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Reduction of $SO_4^=$ Ions in Sulfated Zirconia Catalysts

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Upon reducing sulfated zirconia (SZ) catalysts with hydrogen, roughly 50% of the sulfate groups are reduced to sulfur dioxide which is detected mass spectrometrically; the other 50% are reduced to $S^=$ ions that are retained at the surface. The measured ratio H/S of consumed H atoms to S atoms originally present as $SO_4^=$ ions is thus H/S = 5. In the presence of platinum, either deposited on the SZ, or as Pt/NaY in a physical mixture with SZ, or downstream of SZ in a layered bed arrangement, the SO_2 is reduced further to H_2S, which is detected chemically and by MS. In this case H/S = 8. The TPR peak position is shifted to lower temperature in PtSZ and in physical mixtures of SZ and Pt/NaY. Reduction of sulfate groups lowers the Brønsted acidity of the catalysts, as indicated by the *intensity* of the IR bands of adsorbed ammonia. Brønsted acidity is almost totally eliminated by hydrogen reduction at 400°C. The position of the band of ammonia on Lewis sites is not significantly affected by sulfate reduction, but the temperature at which ammonia is desorbed from these sites is lowered. The H_2S that is formed in the presence of Pt partially poisons the Pt particles; their catalytic signature in the isotope exchange of cyclopentane with D_2 indicates that large Pt ensembles are blocked by adsorbed S atoms even after reduction up to 350°C, but that isolated Pt atoms are still acting as active sites. After complete reduction of the $SO_4^=$ groups, Pt in PtSZ loses its catalytic activity for the isotope exchange reaction.

1. INTRODUCTION

The propensity of sulfated tetragonal zirconia (SZ) to catalyze the isomerization of *n*-butane to *iso*-butane makes this catalyst a crucial test case for the fundamental understanding of solid acid catalysis. SZ apparently violates the general rule that skeletal isomerization of C_4 requires a much higher reaction temperature than isomerization of C_5 and C_{5+} alkanes because of the impossibility of avoiding a *primary* carbenium ion intermediate in C_4 isomerization via a protonated cyclopropane intermediate (1). It has been shown that this exceptional propensity of the SZ catalyst system is due to its ability to produce a C_8 intermediate from two C_4 entities; the C_8 intermediate easily isomerizes and one of its isomers undergoes β-fission to two fragments of *iso*-butane structure (2). In the language of classical carbenium ions, it is the 2,2,4-trimethylpentylcarbocation which decomposes into an *iso*-butyl carbocation and an *iso*-butene molecule; this terminology is used even though in reality the intermediates are more similar to alkoxy groups than to free carbenium ions (3).

Formation of a C_8^+ ion from two C_4 alkanes requires not only strong acidity, but also the formation of C_4 alkenes and their regeneration in the catalytic cycle. Many *n*-butane feeds are known to contain *butene* and *butadiene* impurities at the ppm level or above. These unsaturated compounds may favorably affect the initial activity of the SZ catalyst, but they also control the rate of its deactivation by coke formation. Well defined levels of butene/butane and butadiene/butane ratios can be established in the presence of H_2 over Pt containing catalysts. Such catalysts have been found to display extraordinary stability and a reaction order of +1 in butene (4–6). As the reaction mechanism of C_4 isomerization is, basically, the same in both the presence and the absence of Pt, with H_2 having a negative reaction order in both cases (5, 7), it follows that the SZ catalyst is able to produce olefins from paraffins even in the absence of a transition metal. This focuses attention on the redox function of zirconia, in particular the sulfate groups on its surface (8). However, the Pt enhanced reduction of the sulfate groups might lead to H_2S or sulfides which could deactivate the platinum (9–11). Also, since the acidity of the SZ catalysts is assumed to be associated with the sulfate ions (12–15), any reduction of this sulfate could lead to a lower acidity.

In the present work the reduction by H_2 of the sulfate ions in SZ has been studied by quantitative TPR, both in the presence of Pt and in its absence. As the effect of Pt is very pronounced, catalyst samples which contain Pt directly deposited on sulfated zirconia (PtSZ) have been compared with physical mixtures of SZ and Pt/NaY in a variety of configurations, including layered beds with Pt/NaY either upstream or downstream of SZ. The extent of sulfate reduction is derived quantitatively from the TPR data and gaseous reduction products have been identified by on-line mass spectrometry. The effect of sulfate reduction on catalyst acidity and the effects of gaseous reduction products of

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the sulfates on the propensity of Pt particles to catalyze H/D exchange of cyclopentane with D_2 have been determined.

2. EXPERIMENTAL

2.1. Sample Preparation

Pt-free SZ was prepared by calcination of sulfated zirconium hydroxide, kindly provided by Magnesium Electron Inc. (MEI) in a flow of dry air (100 ml/min) at 650°C for 3 h. ICP analysis showed that this SZ catalyst contained 1.04 wt% of sulfur. Platinum promoted sulfated zirconia (PtSZ) was prepared by sequentially impregnating a MEI $Zr(OH)_4$ with aqueous H_2PtCl_6 and 1 N H_2SO_4 solution, as described elsewhere (4), followed by calcination in flowing dry air at 650°C for 4 h. Two samples of PtSZ with Pt loadings of 0.38 and 2.2 wt% have been used in the present study; they are denoted as 0.4% PtSZ and 2.2% PtSZ, respectively. The sulfur content of both PtSZ samples is 1.35 wt%.

Pt/NaY (Pt load, 4.5 wt% Pt or 0.4 Pt atoms per supercage) was prepared by ion exchange of a dilute solution of $Pt(NH_3)_4Cl_2$ (Strem Chemicals, lot 17649-S) with a NaY slurry (150 ml/g zeolite), as reported in (16). The zeolite used was Linde LZY-52 from Union Carbide (lot 968087061020-S-8); the approximate unit cell formula is $Na_{56}(AlO_2)_{56}(SiO_2)_{136}$.

