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Characterization of the Acid Properties of Tungsten/Zirconia Catalysts Using Adsorption Microcalorimetry and *n*-Pentane Isomerization Activity

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Ammonia adsorption microcalorimetry was conducted on various solid acid tungsten/zirconia catalysts prepared by different techniques. The calorimetric data were compared to catalytic test results using *n*-pentane isomerization as a measure of acid activity. The results show that (1) the co-precipitation method of making the tungsten/zirconia catalyst produces a greater number of acidic sites than impregnating tungsten on hydrous zirconia, resulting in a more active catalyst, and (2) the addition of small amounts of iron to the tungsten/zirconia catalyst increases the acid site strength as determined by ammonia adsorption and improves the paraffin isomerization activity. The calorimetry data indicate that the acid site strength of the tungsten/zirconia materials is similar to or slightly higher than that found in zeolites or sulfated zirconia and is comparable to sulfuric acid. However, the paraffin isomerization activity results suggest that the acid sites of the tungsten/zirconia catalyst should be about four orders of magnitude more active than that of zeolite β on the basis of turnover frequency. Our experimental results indicate a lack of correlation between the heat of ammonia adsorption with catalytic activity. Comparisons of catalytic activity between materials based entirely on acid strength may not be valid, and kinetic probes would be more appropriate. © 1999 Academic Press

Key Words: **calorimetry; acid properties; tungsten/zirconia catalyst.**

INTRODUCTION

In the last few years, a great deal of attention has been given to sulfated and tungstated zirconia materials for their remarkable catalytic activity for acid-catalyzed reactions, in particular paraffin isomerization. Despite considerable efforts, not only is the nature of the acid sites on these materials still in dispute but the many investigations that have measured the Brønsted acid strength of these materials have produced varying results. The direct measurement of the strength of a solid acid is not as straightforward as in a liquid acid. Issues such as heterogeneity of the surface and accessibility of acid sites make the determination of acid strength of solid acids difficult. In addition, it has been demonstrated that in the case of WO_x/ZrO_2 catalysts, the density of strong acid sites responsible for their remarkable catalytic activity is extremely low, $\sim$4 μmol H^+/g catalyst (1). This low density of sites causes difficulties in the characterization of the sites relevant to catalysis.

Typically, the acid strength of a solid catalyst is measured from the interaction of the acid site with a probe base. This interaction could involve the formation of a complex between the acidic hydrogen on the catalyst surface and a base. The strength of this hydrogen bonding, which is usually determined by spectroscopic techniques (IR, NMR, EPR), temperature-programmed desorption, microcalorimetry, or Hammett indicators, is taken as a measure of the site strength of the acid in question (2–5). The acid strength determined by these methods is then correlated to catalytic activity. The generality of this approach is usually assumed. However, Farcasiu and Hancu (6) recently described examples of acid-catalyzed reactions where no apparent correlation exists between the hydrogen bond donor ability and the acid strength, as measured by catalytic activity. From their experimental work, they concluded that a direct correlation among the above properties is possible "only when each group (acid and bases) involved in the comparison consists of very close structural relatives."

In the present work, we compare ammonia adsorption microcalorimetry data and paraffin isomerization activity of WO_x/ZrO_2 catalysts prepared by several methods. Our experimental results indicate a lack of correlation between the heat of ammonia adsorption and catalytic activity, consistent with the ideas proposed by Farcasiu and Hancu (6).

EXPERIMENTAL PROCEDURE

WO_x/ZrO_2 Prepared by Impregnation—W/Zr-IM

This catalyst was prepared according to the procedure given by Arata and Hino (7, 8). Briefly, $Zr(OH)_4$ was

