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$Pt-SO_4^{2-}-ZrO_2$ Catalysts: The Impact of Water on Their Activity for Hydrocarbon Conversion

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A series of experiments were conducted to determine the effect of water on the activity of platinum promoted sulfated zirconia catalysts. The initial set of experiments showed that the catalyst exposed to various water partial pressures generated a Type II adsorption isotherm. The activity measurements, as defined by hexadecane conversions, showed that at a ratio of approximately 0.5 mol H_2O absorbed per sulfate molecule the water was functioning as a poison. A second set of experiments was designed to generate water *in situ* by alcohol dehydration for lower ratios of H_2O to sulfate than 0.5. These activity measurements showed that water was acting as a poison at these lower ratios and the resulting decline in activity was approximately zero order in water. In addition, the data indicate that the active site for hexadecane conversion is not a Brønsted acid site that is generated by an interaction with added water. © 1995 Academic Press, Inc.

INTRODUCTION

Ever since Mrs. Fulhame (1) reported the effect of water on the combustion of methane in 1794, the role of water in determining the rate of chemical reactions has been debated. This debate has been prominent in the area of homogenous and heterogeneous catalysis. For example, Beeck (2) reported that it had been conclusively shown that in the cases of a bright platinum filament and a carbon filament, no dehydrogenation of paraffins, olefins, or alcohols takes place unless traces of water are present.

Since the introduction of metal halide catalysts, such as anhydrous aluminum chloride as an acid cracking catalyst, debate has ensued as to whether a co-catalyst, such as HCl or H_2O, is a necessary component and functions as a promoter of catalytic activity (3). This controversy persists even today. Thus, proponents of the co-catalyst view argue that the role of the HCl or H_2O is to convert the Lewis acid to a stronger Brønsted acid:

$$HCl(H_2O) + AlCl_3 \rightleftarrows H^+ \; AlCl_4^- \; (H^+AlCl_3OH^-). \quad [1]$$

This debate also applies to the case of silica–alumina catalysts, for which many claimed that a small amount of water was necessary to attain the maximum catalytic activity. In this case, the presence of water was considered to convert Lewis acid sites into stronger Brønsted acid sites. The search for confirmation of this role for water is illustrated by the studies of Emmett and coworkers (4) to learn whether "added-back" water caused or enhanced hydrocarbon adsorption on a silica–alumina catalyst. The effects of added-back water and the degree of dehydration on catalytic cracking (5–7), catalytic isomerization (7–10), and rate of exchange (8, 10–16) of the hydrogen of hydrocarbons with deuterium on deuterated silica–alumina catalysts have been studied by many investigators. In these reactions, the adding back of a few tenths of a percent of water vapor has been found to have a pronounced accelerating effect on the reaction rate. In an effort to explain the influence of added-back water, MacIver *et al.* (17, 18) employed a radiotracer technique for the measurement of isobutane chemisorption on a silica–alumina catalyst. They found both reversible and irreversible or nonexchangeable (NE) chemisorption; however, they did not observe any appreciable increase in the amount of reversible or total chemisorption as the amount of added-back water was increased.

Larsen and Hall (19) repeated the study of isobutane chemisorption using a circulating system built so that the equilibrium "adsorption–desorption" rates could be measured. They found two kinds of reversible chemisorption, namely a weak chemisorption (Type I) and a strong chemisorption (Type II); they also found a nonexchangeable chemisorption. Type I and NE adsorption were not affected by the added-back water but the Type II adsorption decreased as water was added.

Matsushita and Emmett (4) studied the effects of added-back water on the cracking and isomerization of 2,2,2-trimethylbutane at 162, 180, and 200°C, as well as of 2-methylpentane at 100°C and of *n*-heptane at 200, 250, and 300°C. The optimum amounts of added-back water were in the range of 0.05 to 0.15%; the increase in the rate of cracking at the optimum amounts was usually about fivefold. For the isomerization of 2-methylpentane it was about 22-fold. The radiotracer adsorption experiments

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with n-heptane-1-^{14}C at 10 mm Hg and 110°C confirmed three types of chemisorption, as reported by Larsen and Hall (19). Matsushita and Emmett concluded that the marked enhancement of catalytic cracking and isomerization rates caused by added-back water was not yet completely explained.