2.2. Temperature-Programmed Reduction (TPR)

TPR experiments were done with a 5% H_2/Ar gas mixture (30 ml/min). The H_2 uptake was monitored by a Gow-Mac thermal conductivity detector (TCD), which was interfaced to a Zenith 158 computer for data collection and analysis. To prevent the interference of SO_2, which is one of the possible sulfate reduction products, and H_2O in the TCD, a pentane/liquid nitrogen trap (−131°C) was placed after the TPR reactor and before the sampling side of the TCD. Another trap, containing an aqueous 0.1 M Pb^{2+} solution, was placed at the outlet of the TCD in order to detect H_2S which is not condensed in the pentane/liquid nitrogen trap. The differences in thermal conductivity between H_2 (186 mW/mK), H_2S (14.6 mW/MK), and Ar (17.9 mW/mK) are large enough to prevent a major interference of H_2S formation and H_2 consumption. In some experiments on-line mass spectrometry is operated to identify gases formed in the TPR process. In these experiments, the pentane/liquid nitrogen trap was not applied, so that all gas phase products could be detected by the MS.

For the TPR's of sulfated zirconia (SZ and PtSZ), a 100-mg sample was loaded in a quartz reactor and calcined in a flow of ultrapure O_2 (>100 ml/min) up to 500°C with a temperature ramp of 8°C/min. The pretreatment was continued for 1 h at 500°C, followed by switching to pure Ar (30 ml/min) at 500°C. After cooling the sample in Ar to RT, the gas flow was changed to 5% H_2/Ar for the TPR with a ramp of 8°C/min. For the TPR's of Pt/NaY 100-mg samples were used; for the physical mixtures of Pt/NaY and SZ 100 mg of each component was used. The temperature ramp during the pretreatment with O_2 was 0.5°C/min and the pretreatment continued for 2 h at 500°C. The termination temperature for TPR was 750°C on SZ, 600–650°C on Pt/NaY, and 700°C on PtSZ and the mixtures of Pt/NaY + SZ. In some cases the pretreatment temperature in O_2 was varied to show the effect of calcination on the TPR profiles of PtSZ. In other runs the TPR reduced sample was cooled in 5% H_2/Ar to RT for hydrogen adsorption, followed by purging with pure Ar at RT for 20 min and a H_2-TPD run.

2.3. H/D Exchange of Cyclopentane

The H/D exchange reaction of D_2 with cyclopentane (CP) was carried out in a recirculation system. The reactor can easily be switched to a flow of different gases facilitating *in situ* pretreatment of the catalyst sample (17). The exchange reaction was performed at 100°C with a molecular D_2/CP ratio of 25 and a total pressure of 52 Torr (18) over 15 mg of 2.2% PtSZ and Pt/NaY, or 30 mg 0.4% PtSZ, or 30 mg physical mixture of Pt/NaY + SZ in a weight ratio of 1 : 1. During the reaction the isotope exchange was monitored by a mass analyzer (Dycor M100) with a variable leak valve from the reaction system. The initial product distribution was calculated according to the method of van Broekhoven and Ponec (19) at less than 7% conversion. The initial rate of the disappearance of undeuterated CP, $[-d(d_0)/dt]$, was corrected for physisorption of CP and calculated by standard means (20). The product distribution of the exchange reaction was expressed by the d_i fraction, which was defined as the ratio of the deutero-cyclopentane molecule with $_i$D atoms to the total number of all deutero-cyclopentane molecules.

2.4. FTIR Measurements

A Nicolet 60SX FTIR spectrometer equipped with a liquid N_2 cooled MCT detector was used for recording the IR spectra. Self-supporting wafers of 6–8 mg/cm^2 were prepared and inserted into an *in situ* quartz cell equipped with NaCl windows and connected to a glass manifold. After certain treatments, spectra were taken in transmittance at RT with 150 scans accumulated at a spectral resolution of 1 cm^{-1}. Anhydrous NH_3 (Matheson, Research grade) was adsorbed to characterize the surface acidity.

3. RESULTS

3.1. TPR of SZ and PtSZ

Figure 1 shows the TPR profiles of the Pt-free (SZ) and Pt-containing (PtSZ) samples. The TPR profile of SZ displays only one large peak, starting near 400°C and peaking

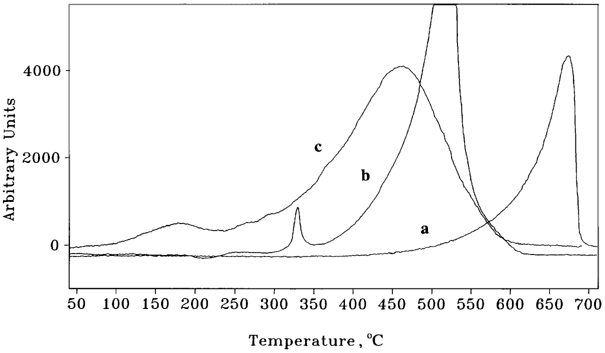

FIG. 1. TPR profiles of sulfated zirconia catalysts. (a) SZ, (b) 0.4% PtSZ, (c) 2.2% PtSZ.

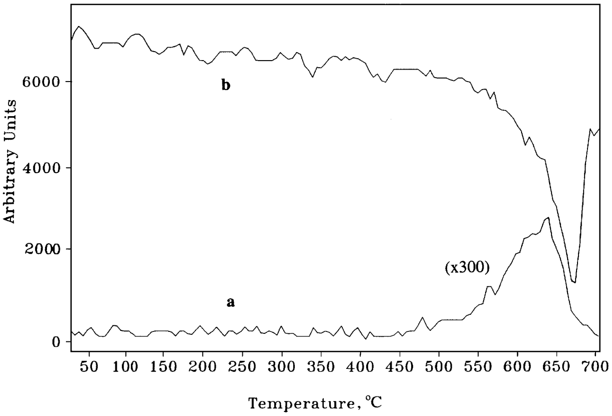

FIG. 2. Mass spectrometric detection of hydrogen consumption and evolution of SO_2 during TPR of SZ. (a) SO_2 evolution, (b) H_2 consumption.

at 660–680°C. Blank experiments confirmed the absence of TPR peaks for unsulfated ZrO_2 in this temperature region. The reduction of PtSZ occurs at temperatures much lower than that of SZ, showing an enhancement of sulfate reduction by Pt. Two peaks are distinguished on the reduction profiles of the Pt-promoted samples; they are located at ca. 180 and 460°C for 2.2% PtSZ and at 325 and 520°C for 0.4% PtSZ, respectively. The low temperature TPR peaks are assigned to oxygen removal from platinum, while the high temperature peaks indicate reduction of sulfate in these PtSZ samples. Although there is some peak overlap, one can see from the shape of the reduction profiles that the onset temperature for sulfate reduction in PtSZ is between 250 and 300°C.