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TABLE 1

Elemental Analyses and BET Surface Areas of WO_x/ZrO_2 Catalysts

Catalyst:	W/Zr-IM	W/Zr-Cop	Fe/W/Zr-Cop
Elemental analysis (wt%)			
Fe	—	—	0.72
W	15.0	15.9	14.8
Zr	63.2	58.6	54.5
Ash (1000°C)	—	100	96.7
Surface area (m^2/g), calcined at 830°C	31	62	63
Crystalline phase of zirconia calcined at 830°C	Primarily tetragonal	Tetragonal	Tetragonal

prepared by dissolving 300 g zirconyl chloride [$ZrOCl_2 \cdot 8H_2O$, Aldrich] in 4.5 liters distilled, deionized water. A 10 M NH_4OH solution was added to precipitate the $Zr(OH)_4$. The final pH of the mixture was approximately 9. The precipitate was filtered and washed with distilled water, and then dried overnight at 85°C. $Zr(OH)_4$ was impregnated, using incipient wetness impregnation, with an ammonium metatungstate [$(NH_4)_6H_2W_{12}O_{40} \cdot nH_2O$, Aldrich, 66.9% tungsten] solution, to a 15 wt% tungsten target loading. The resulting material was air dried overnight at 85°C, and then calcined at 830°C in flowing dry air for 3 h. The elemental analyses and physical properties are shown in Table 1.

WO_x/ZrO_2 Prepared by Co-precipitation—W/Zr-Cop

Five hundred grams $ZrOCl_2 \cdot 8H_2O$ was dissolved by stirring in 7 liters distilled water. A solution containing 263 g concentrated NH_4OH, 500 ml distilled H_2O, and 54 g $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ was added dropwise over a 30–45 min period. The pH of the final composite was adjusted to approximately 9 by the addition of concentrated ammonium hydroxide. The synthesis composition, in terms of the Zr/W molar ratios, was 7.1/1. This slurry was then put in polypropylene bottles and placed in a steambox (100°C) for 72 h. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. Two samples of this catalyst were calcined in flowing air for 3 h, one at 700°C and the other at 830°C. The elemental analyses and physical properties are shown in Table 1.

WO_x/ZrO_2 Prepared by Co-precipitation Containing Iron—Fe/W/Zr-Cop

Five hundred grams $ZrOCl_2 \cdot 8H_2O$ was dissolved by stirring in 6.5 liters distilled water. To this solution was added a mixture of 500 ml distilled water and 7.5 g $FeSO_4 \cdot 7H_2O$. Finally, a solution containing 263 g conc. NH_4OH, 500 ml distilled H_2O, and 54 g $(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$ was added dropwise to the iron/zirconium solution over a 30–45 min period. The pH of the final composite was adjusted to approximately 9 by the addition of concentrated ammonium hydroxide. The synthesis composition, in terms of the Zr/W/Fe molar ratios was 7.1/1/0.12. This slurry was then put in polypropylene bottles and placed in a steambox (100°C) for 72 h. The product formed was recovered by filtration, washed with excess water, and dried overnight at 85°C. A sample of this catalyst was calcined at 830°C in flowing air for 3 h. The elemental analyses and physical properties are shown in Table 1.

The zeolite β ($SiO_2/Al_2O_3 = 35/1$) preparation procedure is described elsewhere (9). The sample was converted to the proton (H-β) form using standard procedures.

Characterization

Powder X-ray diffraction spectra were collected on a Scintag XDS 2000 diffractometer using Cu $K\alpha$ radiation. Surface areas were determined by a multipoint BET measurement using nitrogen adsorption. Chemical analysis of the samples was carried out at Galbraith Laboratories, Knoxville, TN.

Catalyst Testing

n-Pentane isomerization was used as a catalytic test of the acid activity of the various catalyst samples. The catalytic testing was carried out in a down-flow fixed-bed stainless steel reactor. Catalyst samples were crushed and sieved to retain 14/30 mesh particle size. The catalyst was positioned in the central region of the reactor between two layers of sand (Fischer) and calcined at 500°C in flowing dry air for 1 h at atmospheric pressure to remove adsorbed water and/or adventitious carbon. After catalyst pretreatment, the reactor was cooled to ambient temperature and the unit was pressurized with hydrogen (Matheson, UHP) to 350 psig. *n*-Pentane (Aldrich, >99%) was fed into the reactor using a high-pressure ISCO pump. Hydrogen and *n*-pentane flow rates were adjusted to give a 2 $H_2/n\text{-}C_5$ mole ratio. The temperature was then gradually increased to the desired operating temperature. After a Grove Loader back pressure controller, the reactor effluent was diluted with nitrogen, and the combined stream was sent to an on-line gas chromatograph (GC) for analysis. A fused silica capillary column (DB-1, 60 m) run isothermally at 20°C was used to determine product composition. Heating and insulating tapes were wrapped around the stainless steel exit lines connected to the gas chromatograph to maintain the temperature about 150°C to avoid condensation of the reaction products. The results are shown in Table 2.

