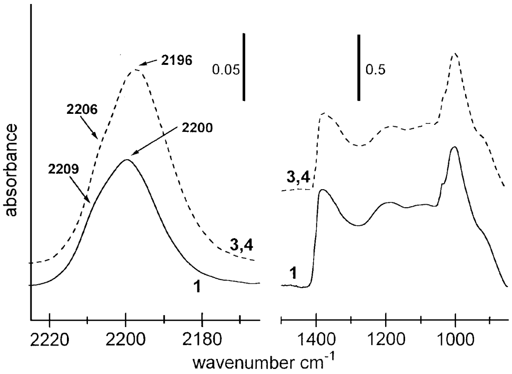


FIG. 5. Segments of the IR spectrum (in the ν_{CO} region, after dosing 100 Torr CO; 2225–2165 cm^{-1}, and in the whole ν_{SO} region, 1450–850 cm^{-1}) of a AZS4 catalyst after the preliminary activation at 400°C (step 1, as defined in the legend to Fig. 3) and after a complete catalytic cycle, i.e., after 2 h reaction at 250°C with *n*-butane/H_2 mixture, followed by both vacuum and oxidation/evacuation treatments at 400°C (steps 3 and 4, as defined in the legend to Fig. 3).

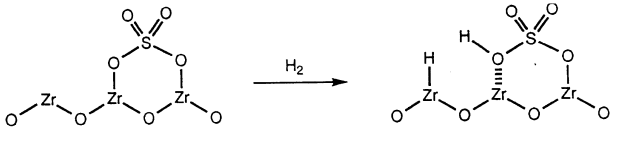
liberated from sulfates so that, after the vacuum activation of step 3, larger portions of the surface may be involved in the formation of coordinatively unsaturated Zr^{4+} sites capable of chemisorbing CO at BT. But this increase of the strong Lewis acidity does not correspond to an increase of catalytic activity, as probably some of the sulfates necessary for the proper catalytic performance of the system were removed during the catalytic cycle. This is demonstrated by the spectra in Fig. 5: after the complete reaction cycle schematically represented by Fig. 3F, the spectrum of surface sulfates on AZS4 is somewhat modified and definitely weaker than it was at the beginning, whereas the spectrum of CO absorbable at BT after completion of the reaction cycle is definitely stronger than at the beginning (as already indicated in Fig. 3F) and the two CO components (typical of monoclinic sulfated zirconias (1)) are located at slightly lower frequencies due to a decreased inductive effect from a decreased amount of surface sulfates.

AZS Catalysts: General Remarks

The data reported in the previous section indicate that, in the catalytic process of *n*-butane isomerization, some redox processes are involved, leading to the formation of water that turns out to be the main agent responsible for the deactivation of working catalysts. It is not quite clear at the moment what is reduced, in the presence of either the sole hydrocarbon or of the hydrocarbon/H_2 mixture. In the case of the stable tetragonal AZS systems, surface sulfates, that can be thought of as the most easily reducible species present, are not observed to decrease to a spectroscopically appreciable extent after a complete catalytic cycle. As for the Zr^{4+} species, the only other reducible species present, the adsorption of CO has not been able to demonstrate the formation of spectroscopically detectable amounts of coordinatively unsaturated surface Zr^{3+} species. On the other hand, it must be considered that the amount of water formed is fairly small, also in the case of the reaction carried out at 250°C.