One area where the requirement for a co-catalyst is not debated is in the production of "magic acids" or superacids (20). For example, the combination of anhydrous HF and SbF_5 produces a Brønsted acid that is so strong that it can even protonate methane:

$$HF + SbF_5 \rightleftarrows H^+ + SbF_6^- \qquad [2]$$

$$H^+ + SbF_5 + CH_4 \rightleftarrows CH_5^+ + SbF_6^-. \qquad [3]$$

Numerous experimental techniques, including NMR, have provided convincing evidence for the role of the co-catalyst in the above system.

The recent interest in sulfated zirconia as a catalyst arises from claims that it exhibits superacid characteristics (21–26). Many research groups, including ours, have experienced difficulties in their early efforts to produce an active catalyst. One reason that was advanced for the inability to reproduce early work was that the presence of some water is essential to produce a very active catalyst (for example, (27–32)). Thus, we have made an evaluation of the catalytic activity of a Pt–SO_4^{2-}–ZrO_2 catalyst containing increasing amounts of water.

EXPERIMENTAL

Two 1-kg batches of sulfated zirconia were prepared using the same procedure. For the purpose of this discussion, the two batches are designated Zr1 and Zr2. Hydrous zirconia was precipitated from 1.14 liters of a 0.5 M solution, prepared from anhydrous $ZrCl_4$ (Alpha Products), at a pH of 10.5 by rapidly adding 1.4 liters of 15 M NH_4OH while vigorously stirring. The resulting precipitate was washed with water in repeated filtration/reslurrying cycles until a negative test for chloride ions was obtained. A final wash with ethanol was done prior to drying overnight at 120°C. The chloride contents of the last wash water were 3 and 1 ppm for Zr1 and Zr2, respectively. The dried filter cake was ground and redried prior to the addition of the sulfate.

The dried sample was sulfated using 10 ml of 1.0 N H_2SO_4 per gram of sample. The slurry was stirred for 1 h, after which the sulfated zirconia was filtered without further washing. The samples were dried at 120°C for 2 h prior to analysis and the addition of Pt. The sulfur contents of Zr1 and Zr2 after sulfation (no activation) were 3.44 ± 0.02 and 3.86 ± 0.08 wt.%, respectively.

The sulfated zirconia was promoted with platinum using an aqueous solution of chloroplatinic acid (Colonial Metals, Inc.) which contained 0.1008 g Pt/ml. Several preparations of the Pt promoted sulfated zirconia catalysts were made from separate portions of each of the 1-kg batches of the sulfated zirconia. The different Pt promoted catalysts prepared from the two 1-kg batches of SO_4^{2-}/ZrO_2 are designated Zr1A through Zr1P and Zr2A or Zr2B, respectively. The appropriate amount of chloroplatinic acid solution to produce a catalyst which contained 0.6 wt% Pt (typically 50 to 75 g) was added to the sulfated zirconia. The platinum analyses of the catalysts ranged from 0.57 to 0.60 wt.% Pt.

All of the catalyst samples were activated for 2 h in air using a temperature of 725°C, unless stated otherwise, prior to activity testing with n-hexadecane and water. In the activity testing experiments using n-hexadecane, the activated catalyst was placed in a dried reactor directly from the muffle furnace and stored in a desiccator to cool to room temperature (typically 15 min). In the H_2O absorption studies, the activated catalysts were cooled to room temperature in a desiccator, weighed, and placed in the appropriate humidification chamber.

The humidification chambers were a series of desiccators containing different H_2SO_4/H_2O solutions to produce the desired relative humidities. The chambers were equilibrated for 72 h prior to use. The weighed, activated catalysts were placed in the chambers prior to activity testing. The catalyst weight gain was measured after 16 and 22 h of exposure to determine the amount of H_2O adsorbed onto the samples.

The activity testing of the catalyst samples was done in a dried 25-ml batch microautoclave. The reactions were carried out using a temperature of 150°C, a residence time of 15 min, 500 psig H_2 (ambient), and an n-hexadecane (4 g)/catalyst (2 g) ratio of 2. Anhydrous n-hexadecane (Aldrich) was used in all of the activity experiments and was further dried by storing over activated 4-A zeolite. After the catalyst and n-hexadecane were loaded, the batch reactor was purged with H_2 (ultrahigh purity) and then pressurized to 500 psig. The reactor was heated to 150°C in a fluidized sand bath and shaken vertically at 400 cpm for the desired residence time. Typical heatup of the reactor to 150°C occurred within 2 min. After the experiment, the reactor was cooled to room temperature (typically within 1 min) and vented. The reaction products were stored in a freezer prior to analysis.