Isomerization forward areal rate constants were calculated assuming a first-order reversible reaction and are reported as molecules of *n*-pentane isomerized per unit surface area per unit time. Liquid hourly space velocity

TABLE 2

n-Pentane Conversion over WO_x/ZrO_2 Catalysts at 190°C and 210°C, 2 H_2/n-C_5 Molar Ratio, 2 LHSV, and 350 psig

Catalyst:	W/Zr-IM	W/Zr-Cop	W/Zr-Cop	Fe-W/Zr-Cop
Calcination temperature (°C)	830	700	830	830
BET surface area (m^2/g)	32	—	62	62
Catalyst weight (g)	6.2	4.8	4.8	4.7
Catalyst vol. (ml) (14/30 mesh)	4.0	4.0	4.0	4.0
LHSV	2.0	2.0	2.0	2.0
WHSV	0.81	1.04	1.04	1.07
Pentane Conv. Temp. (°C)	220	220	220	190
Prod. Dist. (mol%)				
$C_1 + C_2$	0.26	0.05	1.25	0.05
C_3H_8	0.20	0.05	0.72	0.40
i-C_4H_{10}	0.77	0.02	3.67	1.20
n-C_4H_{10}	0.12	—	0.27	0.30
i-C_5H_{12}	55.7	11.6	68.3	70.5
n-C_5H_{12}	42.1	88.1	25.2	25.8
C_6	0.85	0.20	0.63	1.40
i-C_5/total C_5 (%)	56.9	11.9	73.1	73.2
Total cracking products C_4- (mol%)	0.93	0.12	5.91	2.38
$k_v = (\mathrm{LHSV})(X_e)[-\ln(1-X/X_e)]$	2.16	0.26	6.22	5.28
$k_w = (\mathrm{WHSV})(X_e)[-\ln(1-X/X_e)]$	0.88	0.13	3.24	2.82

Note. X_e (210°C) = 0.742. X_e (190°C) = 0.755.

(LHSV) is defined as the volume of n-pentane (ml) contacting a given volume of catalyst (ml) in 1 h at STP. Likewise, weight hourly space velocity (WHSV) is defined as the weight of n-pentane (g) contacting a given catalyst weight (g) in 1 h.

Adsorption Microcalorimetry Procedure

A schematic representation of the microcalorimetry system is depicted in Fig. 1. It consists of a Setaram C80D heat-flow microcalorimeter of the Calvet type with a sensitivity of 0.1 mW, connected to a stainless steel, calibrated, volumetric system. Pressures are measured by means of either a MKS Baratron Model 615 AD capacitance manometer for pressures between 1×10^{-5} and 10 Torr (1 Torr = 133.3 Pa) or a MKS Baratron Model 590 HA capacitance manometer for pressures between 1×10^{-3} and 1000 Torr. The entire calorimetric system is thermally insulated. The temperature of the volumetric system is kept constant at 72°C by using an Omega temperature controller. The temperatures of the cells (matched sample and reference cells) and dosing volume are measured using a pair of precision Platinum Resistance Temperature Devices (RTD). The dosing volume is attached to a diffusion-pumped glass vacuum system with an ultimate dynamic pressure of 4×10^{-7} Torr and to a gas handling and purification system.

Between 700 and 1000 mg catalyst was placed in the sample cell and the cells were slowly evacuated. Following this initial evacuation the catalyst was pretreated at 500°C for 1 h in about 500 Torr static oxygen; then the cells were evacuated. This procedure was repeated to ensure that none of the acid sites were blocked by coke. The oxygen was purified by passage through a molecular sieve (3A) trap at 203°K. To address the possibility that active sites for isomerization may be generated under a reducing atmosphere, an additional calorimetric run was conducted on a reduced sample of W/Zr-Cop. For this experiment, after the oxidation procedure, the cells were evacuated before the sample was exposed to 500 Torr static hydrogen at 500°C for 1 h. This was followed by evacuation and the procedure was repeated. The hydrogen was purified by passage through a molecular sieve (3A) trap at 77°K.