The most generally accepted idea with respect to poisoning of working catalysts is related to a carbon deposition, as a consequence of cracking reactions. The occurrence of the latter reactions is particularly evident at the beginning of the catalytic process, and when the reaction temperature is increased. The data presented in the previous section support this idea, as they confirm that in the case of a reaction carried out without H_2 in the feed at 250°C an oxidative activation of the catalysts is necessary in order to bring the catalysts back to its initial activity. Conversely, in the case of the reaction carried out in the presence of H_2, the formation of water seems to be the only source of catalyst deactivation. In fact, a sufficient pressure of hydrogen in the feed leads to a quasi-steady state situation where carbon would be removed from the surface and a relative stability of the catalyst would be reached under suitable conditions. Indeed, H_2 needs to be activated in order to be able to remove carbon from the surface. It is known that pure ZrO_2 can activate hydrogen and catalyze the hydrogenation of olefins (16), and it seems realistic to suggest that this activation would occur only on free, coordinatively unsaturated Zr^{4+} centers, not covered with sulfate groups (Lewis sites), with the possible assistance of adjacent sulfate groups as is shown in Scheme 1. Note that in this, as in the other schemes, surface sulfates are represented with two S=O bonds, although it is fairly possible that they carry only one S=O bond (17). The actual structure of sulfates is virtually irrelevant to the present discussion, provided that the sulfates have reached upon rehydration (i.e., in the activation step), a covalent configuration.

The possible practical use of sulfated zirconia catalysts is strongly dependent on their catalytic stability on stream, and in this respect feeding hydrogen together with the hydrocarbon, as we have done in this work, has become a common practice since the early report of Garin *et al.* (14). The difficulty to activate hydrogen to keep the catalyst surface clean unavoidably requires an increase in the reaction temperature, i.e., moving to thermodynamically more unfavorable conditions and toward a consequent loss in selectivity. The data reported here seem to show that no real advantage is observed when working in the presence of H_2, unless a relatively high pressure of H_2 is added. Even so, the ability of the catalysts to withstand these conditions is



SCHEME 1

rather limited since a slow deactivation after long reaction times (~1500 min) can be seen even in the best cases.

All these considerations apply to the tetragonal sulfated zirconia systems, whose typical behavior is represented by AZS2. As for the peculiar behavior exhibited by the mainly monoclinic AZS4 catalyst in reactions carried out at 250°C (and especially in the presence of H_2), it stems from a much higher instability of its surface sulfates toward reduction. The origin of this instability is not quite clear, but it could be tentatively related to the presence, only on monoclinic sulfated zirconias, of a family of stronger Lewis sites that can adsorb CO at BT, yielding a second CO adspecies characterized by a ν_{CO} frequency above 2200 cm^{-1}.

PZS Catalysts: Reactivity Data

Reactivity studies in the isomerization of *n*-butane with PZS samples have been carried out at 250°C using hydrogen in the feed. Some preliminary data have been already reported elsewhere (2, 3). In particular, we have observed how the pretreatment conditions affect the activity. As is shown in Table 2 (entries 11 and 12) for PZS-B (but the effect is the same for all Pt-promoted catalysts examined), a further activation in hydrogen at 300°C after the usual preliminary treatment in dry air at 450°C is detrimental for the activity of the catalyst. This is the reason why the reactivity of the PZS samples was tested following an activation in dry air only.

The general decrease in activity that is observed after an activation in hydrogen (reductive treatment) could be ascribed to water formation and therefore to suppression of strong Lewis acid sites as was demonstrated for the AZS catalysts by the IR studies reported above. This behavior is also strongly reminiscent of the suppression of the hydrogen chemisorption capacities of the PZS samples reported in the previous paper (1). Both phenomena occur after an identical reductive treatment and are most likely due to a Pt surface contamination following reduction of some of the sulfate groups, possibly to strongly bound sulfide. Similarly to the chemisorption studies, this surface contamination is reversible, and the maximum activity can be completely recovered after a reactivation in air (oxidative treatment).

If we consider the possible reduction stages of the sulfate groups in the presence of hydrogen, they can be ordered with respect to the amount of hydrogen required (Scheme 2). Stepwise reduction of sulfates has been recently suggested by Le Van Mao *et al.* (18) on the basis of thermal analysis data. It seems reasonable to suggest that, during the activation in hydrogen at 300°C, the process stops at the second reduction stage (bound S^{2-}); in fact, the formation of either SO_2 or H_2S in a flow system would lead to an irreversible loss of sulfur. A process like the one reported in Scheme 2 would result in two negative effects: (i) the contamination of Pt with sulfide and (ii) the contamination of Zr^{4+} Lewis acid sites with water.

$$\text{bound } SO_4 \xrightarrow[-H_2O]{+H_2} SO_2 \xrightarrow[-H_2O]{+H_2} \text{bound } S^{2-} \xrightarrow{+H_2} H_2S$$

SCHEME 2

These observations point out the undesired role played by Pt in promoting the above sequence of hydrogenation steps. On the other hand, Pt being also an oxidation catalyst, it is able to reestablish the original activity of the samples. Clearly, these reduction/oxidation cycles may also lead to a reassembly of the sulfate groups on the surface of zirconia at least in proximity of Pt.