The liquid products were analyzed using a 60 m × 0.32 mm DB-5 capillary column (0.25 μm thick) installed in a HP 5890 Series II gas chromatograph with FID detectors. Conversion was defined by the disappearance of n-hexadecane in the liquid product samples; thus, conversion includes both isomerization and cracking.

In the deactivation experiments, which required very low concentrations of H_2O to be present, 3-methyl-2-buta-

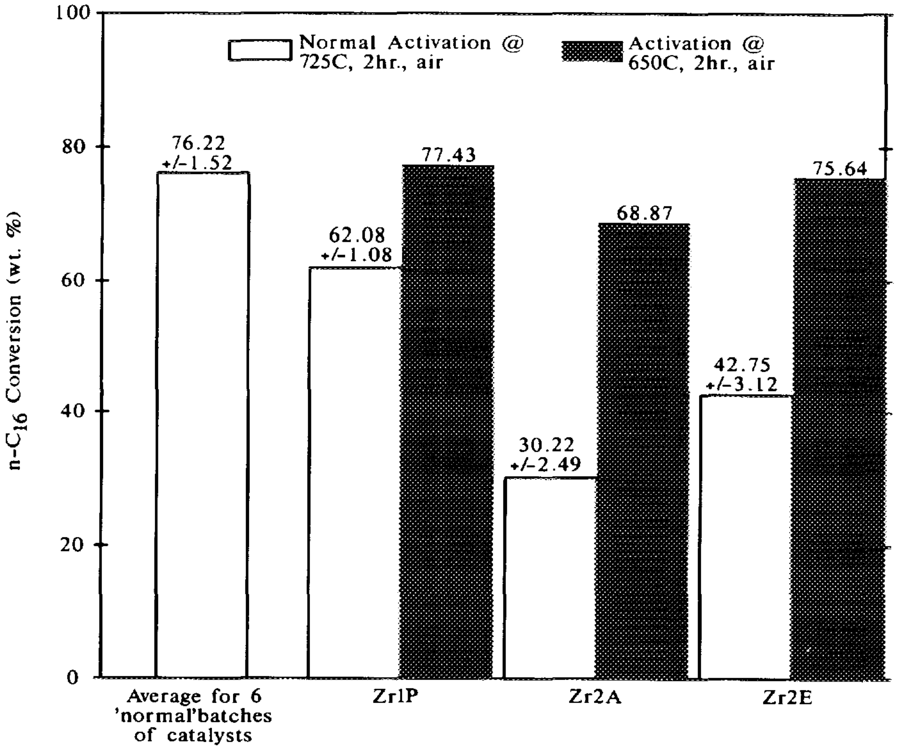


FIG. 1. A comparison of the activity of the two 1-kg batches of SO_4^{2-}-ZrO_2.

nol (Aldrich) was used to generate H_2O during the reaction. The choice of the alcohol was based on the retention time of the 3-methyl-2-butanol on the DB-5 column and on its being easily dehydrated. The elution time of this alcohol did not overlap with the elution times of the cracked and isomerized products derived from the conversion of *n*-hexadecane. Therefore, conversion of the alcohol could be determined. Conversion of the alcohol was defined by the disappearance of the alcohol from the feedstock solution. The feedstock solutions containing the alcohol (0.04–8.71 wt%) and *n*-hexadecane were analyzed prior to the experiments.