After sample activation, the sample was cooled under dynamic vacuum to room temperature. The calorimeter was lifted by a jack to enclose the cells, and the sample was evacuated overnight to allow the system to reach thermal equilibrium at 150°C. Argon was subsequently used to determine the dead volume of the cells.

The ammonia (anhydrous grade, 99.99% purity) used in these studies was purified with a freeze–pump–thaw technique before each run. The ammonia reservoir was kept at 195°K to control the vapor pressure at approximately 4.9 kPa. A known amount of the base (between 1 and 4 μmol) was placed in the calibrated dosing volume. When the pressure in the dosing volume was stable, the probe molecule was dosed into the calorimeter cells, one cell containing the sample, the other serving as a reference. The heat released upon dosing with the base was detected by the calorimeter. The signal from the calorimeter was sent to a strip-chart recorder and to a National Instruments LC analog-to-digital interface. The signal from the calorimeter amplifier, as well as the pressure and dosing volume temperature, was fed to an Apple Macintosh LCII computer.

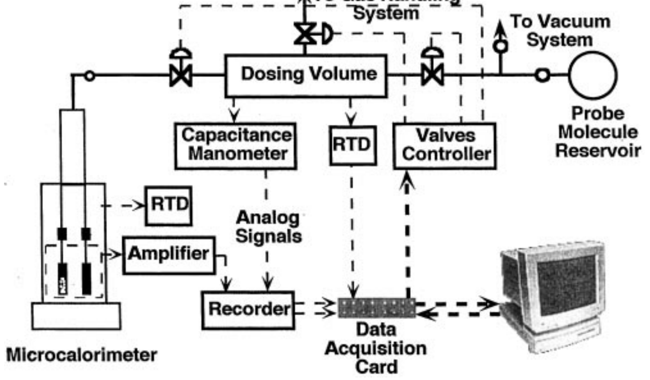

FIG. 1. Schematic representation of microcalorimetric apparatus.

The computer was programmed to integrate the area under the thermogram, calculate the amount of ammonia adsorbed during the dose (Δn), calculate the integral heat of adsorption (Q), and determine the differential heat of adsorption per mole of adsorbed ammonia ($\Delta Q/\Delta n$). The processing of these data provides a complete characterization of the adsorption process. Integral heat and volumetric isotherms give the total heat and total adsorption, respectively, as a function of pressure. Integral heats, Q, as a function of coverage, indicate the overall acid strength of the system. Differential heats of adsorption as a function of coverage provide a description of the acid strength distribution over the surface of the catalyst. When equilibrium conditions were attained after a dose, that is, constant pressure and no deviations from the calorimetric base line, the cells were isolated and the dosing volume was evacuated to decrease the amount of air admitted to the system through small leaks. The above procedure was followed repeatedly. A typical adsorption isotherm was built sequentially from approximately 15 to 60 consecutive doses in 2 to 6 days.

EXPERIMENTAL RESULTS

Table 1 illustrates the elemental analyses and surface area of the WO_x/ZrO_2 catalysts prepared by the different methods. The results in Table 1 indicate that catalysts W/Zr-Cop and Fe/W/Zr-Cop exhibit a surface area of 62 m^2/g compared to 32 m^2/g for the W/Zr-IM catalyst.

Structure determinations of the WO_x/ZrO_2 catalysts were made by X-ray powder diffraction. The results presented in Table 1 indicate that the W/Zr-IM catalyst calcined at 830°C contains primarily tetragonal zirconia with some monoclinic phase. There was also an indication of some WO_3 present. For W/Zr-Cop and Fe/W/Zr-Cop catalysts, only the tetragonal zirconia phase was present; there was no indication of WO_3. The results suggest that the tungsten oxide species in the W/Zr-Cop or Fe/W/Zr-Cop material exist mainly in an amorphous, noncrystalline state or as small crystallites of $\leq$5-nm diameter.