Indeed, on a PZS-B batch that had been reactivated 10 times and kept working for over 1 month, the final sulfate content was found to be 4.5% (initial SO_4^{2-} content: 6.2%) while the activity was only slightly reduced (<10%) with respect to the original one. A similar loss of sulfate was found also on a AZS2 catalyst (SO_4^{2-}%: initial, 5.5; after 1 month 4.1), and therefore seems to be independent of the presence of Pt. More likely, the major responsibility for the loss of sulfate might be ascribed to a simple thermal decomposition, related to the repeated number of reactivations at 450°C in air that was performed on both catalysts. In any event, no matter what the actual origin of the loss of sulfate is, the present results suggest that mostly catalytically inactive sulfate groups are eliminated thermally and/or by reduction, as the catalytic activity declines much more slowly than does the surface sulfate concentration.

The effect of the hydrogen partial pressure on the activity of the catalysts is reported in Fig. 6 for PZS-A and is typical. As can be seen, at low H_2 pressures (H_2/*n*-butane 1/1) a steady state is never attained and a slow deactivation is evident even after long reaction times. This is probably due to a deposition of cracking products that are not adequately removed. On increasing the hydrogen pressure, the activity reaches a maximum (H_2/*n*-butane 3/1) and then decreases

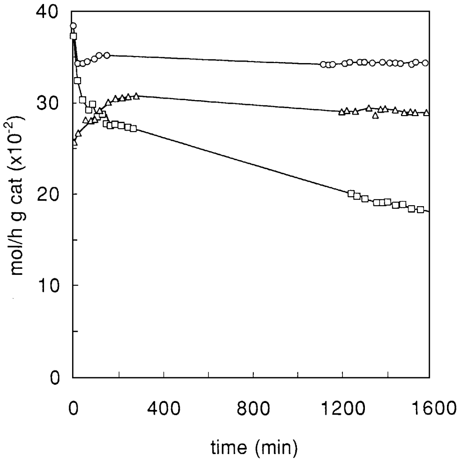


FIG. 6. Effect of hydrogen on the activity of PZS-A at 250°C: squares, H_2/*n*-butane 1/1; circles, H_2/*n*-butane 3/1; triangles, H_2/*n*-butane 6/1.

(H_2/*n*-butane 6/1). In both cases steady-state conditions are reached in about 150 min. This behavior is general and is exhibited by all catalysts, independently of the Pt content.

Indeed, the real activity of the catalysts for 1/1 H_2/*n*-butane ratio cannot be observed because the catalyst never attains steady-state conditions, and therefore the kinetic effect of hydrogen on the reaction is not evidenced by the results reported in Fig. 6. The data seem to show that, for Pt-promoted catalysts, the overall dependence on the H_2 partial pressure is a complex one and is a balance between two opposing effects: (i) the clean-up of the catalyst surface that benefits from an increase in H_2 partial pressure; this effect is demonstrated also by the activity data of Table 2, entries 6–8, for the AZS1 sample and Fig. 3 for the AZS2 system (i.e., for catalysts that do not contain Pt); (ii) a possible negative kinetic effect of H_2 on the reaction rate.