RESULTS

The preparation of large (1-kg) batches of sulfated zirconia is complex and it is difficult to obtain repeat batches with identical catalytic activities. For example, several batches (75 to 100 g) of Pt (0.6 wt.%) containing SO_4^{2-} ZrO_2 were prepared from Zr1 and Zr2. Initially, all of the catalysts were activated under the same conditions (725°C for 2 h in air) and activity tested under the same conditions as described under Experimental. The results of the activity testing are shown in Fig. 1. The majority of the catalysts exhibited similar conversions of *n*-hexadecane. However, three of the catalyst batches (Zr1P, Zr2A, Zr2E) had significantly lower conversions under these conditions. All of the activated catalysts had similar sulfur contents (1.00–1.16 wt.%) after activation at 725°C. Subsequent studies at different activation temperatures and times showed that the levels of conversion of the lower activity batches could be restored to levels of conversion similar to those of the "normal" catalyst batches by lowering the temperature of activation to 650°C. One of the lower activity catalysts (Zr2E) was included in this study (activated at 725°C, 2 h, air) to provide a range of catalyst activities in the *in situ* H_2O generation experiments. In addition to the lower activity catalysts, a single batch (Zr1F) activated at 725°C for 2 h in air exhibited significantly higher conversion (92.90 ± 1.92 wt.%). This catalyst was also included in the *in situ* water generation experiments to provide a range of activities. It should be noted that with the exception of the Zr2E and Zr1F catalyst batches described above, all the subsequent experiments were done with a catalyst batch (Zr1N) which was representative of the reproducible series of catalysts produced.

A sample of an activated Pt–ZrO_2 catalyst was exposed to water partial pressure to generate an equilibrium adsorption isotherm (Fig. 2). The isotherm is Type II according to the Brunauer *et al.* classification (33, 34). After 22 h of exposure to a range of water vapor pressures, the activity of these catalysts was determined under standard conditions. These activity measurements clearly show

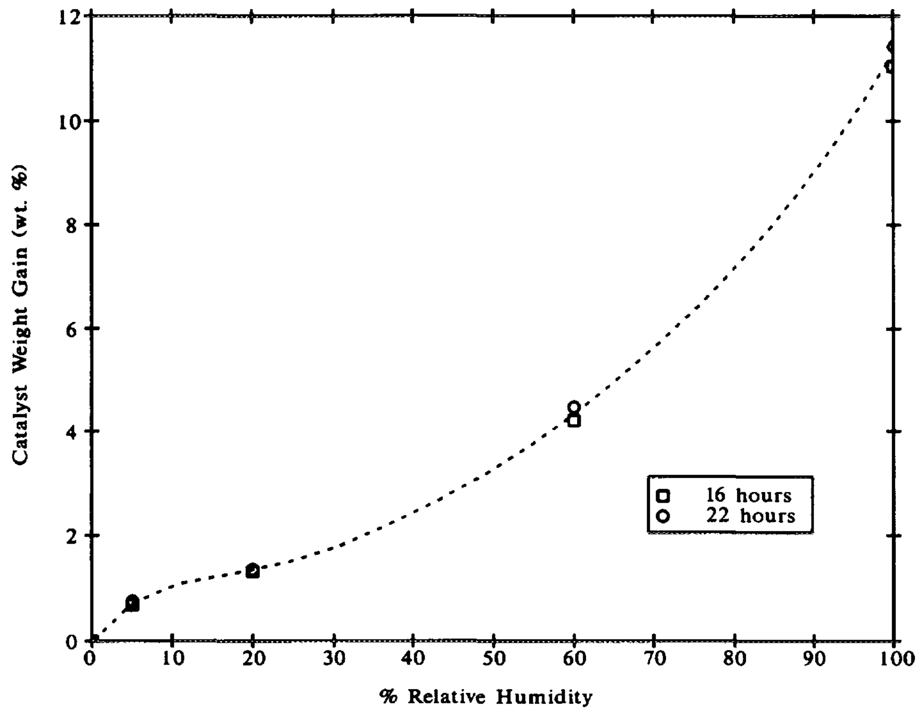


FIG. 2. Catalyst weight gain as a function of relative humidity.

that water is functioning as a catalyst poison rather than as a promoter for all water levels above approximately 0.5 mol of adsorbed water per sulfate molecule in the catalyst (Fig. 3). It was possible that it was the 22-h period allowed for water equilibration, and not the water, that led to the low activity of the catalysts. This was shown not to be the case since the conversion of an activated catalyst that was stored in the reactor at room temperature and under H_2 (500 psig) for 5.23 or 22.28 h had essentially the same activity as the sample that was used for activity