Integration of the TPR peaks yields hydrogen consumption data compiled in Table 1. They are reproducible within <10%. While the reduction of SZ consumes on the average five H atoms per S atom of the surface sulfate (H/S = 5), a value of H/S = 8 for PtSZ demonstrates total reduction of all sulfur atoms from the oxidation state of +6 in sulfate ions to a state of −2 in H_2S or sulfide ions. Formation of H_2S during the TPR experiments of PtSZ is confirmed by the observation of a black PbS precipitate in the aqueous Pb^{2+} trap placed at the outlet of the TPR detector. A blank test during the TPR experiment of the Pt-free SZ was negative. Gaseous products formed during the reduction of SZ have been trapped in the *n*-pentane/liquid nitrogen cooled trap at −131°C. Upon purging the trapped condensate and releasing it into the aqueous Pb^{2+} solution trap, formation of a white precipitate is observed, presumably $PbSO_3$. It follows that SO_2, not H_2S, has been formed during the reduction of the Pt-free SZ.

TABLE 1

Quantitative Hydrogen Consumption in TPR of SZ and PtSZ

Sample	H/Pt	H/S	SO_4 reduction peak (°C)
SZ		5.1	660–680
0.4% PtSZ	2.9	8.2	515
2.2% PtSZ	0.6	8.3	460

On-line mass spectrometric analysis during the TPR runs with SZ and PtSZ confirmed the identity of the reduction products in the gas phase. For SZ Fig. 2 shows that SO_2 is the only product, besides water. However, the H_2 consumption curve does not match that of SO_2 evolution. From the fact that the maximum of H_2 consumption coincides with the temperature where SO_2 evolution is fading out, it is deduced that the reduction product which is formed at higher temperatures must be retained by the surface of the reduced SZ. To check this point, a TPR reduced SZ sample was reoxidized in a flow of oxygen at 500°C and then cooled in Ar to RT and a second TPR was performed. Figure 3 compares the reduction profiles of the two consecutive TPR experiments, which indicates that 50% of the sulfur originally present on the freshly calcined SZ sample is retained on the surface after the first TPR experiment. A calculation of the oxidation state of the surface retained sulfur from the hydrogen consumption (H/S = 5) and SO_2 evolution discloses that the TPR reduced SZ retains 50% sulfur as surface sulfide.

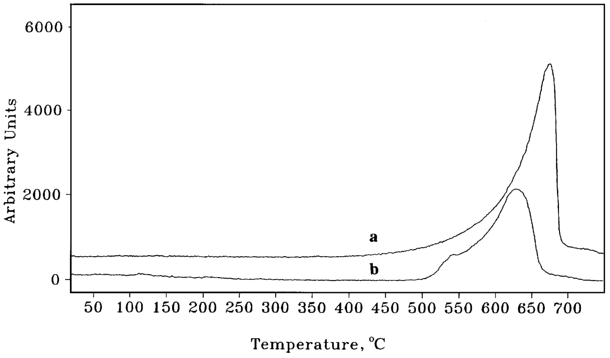

FIG. 3. Comparison of two consecutive TPR profiles of SZ. (a) 1st TPR, (b) 2nd TPR.

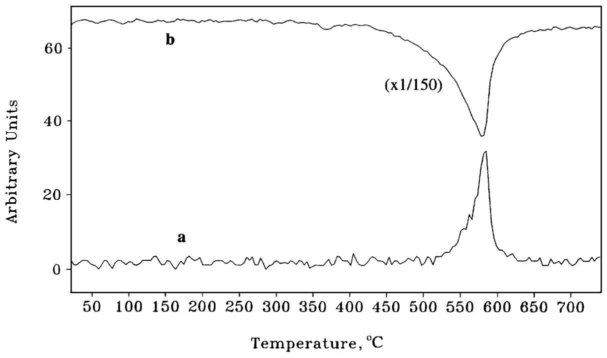

FIG. 4. Mass spectrometric detection of hydrogen consumption and evolution of SO_2 during TPR of 0.4% PtSZ. (a) H_2S evolution, (b) H_2 consumption.

TABLE 2

Effect of Pt/NaY on the Reduction of Sulfate in SZ

Experiment No.	Sample	H/Pt	H/S	SO_4 reduction peak (°C)
1	SZ (single phase)		5.1	660–680
2	Pt/NaY (single phase)	1.9		
3	Pt/NaY (upper) + SZ (lower)[a]	2.2	5.6	670
4	SZ (upper) + Pt/NaY (lower)[a]	2.2	8.6	660
5	SZ+Pt/NaY (mixed phases)	1.8	8.4	500–520

[a] The two phases were separated by a 10-mm in-between quartz-sand layer and a 3-mm glass wool layer. The glass wool was placed just beneath the upper layer sample and assured no contamination between the sample phases.

Gas analysis of the TPR products from PtSZ confirms the formation of H_2S. As it is seen in Fig. 4 for 0.4% PtSZ, the evolution of H_2S matches the consumption of H_2 by the PtSZ samples. These data are in agreement with the result that all the sulfate in PtSZ is reduced to H_2S or $S^=$ ($H/S = 8$).