n-Pentane Isomerization

Isomerization of *n*-pentane to isopentane was chosen as a test reaction to determine the relative acid activity of the different WO_x/ZrO_2 catalysts. Total product distribution and isomerization rates obtained over these catalysts are given in Table 2. No catalyst deactivation was observed during the 2–3 day test period. The data presented in Table 2 were obtained after approximately 40 h on stream. The isomerization data were interpreted kinetically in terms of a reversible first-order reaction, for which the integrated rate expression is

$$-\ln(1 - X/X_e) = k_A(t/X_e) \quad \text{or}$$

$$k_A = (1/t)(X_e)[-\ln(1 - X/X_e)],$$

where

X_e = equilibrium conversion

$1/t$ = superficial space velocity = molecules of n-C_5 feed/cm^2 of catalyst per s

k_A = forward areal rate constant = molecules of n-C_5 isomerized/cm^2 of catalyst per s

The calculated equilibrium conversions at 210°C (74.2% i-C_5/total C_5) and at 190°C (75.5%) are in agreement with those reported by others (10).

For practical purposes, forward isomerization rates based on mass (k_w) and volume (k_v) are given in Table 2. Units for k_w are g *n*-pentane per g catalyst per h, and for k_v, the units are cc *n*-pentane per cc catalyst per h.

Comparison of the forward areal rate constants (k_A), defined as molecules of *n*-pentane isomerized per unit surface area per s (11), among the catalysts indicates that the acid site density of the W/Zr-Cop, is at least two times higher than that of the W/Zr-IM catalyst (Table 2). Notice that the % i-C_5/total C_5 value of the W/Zr-Cop catalyst is very close to equilibrium, and one could argue that the activity of the catalyst as estimated by the forward isomerization rate constant may be underestimated. We propose that the higher acid site density of the W/Zr-Cop material is due to a larger number of tungstate ions interacting with the hydroxyl groups of the $Zr(OH)_4$ formed during the coprecipitation step (1).

The higher acid activity of the W/Zr-Cop material is also reflected in the formation of higher amounts of cracked products, C_4-. It is worthwhile to mention that the cracked product distribution indicates that these products are mainly formed via oligomerization–β scission processes involving carbenium ion chemistry, i.e., acid catalysis. This is reflected, for example, by the higher selectivity of isobutane compared to *n*-butane since carbenium ion chemistry favors the formation of tertiary fragments, precursors of isobutane, over the formation of secondary or primary ion fragments, precursors of *n*-butane (12, 13). In addition, the moles of butanes formed exceed those of methane, the other expected product of direct pentane cracking.

Also shown in Table 2 is the effect of calcination temperature on the isomerization activity of the W/Zr-Cop catalyst. The W/Zr-Cop catalyst exhibited little catalytic activity when calcined at 700°C compared to near equilibrium conversion when calcined at 830°C.

We also show the isomerization results of Fe/W/Zr-Cop (calcined at 830°C). These evaluations were conducted at 190°C due to the higher isomerization activity of the catalyst compared to W/Zr-IM and W/Zr-Cop. Fe/W/Zr-Cop, calcined at 700°C, was not very active for pentane isomerization, exhibiting a pentane conversion to isopentane of approximately 12%, comparable to the results shown in Table 2 for the W/Zr-Cop catalyst.

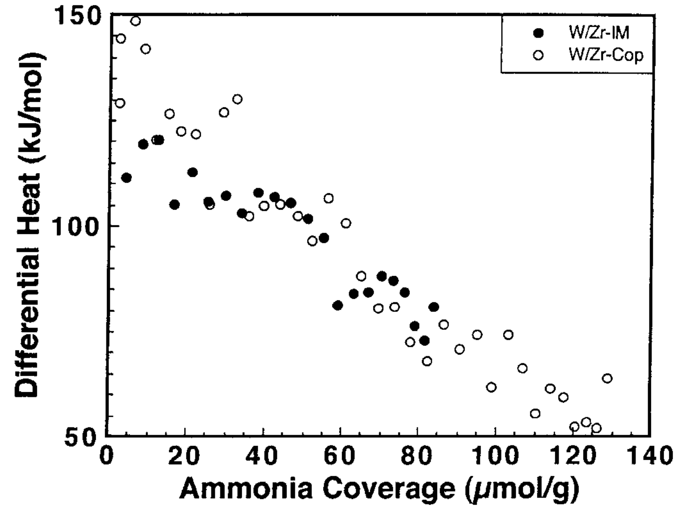

FIG. 2. Differential heat of ammonia adsorption at 150°C on W/Zr-IM calcined at 830°C (●) and W/Zr-Cop calcined at 830°C (○).