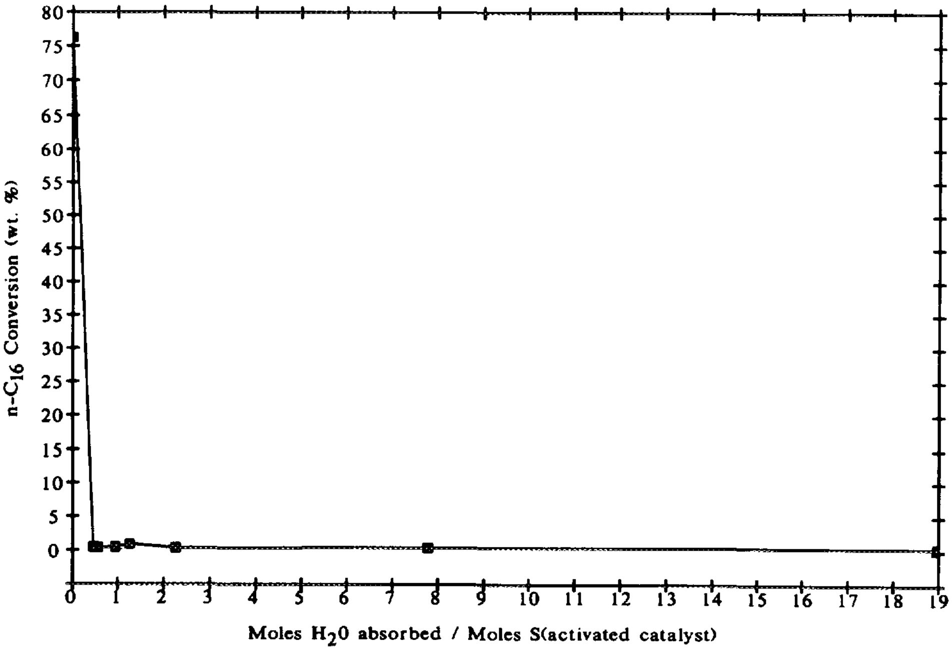


FIG. 3. Conversion of *n*-hexadecane plotted as a function of the moles of H_2O absorbed per mole of sulfur in the activated catalyst.

measurements immediately following the activity step (Fig. 4).

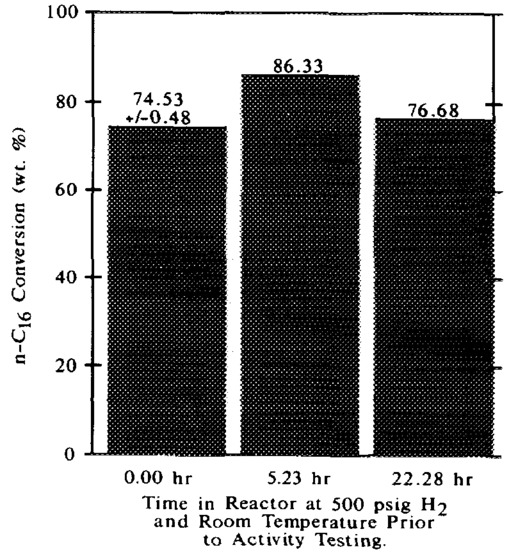


FIG. 4. A comparison of *n*-hexadecane conversions under zero humidity conditions in the reactors under pressure for 5.23 and 22.28 h.

It is difficult to use the concentrated sulfuric acid to obtain the low partial pressures of water that are needed to obtain the low ratios of H_2O/SO_4^{2-}. In fact, it was found that the catalyst sample activated at 725°C for 2 h and then exposed to concentrated sulfuric acid in the desiccator for 24 h had a low activity, similar to those shown for the water-containing samples in Fig. 3. It appeared that the sample could not be maintained in the activated state while being stored for a 24-h period in the evacuated desiccator or a vacuum oven at room temperature (Table 1). Therefore, a method for attaining low levels of H_2O in the reactor was investigated.

To investigate the role of water at low water-to-sulfate ratios, the water was generated *in situ* by the dehydration of 3-methyl-2-butanol. Thus, the appropriate amount of the alcohol was added to *n*-hexadecane to produce various ratios of water/sulfate covering the range from 0 to 1.0. The decline in activity was nearly linear with respect to the water/sulfate ratio (Fig. 5). It was determined that essentially all (95–100%) of the alcohol had been converted during the 15-min reaction time. It is apparent that the conversion decreases more rapidly than would be the case if each sulfate represented an active site that required at least one water molecule per site to eliminate the activity. It is believed that the curvature of the experimental data in Fig. 5 is due to the time needed to completely dehydrate the alcohol as the alcohol/*n*-hexadecane ratio increases. Thus, it is believed that the decline in the activity is actually more rapid than is represented by the experimental data in Fig. 5. The data in Fig. 6 show a similar trend for the impact of water from alcohol on the conversion of *n*-hexadecane for three catalysts. These data show that the influence of water in decreasing the activity of the catalyst for hydrocarbon conversion is not limited to a special catalyst.