3.2. *TPR of Physical Mixtures of Pt/NaY with SZ*

A physical mixture of Pt/NaY (4.5 wt% Pt) with SZ was studied by TPR to show the enhancement of sulfate reduction by Pt, even when not in direct contact. The two powders were physically mixed in the quartz reactor by shaking for 3 min. In different experiments the SZ and Pt/NaY powders were arranged as two layers, separated by a 10-mm layer of quartz powder and a 3-mm layer of glass wool. Figure 5 (left) compares the TPR profiles of the mixtures with those of "pure" Pt/NaY and SZ. The reduction profile (a) of Pt/NaY shows two peaks of Pt reduction at about 85 and 225°C. The negative peaks above 400°C are due to a reoxidation of metallic Pt by zeolite protons, which were formed by H_2 reduction of Pt^{2+} (21). In the 1/1 physical mixture (b-1) of Pt/NaY and SZ, small TPR peaks are observed below 400°C, similar to those in (a) for Pt reduction in Pt/NaY. The two profiles in Fig. 5 (left) (a) and (b-1), are shown at the same scale. In Fig. 5 (right) profile (b-1) is replotted at a larger scale, as (b-2), to facilitate comparison with the double layered configuration (c) with Pt/NaY downstream, and pure SZ (d). While it is obvious that Pt in Pt/NaY is completely reduced below 400°C, the large peaks which appear above 400°C are due to reduction of sulfate in SZ. A quantitative presentation of hydrogen consumption in these experiments is given in Table 2. The H_2 consumption of $H/Pt = 2$ below 400°C is further proof that these peaks are due to the reduction of Pt. Comparison of Profile (b-2) and (c) shows that the sulfate reduction peak is shifted by ca. 160°C to lower temperatures in the physical mixture with Pt/NaY in comparison to SZ.

The ratio of $H/S = 8$ for the physical mixture (Table 2, Experiment 5) indicates complete reduction of sulfate to H_2S. When the Pt/NaY is placed as a separate layer upstream of the SZ it does not affect the reduction of SZ (Table 2, Experiments 1 and 3). However, when the Pt/NaY layer is positioned downstream to the SZ layer (Experiment 4) the sulfate is found, again, completely reduced to H_2S ($H/S = 8$). The shape of the hydrogen consumption profile of SZ is not affected by this positioning (compare c and d in Fig. 5). Obviously, SO_2 produced by the reduction of the

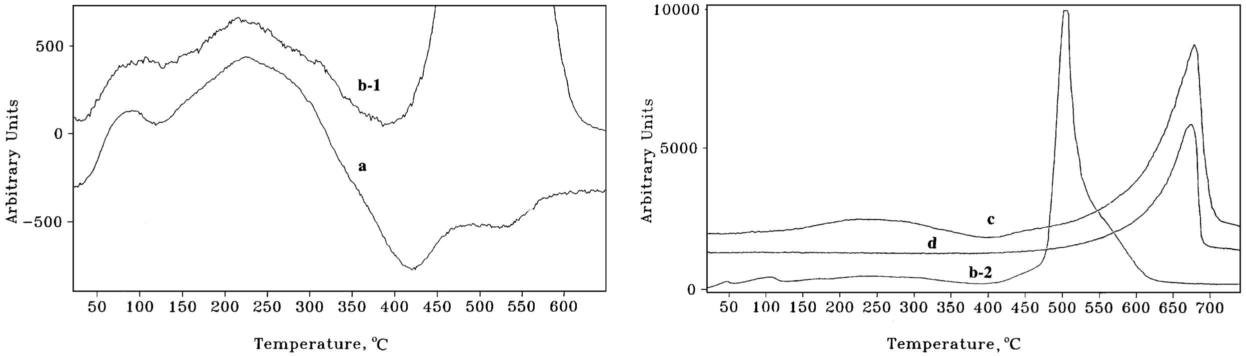

FIG. 5. (Left) TPR profiles of Pt reduction in Pt/NaY and a physical mixture of SZ+Pt/NaY. (a) Pt/NaY, (b-1) a 1 : 1 (weight) physical mixture. (Right) TPR profiles of sulfate reduction. (b-2) Same as (b-1) on left, but plotted at different scale, (c) Double layered configuration with Pt/NaY layer downstream of SZ layer, (d) pure SZ.

SZ layer (Fig. 2) is further reduced to H_2S when it passes over the Pt/NaY layer. Since only half of the sulfate has been reduced to SO_2, while the other half is retained on the surface of the reduced SZ, the overall value of $H/S = 8$ confirms that the sulfur species that was retained at the surface of the reduced SZ must be a surface sulfide.

3.3. H/D Exchange of CP

Table 3 shows the initial activity of PtSZ samples for the H/D exchange of CP with D_2 at 100°C. The corresponding initial product distribution pattern of the exchange reaction is given in Fig. 6. As a blank experiment, 60 mg of the Pt-free SZ sample was used for the exchange reaction under the same conditions. The result showed no exchange between D_2 and CP; one thus can disregard any exchange activity of the acid sites on the PtSZ. The pronounced activity and the typical *double-U shaped* exchange pattern over the calcined, unreduced PtSZ samples (Figs. 6a and 6b) are indicative that metallic Pt is the active site for this exchange (17, 18, 22, 23). When PtSZ is reduced up to the temperature at which Pt reduction is complete, the 2.2% PtSZ sample (TPR to 240°C) has become 2.5 times more active than the unreduced 2.2% PtSZ; the 0.4% PtSZ (TPR to 350°C) loses, however, 1/3 of its activity after calcination. Likewise, the distribution of the exchange product is different between these PtSZ samples; the characteristic *double-U shaped* pattern (similar to Figs. 6a and 6b, but not shown in the figure) is maintained over the 2.2% PtSZ reduced to 240°C, while over the 0.4% PtSZ reduced to 350°C the observed pattern is dominated by the d_1-product (Fig. 6c).

The last three rows of Table 3 present the activities of the TPR reduced mixtures of Pt/NaY and SZ. Figure 7 compares the product distributions of the exchange reaction over the TPR reduced Pt/NaY and the mixture. Clearly, the activity of Pt/NaY for the exchange reaction is greatly reduced when it is mixed and reduced with SZ. However, when the reduction on the mixture is carried out up to 400°C and then stopped, so that little sulfate reduction in SZ can occur, the activity of Pt/NaY in the mixture becomes slightly higher than that of Pt/NaY after reduction to 700°C. The exchange pattern over the reduced Pt/NaY catalyst is dominated by the D-rich products d_8, d_9 and d_{10}, with a maximum at d_9 (Fig. 7a). This indicates that exchange equilibrium has been reached over this catalyst at a very early state of the reaction (18). The exchange pattern over the mixture which has been reduced up to 400°C (not shown in the figure) is basically the same as in Fig. 7a, thus suggesting that SZ in this mixture does not interfere with the Pt catalyzed exchange reaction. In contrast, when the mixture is reduced up to 700°C, to achieve complete reduction of the sulfate to H_2S (Table 2), a double-U shaped pattern (Fig. 7b) is