We have tried to separate the two effects and evidence only the latter, by carrying out the following experiment: a PZS-B catalyst, initially activated in air according to the usual procedure, was tested toward a change of H_2 partial pressure by modifying the feed *in situ*, without loading a freshly activated catalyst at each pressure change. This leaves the catalyst surface "equally contaminated" at each H_2 pressure change, allowing a comparison under similar surface conditions and evidencing the kinetic effect of H_2 on the reaction rate. The results are shown in Fig. 7 and indicate that the observed dependence on hydrogen partial pressure is indeed of kinetic origin and of negative order. This might evidence a direct role of Pt in the organic transformation similar to that observed for bifunctional catalysts, as suggested by other authors (19, 20).

Moreover, if we consider the maximum activity displayed by the catalysts under H_2/*n*-butane 3/1 and reported in Table 2, entries 14, 16, and 17, it is quite evident that it is practically independent of the Pt content. In fact, the conversion vs time curve of PZS-A (Pt 0.65%) is superimposable with that of PZS-C (Pt 4.96%) and only slightly higher than that of PZS-B (Pt 1.04%). If compared with the data reported in entry 7 of Table 2 for AZS1 (that has the same sulfate content), the data of entries 14, 16, and 17 indicate that there is a definite effect of Pt in promoting the catalytic activity, but also indicate that a relatively small amount of Pt centers is necessary to attain the maximum activity.

Finally, in Table 2, entries 18–20, the effect of the reaction temperature is reported. At 220°C the activity is constant since the beginning, no propane or pentanes are found in the reaction mixture, and the selectivity to *i*-butane is >99%. Increasing the temperature to 250°C leads to a significant increase of activity and to a selectivity that stabilizes at 93% at steady-state conditions with propane, pentanes, and methane as by-products. At 280°C, the initial conversion is very high and is associated with a considerable amount of by-products; however, the activity drops down rapidly, and under steady-state conditions is the same as at 250°C, though with a lower selectivity (85%).

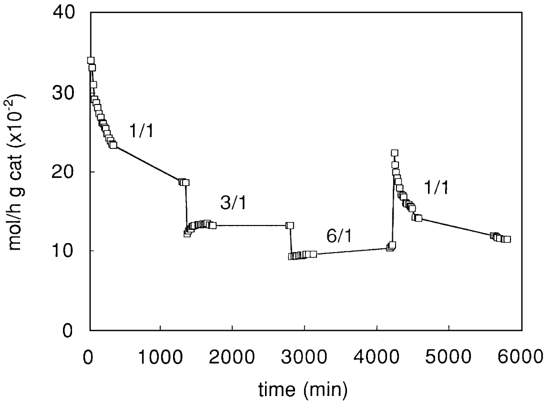


FIG. 7. Effect of hydrogen on the activity at 250°C of a PZS-B catalyst, without regeneration of the catalyst when changing the H_2 partial pressure. H_2/*n*-butane ratios as indicated in the figure.

PZS Catalysts: IR Data

In the case of Pt-promoted catalysts, we chose to investigate in more detail the PZS-B catalyst (Pt 1.04%), because it represents the best compromise between promotion of catalytic activity and observability of the spectral features deriving from the presence of Pt. As in the case of the unpromoted catalysts dealt with in a previous section, with PZS-B we tried to reproduce the conditions experienced in the reactor during the catalytic reaction, in order to test how surface sulfates and all other surface features are modified by contact with the reactants flow.

Figure 8 reports the spectra of the CO interaction (100 Torr at BT) with the PZS-B catalyst in the usual four steps of a typical catalytic cycle. It is noted that:

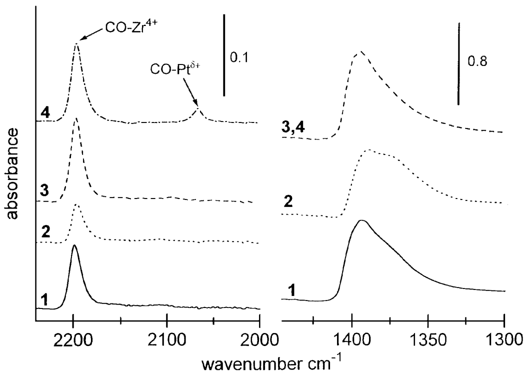


FIG. 8. Segments of the IR spectrum (the ν_{CO} region; 2270–2000 cm^{-1}, and the $\nu_{S=O}$ region; 1450–1300 cm^{-1}) of a PZS-B catalysts after the addition of 100 Torr CO in the various steps of a catalytic cycle. 1, Vacuum activated at 400°C; 2, after 2 h reaction at 250°C with *n*-butane/H_2 mixture (1 : 3) and evacuation at the reaction temperature; 3, after vacuum activation at 400°C; 4, after oxidation/evacuation at 400°C.