DISCUSSION

The nature of the adsorbed water has been investigated using a combined thermal gravimetric/differential scanning/mass spectrometry (TGA/DSC/MS) technique. A catalyst sample, following 2 h calcination at 725°C, was exposed to water vapor for 22 hr to effect saturation. Heating at 20°C/min shows that a significant fraction of the water is retained by the sample (Fig. 7). However, the weight decline due to loss of adsorbed water has been essentially completed by the time the sample has attained 150°C, the temperature of the reaction. Although this heating experiment documents the weakly bonded nature of the adsorbed water, the data were obtained in a flow system where the water is removed from the region of the sample as it is desorbed. In the reactor system, the adsorption/desorption would attain a dynamic equilibrium since water is not removed during the reaction run.

The difference in the amount of water remaining on the sample at 150°C and that lost upon heating to 400°C corresponds to 0.2% of the original sample, or 0.24% based upon the weight of the sample after heating to 150°C. As shown by the traces of the 18 and 34 mass peaks, the weight loss that begins at about 400°C in a hydrogen flow corresponds to the evolution of both H_2O and H_2S. The total weight loss in the 400–700°C temperature range, based upon the weight of the sample heated to 150°C, is 2.42%. This weight loss between 400 and 700°C agrees very well with that expected for a material containing 1 wt.% sulfur and a reaction according to

$$\geqslant\mathrm{Zr{-}O{-}SO_3} + 4\tfrac{1}{2}\,\mathrm{H_2} \longrightarrow \geqslant\mathrm{Zr{-}OH} + 3\mathrm{H_2O} + \mathrm{H_2S}. \quad [4]$$

TABLE 1

The Effect of "Moisture-Free" Atmospheres on Activity

Atmosphere	Exposure time (h)	Catalyst weight gain (wt.%)	*n*-Hexadecane conversion (wt.%)
100% H_2SO_4	22	0.16 ± 0.9	0.53 ± .04
Desiccator	22	0.08 ± 0.9	0.52 ± 0.1
Vacuum oven (21°C)	22	1.78	0.5
Normal experimental procedure	—	—	76.25

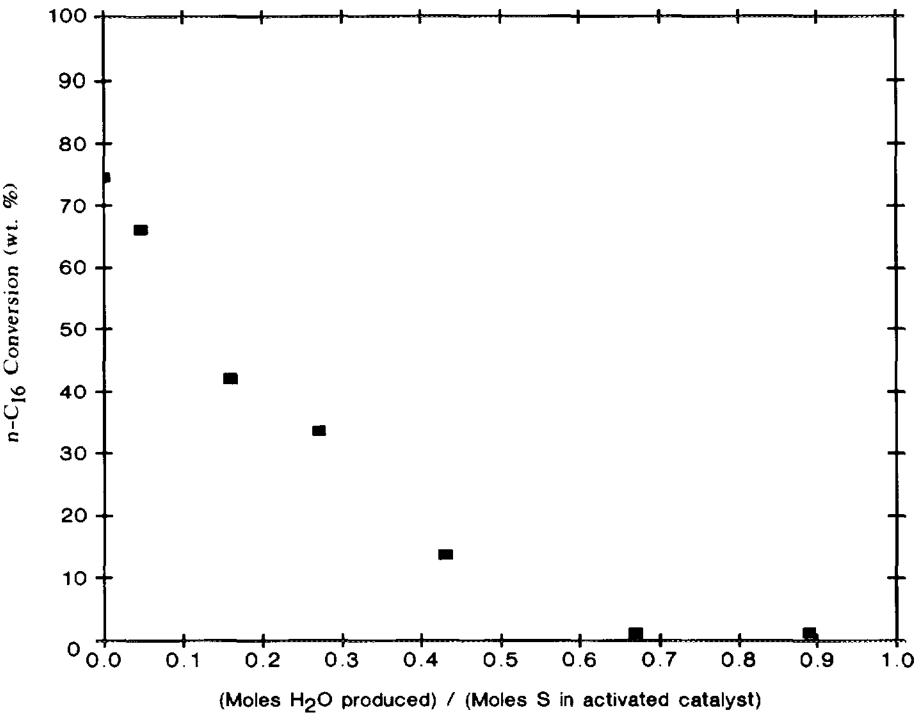


FIG. 5. The conversion of *n*-hexadecane obtained in the *in situ* generation of H_2O experiments.