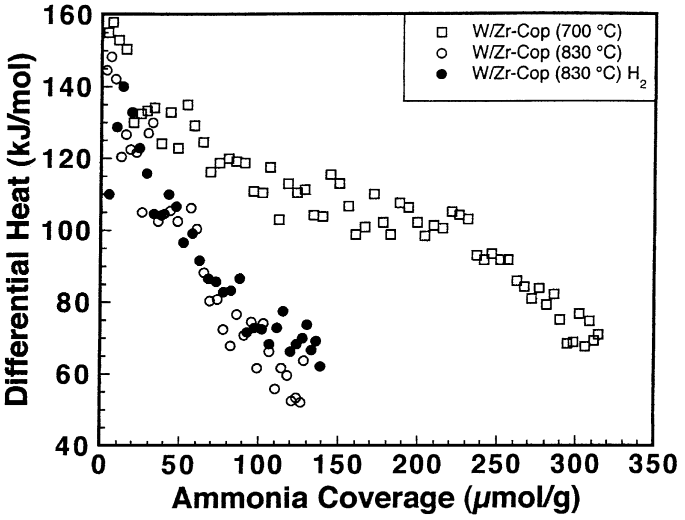

FIG. 3. Differential heat of ammonia adsorption at 150°C on W/Zr-Cop, (□) calcined at 700°C, (○) calcined at 830°C, and (●) calcined at 830°C and then reduced in hydrogen at 500°C.

Microcalorimetry Results

The adsorption microcalorimetry results are depicted in Figs. 2 through 5 and summarized in Table 3. Note that in this table we have defined the total acidity as the coverage when the differential heat drops to 70 kJ/mol. We chose this value because it is the differential heat of ammonia adsorbed at 150°C on silica (14). The differential heats of ammonia adsorption for the W/Zr-IM and W/Zr-Cop samples calcined at 830°C are shown in Fig. 2. The total number of acid sites for both samples is about the same, but the coprecipitation method of preparing the WO_x/ZrO_2 catalyst increases the initial heat of adsorption from about 120 to 148 kJ/mol. About 30 μmol/g acid sites increase their strength from about 105–120 kJ/mol to 120–148 kJ/mol. Within that range the average integral heat increases from 113 to 128 kJ/mol. The overall average integral heat increases from about 99 to 102 kJ/mol. Prereducing the W/Zr-Cop catalyst did not cause a significant change in the acid strength distribution as shown in Fig. 3. There is only a slight increase in the total number of acid sites and a small decrease of the initial heat. Lowering the calcination temperature to 700°C, however, causes a major change in the acid strength distribution as shown in Fig. 3. There is a marked increase in both the acid strength and total acidity. More than 230 μmol/g acid sites have heats of adsorption between 100 and 155 kJ/mol. Also the total acidity increases to almost 310 μmol/g, while the overall average integral heat of adsorption increases to 107 kJ/mol.

Adding iron to the WO_x/ZrO_2 catalyst (Fe/W/Zr-Cop), calcined at 830°C, increases the acid strength of all sites present on the catalyst as compared to the W/Zr-Cop (iron-free WO_x/ZrO_2 catalyst) also calcined at 830°C as shown in Fig. 4. The initial heat of adsorption increases to about 170 kJ/mol, the total acidity to 118 μmol/g, and the average integral heat of adsorption to 112 kJ/mol.

TABLE 3

Summary of Calorimetry Results

Catalyst (calcination, °C)	Initial heat (kJ/mol)	Total acidity[a] (μmol/g)	Average integral heat[b] (kJ/mol)	Acidity with $q > 140$ kJ/mol (umol/g)	Acidity with $q > 120$ kJ/mol (umol/g)
W/Zr-IM (830°C)	120	~90	99	0	12
W/Zr-Cop (830°C)	148	93	102	8.7	30
W/Zr-Cop (830°C) H_2	140	118	96	14	25
Fe/W/Zr-Cop (830°C)	170	118	112	24	59
W/Zr-Cop (700°C)	155	308	107	16	80
Zeolite β	146	568	100	16	97

[a] Coverage when differential heat drops to 70 kJ/mol.

[b] Average integral heat of ammonia adsorption when differential heat of adsorption decreases to 70 kJ/mol. $\{q_{av} = Q_{95}/n_{95}\}$.