(i) After the initial vacuum activation (step 1), catalytically "important" sulfates are in the covalent state ($\nu_{S=O}$ ~1400 cm^{-1}), the activity of Zr^{4+} sites toward CO is fairly high (ν_{CO} ~2200 cm^{-1}; normalized integrated absorbance ~1.75), and no CO adsorbs on Pt sites (no ν_{CO} bands in the 2100–2080 cm^{-1} interval), as already discussed in (1).

(ii) After a 2- to 4-h treatment at 250°C with *n*-butane/H_2 mixture (step 2), the Zr^{4+} activity toward CO is reduced by some 50% and the broadened profile of the $\nu_{S=O}$ vibration at ~1400 cm^{-1} indicates that, also in the presence of Pt, a redox process is involved and leads to the formation of small amounts of water.

(iii) After a vacuum activation at 400°C (step 3), the profile of the sulfate bands and the activity of Zr^{4+} sites toward CO is fully recovered indicating that all the rehydration was reversed, and that other possible catalyst poisoning processes did not interfere with the strong Lewis acidity of the system.

(iv) The latter observation is confirmed by the spectrum of CO adsorption after a subsequent oxidation/outgassing treatment of the catalyst (step 4): no changes are noted in the spectral position and intensity of the band due to Zr^{4+} interaction. Meanwhile, CO adsorption brings about the formation of a weak band at ~2065 cm^{-1}, ascribed in the previous work (1) to a CO/$Pt^{\delta+}$ interaction and confirming that a mild oxidative treatment is needed to render the surface Pt of these Pt-promoted systems active toward CO uptake.

Mechanism and Role of Platinum

We have already pointed out for other ZS catalysts that the high catalytic activity of this class of catalysts is related to the availability of strong Zr^{4+} Lewis acid centers (10, 11). We have also observed in the present and in previous papers (1, 8) that the catalytic properties of these materials are always associated with the occurrence in the IR spectra of a definite class of sulfate bands centered at ~1400 and ~1010 cm^{-1} and corresponding to sulfate groups adsorbed on flat regular faces of the ZrO_2 particles and surrounded by highly coordinatively unsaturated Zr^{4+} centers, probably located at corners, kinks, and edges. A schematic view of this topology in shown in Fig. 9. These sulfate groups are tightly bound and are among the most resistant ones to thermal treatment. However, in other sulfate families and, probably, also within this family of sulfates those important for the catalytic activity are limited in number, as is demonstrated by the observation that even a significant loss of sulfate content and a decrease in intensity of the overall sulfate bands envelope over a 1-month operation time has a modest effect on the catalytic activity. The activation in air at 400–450°C (oxidative activation) is aimed at reestablishing this class of active centers on the surface, by elimination of contaminants deposited during storage (mainly water) that would change the acidic nature of the active centers.

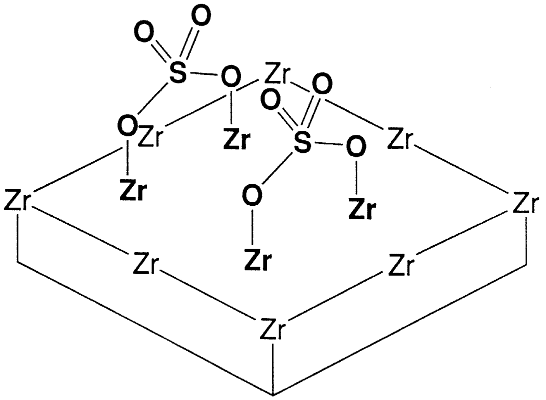
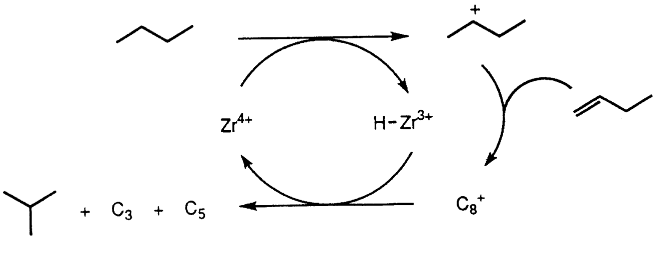