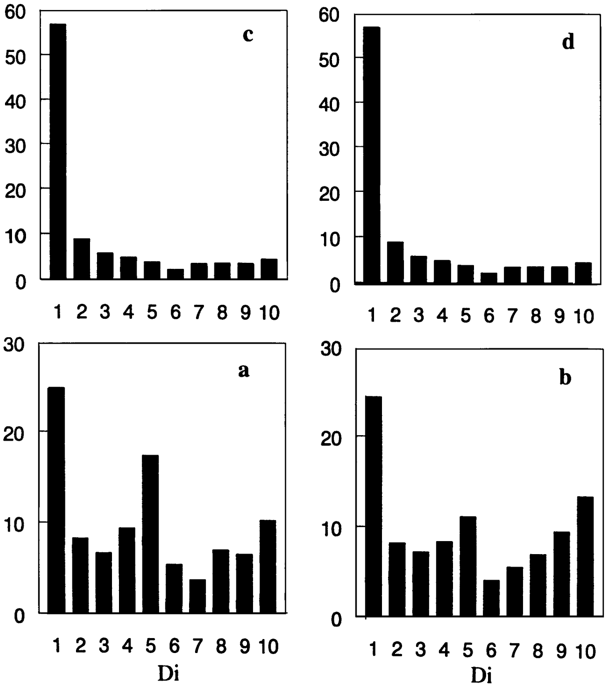

FIG. 6. Initial product distribution of H/D exchange of cyclopentane over PtSZ catalysts after different pretreatment. (a) As-calcined 0.4% PtSZ, (b) as-calcined 2.2% PtSZ, (c) 0.4% PtSZ reduced (TPR) up to 350°C, (d) 2.2% PtSZ reduced at 350°C.

TABLE 3

Initial Activity of H/D Exchange of Cyclopentane (Reaction Temperature 150°C; $H_2/CP = 25$)

Sample pretreatment	Initial rate (%/min 15 mg)
2.2% PtSZ	
As calcined	10.76
TPR to 240°C	24.95
TPR to 700°C	0.27
0.4% PtSZ	
As calcined	0.69
TPR to 350°C	0.43
TPR to 700°C	0.10
4.5% Pt/NaY, TPR to 700°C	38.10
TPR to 400°C	42.61
4.5% Pt/NaY + SZ, TPR to 700°C	7.76

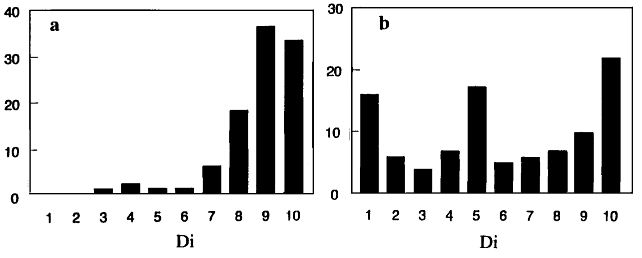

FIG. 7. Initial product distribution of H/D exchange of cyclopentane. (a) Over TPR (to 700°C) reduced Pt/NaY, (b) over TPR (to 700°C) reduced physical mixture of SZ and Pt/NaY.

obtained, one which differs, however, from that in Fig. 6 by a much higher d_{10} content.

3.4. *FTIR Spectroscopy*

Reduction of PtSZ was also examined with FTIR. A self-supporting wafer of 0.4% PtSZ (6–8 mg/cm^2) was dehydrated in the IR cell with Ar at 450°C for 2 h; the IR spectrum after this treatment is shown in Fig. 8a. This spectrum is typical of sulfated zirconia and metal promoted sulfated zirconia catalysts (24–27). When the same sample wafer was subjected to a hydrogen flow at 400°C for 40 min, followed by another dehydration at 450°C, the spectrum shown in Fig. 8b was obtained. Clearly, a drastic decline of sulfate absorption bands (1400–950 cm^{-1}) demonstrates a severe hydrogen reduction of the surface sulfate. The reduction of sulfate also results in a change of the OH groups on the surface. In Fig. 8, the unreduced 0.4% PtSZ sample shows an OH band at 3640 cm^{-1}, which was considered responsible for strong Brønsted acidity of sulfated zirconia catalysts (13, 27, 28). After reduction at 400°C this OH band has shifted to 3680 cm^{-1}; a new band appears at 3775 cm^{-1} (Fig. 8b). The frequencies of these OH bands (3680 and 3775 cm^{-1}) are the same as those of the bridging (3680 cm^{-1}) and terminal (3780 cm^{-1}) OH groups on sulfate-free zirconia (29, 30), thus suggesting that after reduction the OH groups on PtSZ become like those of sulfate-free zirconia. Interestingly, separate XRD data show that the tetragonal phase still dominates in the reduced sample; compared to the unreduced sample, the concentration of this phase decreased be less than 10%.

Figure 9 compares the acidity of SZ, 0.4% PtSZ and the hydrogen reduced 0.4% PtSZ by using the IR bands of adsorbed NH_3. Apparently, SZ and 0.4% PtSZ have similar acidity (Figs. 9A and 9B). Lewis as well as Brønsted acidity are characterized in these spectra by absorption bands at 1610 and 1445 cm^{-1}, respectively. While NH_3 adsorbed at RT and remaining undesorbed at 200°C shows a strong absorption band (1445 cm^{-1}) for Brønsted acidity, the spectra after desorption at 400°C show the characteristics of Lewis acids (1610 cm^{-1}). No significant change in Lewis acidity is observed when the desorption temperature is raised from 200 to 400°C. This seems to suggest that the strongest acid sites on SZ and PtSZ are of the Lewis acid type; this is consistent with data of Dumesic *et al.* (31).