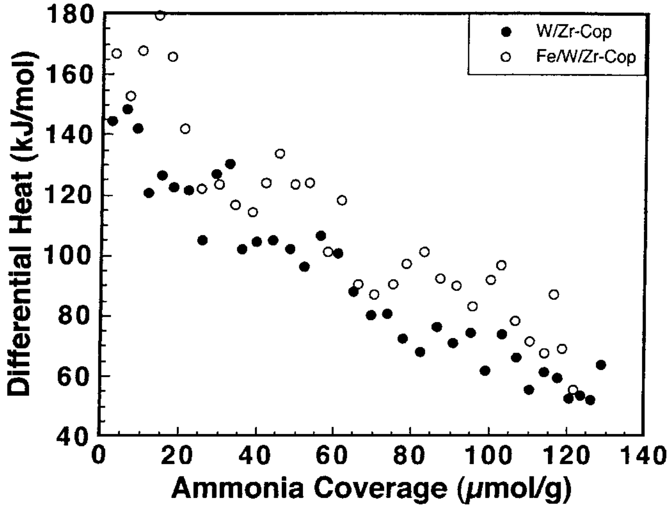

FIG. 4. Differential heat of ammonia adsorption at 150°C on W/Zr-Cop and on Fe/W/Zr-Cop calcined at 830°C.

The highest initial differential heats of ammonia adsorption found for all of these tungsten/zirconia catalysts are consistent with the range of values reported in the literature for zeolites and are slightly higher than the highest heats reported for sulfated zirconia (15–20). In addition, Adena *et al.*, based on NMR and FTIR studies, concluded that sulfated zirconia and iron-promoted sulfated zirconia did not exhibit superacidity (19). In fact, the authors concluded that the sites were less acidic than those of HZSM-5 and HY. A comparison of the acid strength for zeolite β and the W/Zr-Cop catalyst calcined at 700°C is given in Fig. 5. The total acidity of the zeolite β is the highest among all samples studied. The initial heat of adsorption for zeolite β is about the same as that for W/Zr-Cop calcined at 830°C, is higher than the initial heat found for W/Zr-IM, and is lower than the initial heats for the Fe/W/Zr-Cop sample. Therefore, the addition of iron to the WO$_x$/ZrO$_2$ catalyst appears to generate stronger acid sites as determined by calorimetry than those present in zeolite β and on sulfated zirconia.

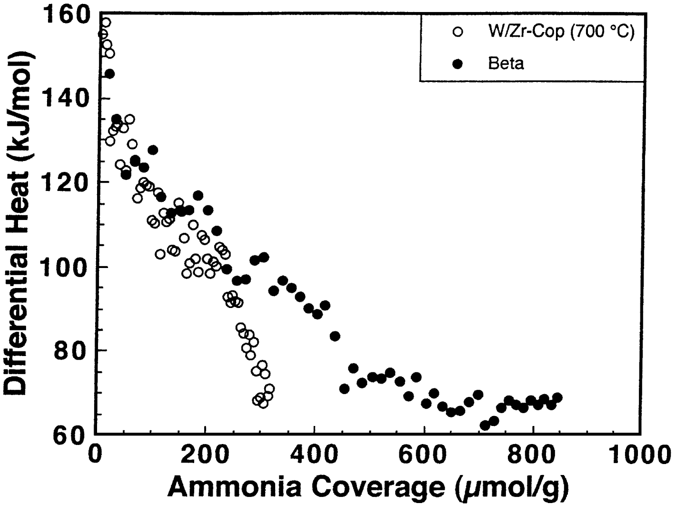

FIG. 5. Differential heat of ammonia adsorption at 150°C on W/Zr-Cop calcined at 700°C (○) and on the hydrogen form of zeolite β (●).

DISCUSSION

The question arises, How do we explain the apparent difference between the catalytic activity of these zirconia-based catalysts for paraffin isomerization and the calorimetric determination of the stength of the acidic sites? Earlier work indicated that zeolite β ($SiO_2/Al_2O_3 = 35$) is not active for *n*-pentane isomerization at 210°C, with only about 1 wt% isopentane obtained (1). Even at 260°C the isopentane yield is a fraction of that obtained over the WO$_x$/ZrO$_2$ catalyst at 210°C. On the basis of turnover frequency, these results implied that the acid sites on WO$_x$/ZrO$_2$ are about four orders of magnitude more active than those sites present in the zeolite β for paraffin isomerization (1).