FIG. 9. A schematic view of the topology of active sulfate centers (see text).

Recently, Sachtler and co-workers (21) have convincingly demonstrated, on the basis of thermodynamic considerations and kinetic analysis of the *n*-butane isomerization reaction, that the mechanism of action of these catalysts is most likely of an intermolecular type, involving the initial formation of a C4 carbenium ion, followed by dimerization with butene and fragmentation of the C8 intermediate to give *i*-butane. The necessity of butene to sustain the reaction has been demonstrated by same authors (21).

In general terms our experimental results on PZS samples are in agreement with the findings of these authors: clear evidence for dimerization is provided by the observation of C3 and C5 by-products, while the negative kinetic effect of hydrogen observed for PZS samples accounts for the formation of butene. Scheme 3 summarizes the reaction pathway. The mechanism suggested implies the formation of cracking products, as evidenced by the formation of methane, that increase upon increasing the reaction temperature, and are obvious responsible for the continuous deactivation of the catalysts. The use of hydrogen in the feed is essential to get rid of this problem, and in this respect the effect of hydrogen on the catalytic activity should be positive. If Pt is not present (AZS samples) the necessary activation of hydrogen may be performed by some Zr^{4+} sites (Scheme 1), although, as expected, activity data demonstrate that these sites are far less efficient compared