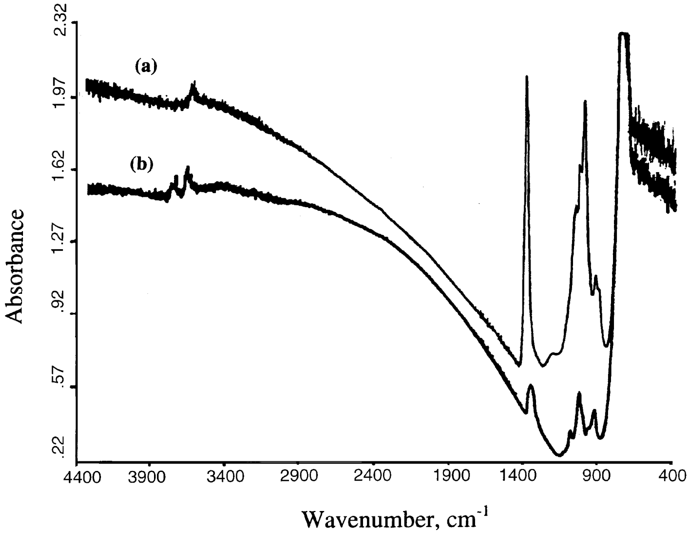

FIG. 8. IR spectra of 0.4% PtSZ dehydrated at 450°C. (a) Before reduction, (b) after reduction in H_2 at 400°C for 40 min and a second dehydration at 450°C.

The hydrogen reduction of 0.4% PtSZ at 400°C almost eliminates the Brønsted acidity as is shown in Fig. 9C. Although the absorption band for Lewis acidity does not change significantly after desorption at 200°C, its disappearance after desorption at 400°C (not shown in the figure) indicates that Lewis acidity of sulfated zirconia is also weakened after the reduction.

4. DISCUSSION

4.1. *Reduction of Pt-Free SZ*

TPR studies of SZ were previously reported by Sayari *et al.* (32, 33) and Srinivasan *et al.* (34). The TPR profile of the Pt-free SZ (Fig. 1) basically reproduces theirs. The observation of SO_2 evolution during TPR (Fig. 2) is also in agreement with results reported by Sayari *et al.* (33). Srinivasan *et al.* (34) observed that formation of SO_2 (566°C) was accompanied by H_2S formation at a slightly higher temperature (591°C) when an uncalcined SZ (3.46 %S) precursor, probably $SO_4/Zr(OH)_4$, was heated in 34% H_2/Ar. They also reported that after reduction to 800°C of a 725°C calcined SZ (1% S), ca. 50–60% of the sulfur was retained on the reduced surface. Le Van Mao *et al.* (35) reported that the sulfate of a 600°C calcined SZ of higher sulfur content (5.0% S) was completely reduced to H_2S in 40% H_2/N_2, though these authors did not detect H_2S directly. In the present study, no H_2S formation was found in the absence of Pt; this may suggest that the reducibility of the sulfate in SZ is dependent on the sulfur content and/or the calcination temperature. However, the finding of Srinivasan *et al.* (34) that almost half of the sulfur in SZ was retained on the reduced SZ surface is reproduced in the present study.

The average hydrogen consumption of the Pt-free SZ is $H/S = 5$ (Table 1); this fact and the observation of HSO_2 as the sole gaseous reduction product of SZ prove that the second reduction product, which is retained on the surface, must be a surface sulfide. This conclusion is confirmed by the fact that subsequent reduction of the primary SO_2 over a separate layer of Pt/NaY brings the total H/S ratio from 5 to 8. This completes the material balance for total reduction of S^{6+} to S^{2-}. It is concluded that in the absence of Pt one half of the sulfate in SZ is reduced to SO_2, while the other half is reduced to sulfide and retained by the zirconia.