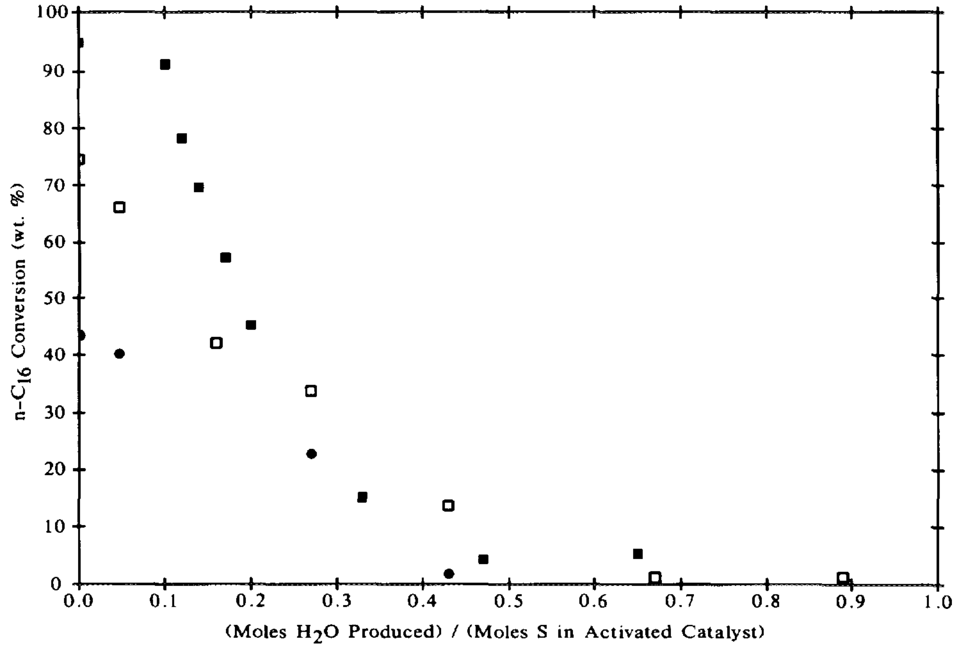


FIG. 6. A comparison of the deactivation of different activity Pt-SO_4^{2-}-ZrO_2 catalysts in the *in situ* H_2O generation experiments (■, Zr1F; □, Zr1W; ●, Zr2E).

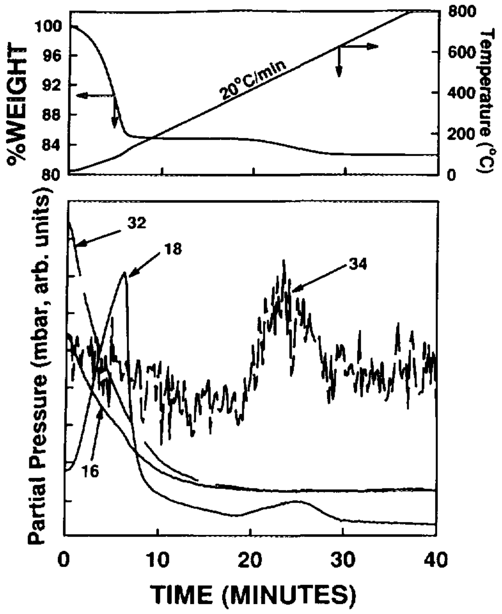
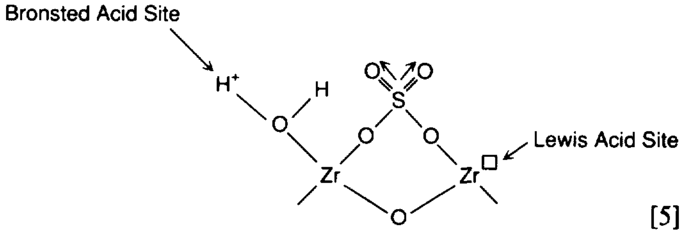


FIG. 7. (Top) Weight loss and temperature profile of a Pt–SO_4^{2-}–ZrO_2 sample activated at 725°C for 2 h and then exposed to a 100% humidity atmosphere for 24 h, when heated in hydrogen. (Bottom) Mass spectrometry traces corresponding to the heating curve in the upper figure for water (18), oxygen (16,32), and H_2S (34) (peaks corresponding to SO and SO_2 (48, 64) were not observed).