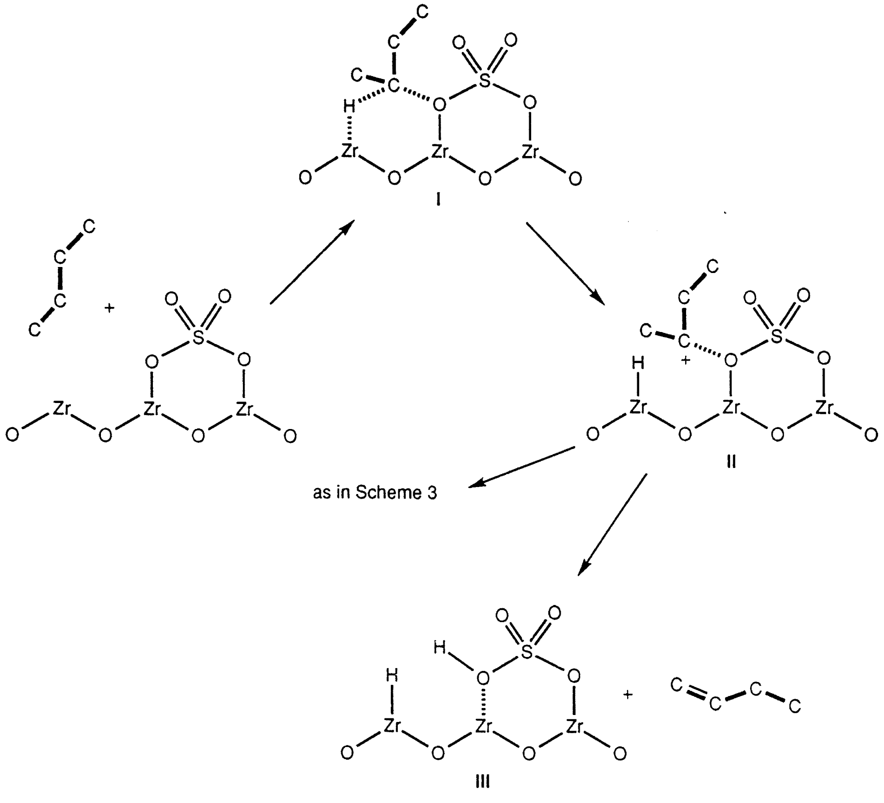
SCHEME 3

to Pt. The positive effect of hydrogen observed in the case of AZS samples reflects this view and is in agreement with previous observations by Garin *et al.* (14). These authors also reported that, if the H_2/butane ratio is checked in a wide range (up to ~350), the occurrence of an inversion in the effect of hydrogen on the catalytic activity could also be observed. This second regime was observed by Sachtler at high H_2 pressure and is consistent with the intermediate formation of butene required by the intermolecular mechanism proposed (21).

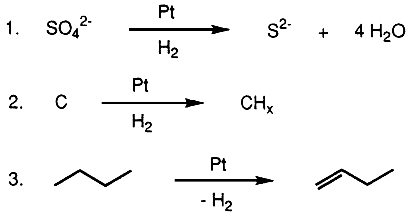
However, as shown in Scheme 3, to account for the evidence found in previous work by us (10, 11) and other authors (22) on the involvement of Lewis acid centers as crucial components for an active catalyst, we suggest Zr^{4+} Lewis acid centers as the major factors responsible for the generation of the initial C4 carbenium ion. Indeed, the early assumption of the superacid nature of sulfated zirconia materials has been severely questioned, and it is now accepted that the Lewis Zr^{4+} sites are far weaker acids than, for instance, the exposed Al^{3+} ions at the surface of dehydrated aluminas (23). We suggest that the first hydride abstraction with formation of the initial C4 carbenium ion would occur on coordinatively unsaturated Zr^{4+} centers with the assistance of the adjacent sulfate groups (Scheme 4), a topology that we have found from IR data to be crucial for the activity of the catalysts (Fig. 9) and that contributes significantly to the stabilization of the transition state (species **I** in Scheme 4). A pathway of this type is in agreement with the suggestions of Sachtler and co-workers on the stabilization of the surface intermediates on sulfated zirconia catalysts (21) and is analogous to Kazansky's (24) and van Santen's (25) conclusions for acid zeolites. Once the adsorbed C4 carbenium ion is formed (species **II** in Scheme 4), it will either react with butene as in Scheme 3 or transfer a proton to the sulfate group to yield butene and **III**.

In the absence of Pt, this pathway would account for both the formation of butene and the negative effect of hydrogen observed at high pressure (21). In fact, the step from **III** to the starting species is the equilibrium depicted in Scheme 1. Moreover, Scheme 4 is in general agreement with the pathway suggested by several authors (26) for the dehydrogenation of alkanes on solid acids.

The various roles played by platinum as a component of Pt-promoted SZ catalysts are summarized in Scheme 5. Activation of the catalyst must be performed in dry air only (oxidative activation), to avoid reaction 1 that leads to masking of the Pt centers. The two major roles of Pt in the catalysis are those indicated in reactions 2 and 3. The former benefits from an increase in hydrogen pressure, the latter implies a negative hydrogen effect. Indeed, some previous analysis on Pt containing systems have evidenced either a positive hydrogen effect, as found by Garin at low



SCHEME 4



SCHEME 5

hydrogen pressure (7) and related to the clean-up of the catalyst surface (reaction 2), or a negative kinetic effect (reaction 3), as reported by Sachtler and observed at high hydrogen pressure (21). The conditions chosen in this work have allowed us to observe the inversion point, providing the first experimental evidence for the coexistence of both effects and complementing the above works. Only relatively few centers of Pt seem to be necessary to perform the above, as is shown by the relative independence of the catalytic activity on the Pt content in the 0.65–4.96% range. The direct involvement of Pt in the formation of butene is further demonstrated by a comparison of the activity between the unpromoted and the Pt promoted catalysts: the latter are about three times more active than the former under optimum reaction conditions. The comparison is particularly appropriate and significant, because the two classes of catalysts have been prepared according to the same procedure and, except for the presence of Pt, possess very similar structural and morphological properties.

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