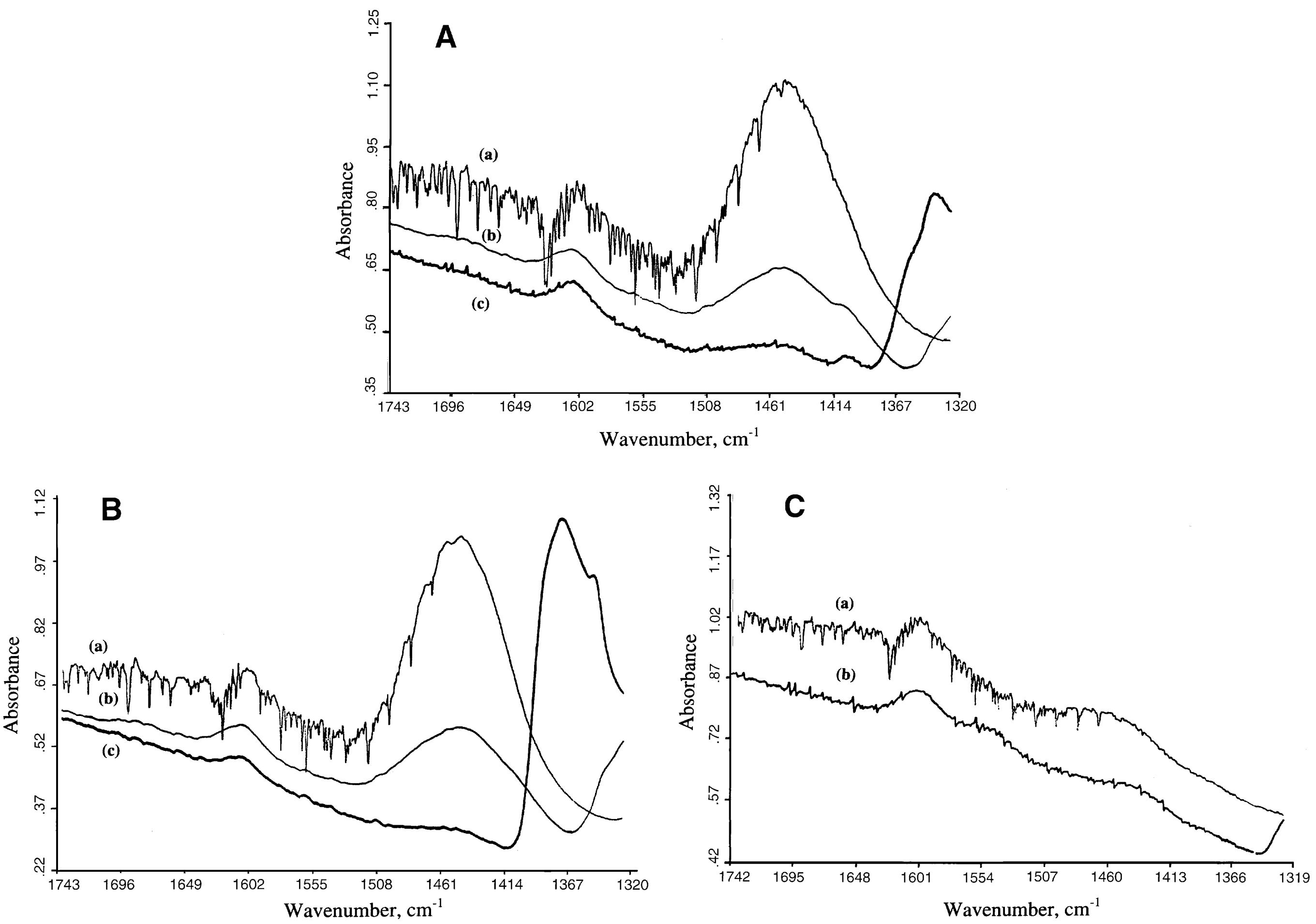

FIG. 9. IR spectra of adsorbed NH_3 on SZ (A), 0.4% PtSZ (B), and H_2 reduced 0.4% PtSZ (C). (a) After desorption at RT, (b) after desorption at 200°C, (c) after desorption at 400°C.

4.2. Effect of Pt on the Reduction of SZ

The TPR results of both PtSZ and the physical mixtures of Pt/NaY and SZ show that the presence of Pt not only changes the nature of the gaseous reduction product, it also lowers the reduction temperature of sulfate in sulfated zirconia (Figs. 1 and 5). Enhancement of sulfate reduction by Pt has also been reported from other laboratories (10, 33–35). It is remarkable that Pt, even if not supported on the same zirconia as the sulfate groups, facilitates the quantitative reduction of all sulfate groups in SZ. In a merely phenomenological way this phenomenon can be described as hydrogen spillover, but this term does not identify the physical nature of the migrating species. A satisfactory analysis of this phenomenon, though quite challenging, is outside the scope of the present paper. The present data show that not only the secondary reduction of SO_2 to H_2S, but also the onset of the reduction of sulfate or bisulfate groups on zirconia is affected by the presence of Pt, even at some distance from the reducible sulfur species. It is remarkable that the TPR peak for sulfate reduction on SZ is lowered by ca. 160°C when SZ is physically mixed with Pt/NaY (Fig. 5b), whereas this TPR peak does not shift significantly when SZ and Pt/NaY are separately layered without physical contact (Fig. 5c).

The reduction of sulfate in PtSZ peaks at 515°C for 0.4% PtSZ, but at 460°C for 2.2% PtSZ (Fig. 1). However, with both samples the *onset* of reduction is observed at the same temperature, viz. 250°C. With the physical mixtures, Pt's apparent effect on the peak temperature seems to depend on the amount of Pt present, but it seems to have little effect on the *onset* temperature of sulfate reduction. Even, for mixtures with higher overall Pt/SO_4 ratios than in the present PtSZ samples, *onset* of the reduction is observed only near 400°C, which is close to the onset temperature over Pt-free SZ. TPR peak positions are, of course, the result of competing rates which depend on the reduction rate and the reductant flow rate, whereas *onset temperatures* are indicative of the activation energy of the reduction process. It thus seems that proximity of Pt on the same support as the reducible sulfate or bisulfate groups has a significant effect in lowering the activation energy for the reduction of these reducible moieties. In contrast, Pt at some distance, as in the physical mixtures, affects the rate of reduction only at temperatures at which this rate is also measurable in the absence of platinum.

4.3. *Effect of Sulfate Reduction on Pt and Surface Acidity*

The low temperature peak in the TPR profile of PtSZ (Fig. 1) registers a reduction of platinum. Hydrogen consumption under this peak gives a H/Pt ratio of 0.6 on 2.2% PtSZ and 2.9 on 0.4% PtSZ (Table 2). The very low H/Pt ratio of 0.6, compared to the theoretical value of 4.0, indicates that a major portion of the platinum has been reduced to the metallic state during the calcination of the 2.2% PtSZ sample. Even for the low Pt sample (0.4% PtSZ), an extensive reduction of Pt also occurs during the calcination. The much higher "H/Pt" ratio (2.9) for 0.4% PtSZ is an overestimated hydrogen consumption of the Pt reduction because it involves some reduction of sulfate (see below). To confirm this statement, the as-calcined PtSZ samples have been analyzed carefully by x-ray diffraction. Indeed, small crystals of Pt-metal have been detected on the as-calcined PtSZ samples (Figs. 10a and 10b). It should be mentioned that TPR profiles presented so far in the present report are obtained after an *in situ* treatment in O_2 at 500°C. This oxidation treatment may cause a reoxidization of the Pt-metal formed during the preceding preparative calcination at 650°C. Interestingly, additional TPR experiments with freshly calcined PtSZ samples do not show any significant difference to the TPR profiles obtained after the *in situ* O_2 treatment at 500°C (Figs. 11a and 11b). However, if the oxidation temperature is raised from 500 to 650°C the hydrogen consumption under the Pt reduction peak is found to increase from 0.6 to 2.4 for 2.2% PtSZ (Fig. 11c). When taken at face value, these results are not in contradiction with statements by Sayari *et al.* (32, 33) and Davis *et al.* (36, 37), that Pt is reduced to the metallic state by calcination in air above 600°C. However, the present data also show that reduction of Pt is not complete at a calcination temperature of 650°C and that reoxidation of this Pt requires a temperature above 500°C.

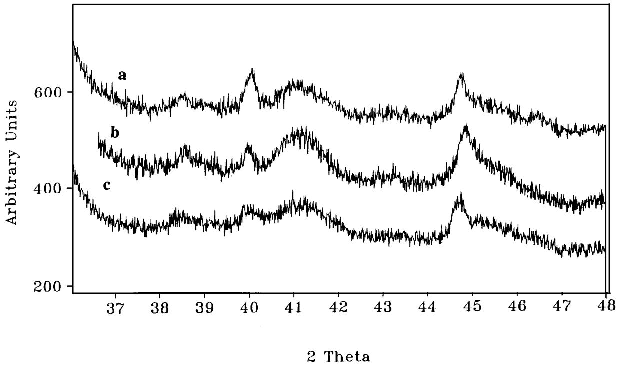

FIG. 10. XRD detection of Pt metal. (a) Calcined 2.2% PtSZ, (b) calcined 0.4% PtSZ, (c) TPR reduced 2.2% PtSZ.