Two $\geq$Zr–OH groups may undergo dehydration to produce additional H_2O; however, the weight loss is not dependent on this occurrence. Thus, the TGA/MS data do not provide evidence for the loss of an amount of water above 400°C that corresponds to an amount equal to the SO_4^{2-} present at 400°C.

The decline in activity for the lower ratios of water/sulfate is approximately linear in water concentration. Alcohol dehydration, at higher pressures on metal oxide and silica–alumina catalysts, is a zero order reaction but becomes first order at low partial pressures of alcohol (35, 36). The nearly linear dependence on alcohol (water) concentration, with deviations from this at higher concentrations, is consistent with the alcohol dehydration to produce the water needed to poison the catalytic site being diffusion controlled. Thus, the decline in activity is probably more rapid than is indicated by the data in Fig. 6.

The data in the present study clearly show that water is not a promoter for the development of catalytic acid sites through the interaction of water with the activated catalyst to convert Lewis to Brønsted acid sites to produce the structure that has been represented as (21)



[5]

Thus, the present data indicate that if water is a necessary copromoter it must be retained at the site during 2 h of activation at 725°C or to be reabsorbed during the rapid transfer of the hot (>400°C) sample to a reactor immediately following activation. The data show that the decline in activity is not due to solid-state changes that occur during the 24-h period following activation and must therefore be due to the added water. Furthermore, the activated solid appears to be able to adsorb sufficient water to eliminate the measurable catalytic activity even in the presence of 100% sulfuric acid; this implies that the activated catalyst is a stronger acid, based upon competition for water, than 100% sulfuric acid.

The poisoning data shown in Fig. 6 make it clear that a water molecule eliminates the catalytic activity of more than one site if all sulfate groups serve as sites of equal activity. This type of poisoning could occur if the strengths of the acid sites were heterogeneous and the more active ones were poisoned first. We believe that a more likely explanation is that the sulfate groups are distributed both on the surface and in the bulk of zirconia, and that either the bulk sulfate groups do not generate catalytic sites or, if they do, they are not accessible to the alkane reactant. Thus, the number of sulfate groups that are located upon the surface will depend upon a number of factors such as catalyst preparation and activation. The data in Fig. 6 suggest that only about one-third of the sulfate groups are responsible for the generation of acid sites that are active for the conversion of alkanes under the low temperature conditions used in the present study.

The TGA/MS data obtained previously (37) show that heating the sample in an inert gas results in the loss of water during heating to 400°C. However, while SO_2/SO/O are observed when the sample is heated from 400 to 800°C, no evidence is obtained for the evolution of water that should occur if it were present as shown in the above structure (Eq. [5]). On the other hand, when the activated sample, resaturated with water at 25°C, is heated in hydrogen, the adsorbed water is lost at temperatures less than 400°C. Heating the sample above 400°C in hydrogen results in the loss of both H_2O and H_2S; the weight loss in this region is the amount expected for the loss of SO_3 (as

H_2O and H_2S). It is therefore concluded that insufficient water is present on the catalyst after heating to 725°C, the pretreatment to produce an active catalyst, for the structure shown above (Eq. [5]) to represent all, or even a significant fraction, of the SO_4^{2-} groups that remain in the catalyst.

In summary, it is clear that water does not function as a co-catalyst for the Pt–SO_4^{2-}–ZrO_2 catalyst by a mechanism similar to that envisioned for other superacid systems such as the HF/SbF_5 pair. Furthermore, the data indicate that the site that is the seat of the catalytic activity for hydrocarbon conversion is not a Brønsted acid site generated by an interaction with water with the activated catalyst (38, 39).

ACKNOWLEDGMENTS

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