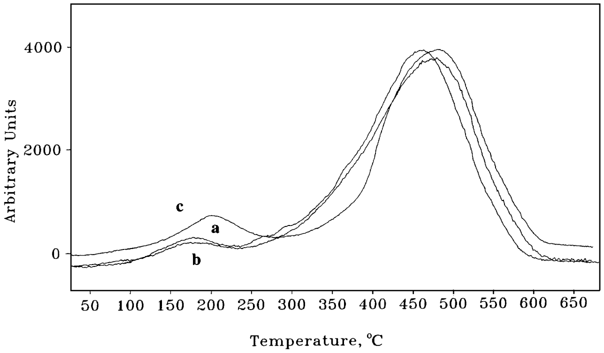

FIG. 11. TPR profiles of 2.2% PtSZ after different pretreatments. (a) Calcined, (b) after calcination in O_2 at 500°C, (c) after calcination in O_2 at 650°C.

In the case of 2.2% PtSZ, Pt reduction at low temperature is strongly supported by the hydrogen chemisorption data measured by H_2-TPD (Table 4). While the calcined sample hardly chemisorbs hydrogen (H/Pt < 0.1), the hydrogen chemisorption capacity is increased to H/Pt $= 0.36$ by treatment in flowing hydrogen up to 240°C, i.e., below the temperature where sulfate reduction can occur. In the case of 0.4% PtSZ, reduction of Pt cannot be completely separated from the reduction of sulfate; consequently, no significant change in hydrogen chemisorption is observed, because extensive reduction is counteracted by poisoning with traces of sulfur. The data shown in the last row of Table 4 are the results of the TPR (to 700°C, as in Fig. 1) reduced samples. While poisoning of Pt by sulfur is conceivable for the very low hydrogen chemisorption of the TPR reduced samples, the reason that the freshly calcined samples fail to show higher hydrogen chemisorption remains unexplained here. We have attempted to detect Pt particles with high resolution transmission electron microscopy (HRTEM) on every sample shown in Table 4; unfortunately no definite image for metallic Pt particles has been observed.

The H/D exchange of CP has been proven a powerful probe for metal catalysis because it counts only exposed metal surface atoms (17). In addition, the product pattern of this exchange reaction is a diagnostic tool for the exchange mechanism (38) and is sensitive to sulfur poisoning of metal catalysts (39). The typical *double-U shaped* exchange pattern indicates a prevailing multiple exchange mechanism

TABLE 4

Pt Dispersion (H/Pt) by H_2-TPD

Sample	0.4% PtSZ	2.2% PtSZ
As-calcined (650°C, 3 h)	0.078	0.075
Pt-reduced (TPR)	0.066	0.36
SO_4-reduced	0.061	0.10

over the freshly calcined PtSZ samples (Figs. 6a and 6b). The fact that 2.2% PtSZ after reduction up to 240°C displays much higher activity (Table 3) and the same product pattern solidifies the assignment of Pt reduction under the low temperature peak (180°C, Fig. 1c). In the case of 0.4% PtSZ, a similar treatment (TPR to 350°C) (Fig. 1b) results in lower activity and a stepwise exchange product pattern (Fig. 6c). This indicates that the size of the Pt ensembles has been reduced by chemisorbed S or SH groups. As expected, the toxicity of sulfur for the multiple exchange is 20 times higher than for the stepwise exchange (39). In other words, the peak at 325°C in Fig. 1b involves reduction of some sulfate, which means that the hydrogen consumption ($H/Pt = 2.9$, Table 1) under this peak may not exclusively be ascribed to Pt reduction. Reduction of 2.2% PtSZ with hydrogen at 350°C also causes sulfur poisoning of Pt, as shown in Fig. 6d. The loss of catalytic activity of the completely reduced PtSZ (TPR to 700°C) samples for the exchange reaction demonstrates total sulfur poisoning of Pt.

The observation that the TPR reduced physical mixture of SZ and Pt/NaY is five times less active for the H/D exchange reaction than the reduced Pt/NaY catalyst (Table 3) identifies the sulfur poisoning of Pt in the reduced mixture. Since there are many more Pt atoms but fewer sulfur atoms in the mixture, the poisoning of Pt in this reduced mixture is less severe than in the reduced PtSZ samples. As a result, some Pt in the mixture is able to survive the reduction and remains active for the exchange reaction. Over the unpoisoned Pt/NaY catalyst, equilibrium between the isotopic products is easily attainable because every reacting CP molecule has a high probability to react with deuterium many times before it can finally diffuse out of the zeolite crystal. Although this probability is lowered over the Pt/NaY in the reduced mixture because of sulfur poisoning of Pt, the much higher d_{10} content in the exchange pattern (Fig. 7b) suggests that some of the D-rich products are formed by secondary exchange reactions that occur when the primary isotopic products diffuse out of the zeolite crystal.

The IR observation that OH groups on PtSZ become like those of sulfate-free zirconia after hydrogen reduction is in good accordance with the TPR results that hydrogen reduction of sulfated zirconia removes sulfate from the surface. These results and the lower acidity of the reduced sample (Fig. 7b) demonstrate the role of sulfate promotion in surface acidity (25). Although the structure of the acid sites in relation to sulfate is still an issue of some debate (13–15, 28), the present work shows that removal of sulfate from the surface eliminates the Brønsted acidity and weakens the Lewis acidity.

5. CONCLUSIONS

Temperature programmed reduction of Pt-free SZ in 5% H_2/Ar releases 50% of the sulfate groups as SO_2 and retains the other 50% on the surface as sulfide. When Pt is present, either deposited on the SZ or as Pt/NaY in a physical mixture with SZ, the sulfate groups in SZ are quantitatively reduced to $S^{=}$. The H_2S poisons the Pt particles, so that first the large Pt ensembles are blocked and only stepwise H/D exchange CP occurs; ultimately Pt supported on SZ loses its catalytic activity altogether. Reduction of the sulfate groups markedly lowers the Brønsted acidity of the catalysts, while the strength of the Lewis sites is only slightly lowered.

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