In our earlier study it was found, using catalytic titration experiments, that the W/Zr-Cop catalyst calcined at 830°C has about 4.2 μmol/g strong Brønsted sites that appear to be active sites for paraffin isomerization (1). A complementary result using XPS of chemisorbed 2,6-dimethylpyridine and pyridine indicated that the W/Zr-Cop catalyst had about 13 μmol/g Lewis acid sites and 11 μmol/g strong Brønsted sites. Let us assume that the number of strong Brønsted sites and Lewis sites is about the same and that they correspond to the strongest sites on the sample. Based on the results from the catalytic titration experiments and the microcalorimetry results for W/Zr-Cop calcined at 830°C, these sites have heats higher than 140 kJ/mol while, based on the results from the XPS, the sites would have heats higher than 120 kJ/mol. Note in Fig. 2 that at about 10 μmol/g, the differential heat of adsorption drops from about 142 to 125 kJ/mol, probably indicating the presence of a significantly different acid site at higher ammonia coverages. The coverage where this happens is close to twice the number of strong Brønsted sites that are found using catalytic titration. Using the heats determined above, we summarize the corresponding coverages for all samples studied in Table 3. For zeolite β, if we assume that the sites with heats higher than 140 kJ/mol are the active sites for paraffin isomerization, the turnover frequency at 210°C would be 4.9×10^{-3} molecules converted per active site per s. Thus the sites present on W/Zr-Cop are about 800 times more active than on zeolite β.

The calorimetric results suggest an activity difference (based on the number of strong acid sites) of about two to three orders of magnitude between zeolite β and the W/Zr-Cop catalyst. The isomerization activity data suggest that this difference is closer to four orders of magnitude (based on turnover frequency). However, the calorimetric data also suggest that W/Zr-Cop calcined at 700°C should be more active than W/Zr-Cop calcined at 830°C (see Table 3) and that W/Zr-IM should be much less active. The catalytic data presented in Table 2 indicate just the opposite. This difference can not be explained by the acid strength or number and might be related to a difference in chemistry. That is, we need to identify which are the active sites and determine their concentration.

If we accept the Hammett acidity value ($Ho < -14.52$) for activated WO_x/ZrO_2 given by Hino and Arata (7), this difference in activity would imply that the acidity of zeolite β is similar to ~90% H_2SO_4. This is in general accord with the ranking of solid acids devised by Haw *et al.*, based on the acid strength of carbocations and other electrophiles in various media (21). It should be noted, however, that in the case of sulfated zirconia, which also catalyzes *n*-alkane isomerization, there is increasing evidence that its acidity does not exceed that of 100% H_2SO_4 (22, 23). This of course assumes a simple relationship between catalyst Brønsted acidity and paraffin isomerization rate, such as that expressed by the classic Brønsted law. However, the present microcalorimetry results suggest a more complicated picture, at least for catalysts such as tungsten/zirconia. Others have commented on the problematic nature of the relationship between acid strength and catalytic activity (24, 25). The problems associated with the use of Hammett indicators on solids are well known and will not be further discussed. On the catalyst surface, acid sites may have a distribution of strengths and some sites may be irrelevant to the reaction in question. Another possibility is that we are measuring the acid strength of the surface sites with the wrong probe molecule. Perhaps ammonia is too strong a base to differentiate the sites responsible for paraffin isomerization activity. Recently, Han *et al.* suggested another probe molecule, diethyl ether, for evaluating the acid properties of these mixed metal oxides (26). The reaction mechanism must also be considered. If the rate-limiting step is hydride transfer and not protonation, then Lewis sites or other mediators may be implicated (27). For tungsten/zirconia or any catalyst with a reducible component, one-electron transfers generating radical cations, and then olefins which would be rapidly protonated, cannot be discounted (28). The reaction may proceed through a cationic chain mechanism where an initiation step is followed by bimolecular hydride transfer. Over sulfated zirconia, other researchers have suggested that the isomerization of butane involves the formation of olefins in the initial step (16, 29). From these considerations, we submit that use of kinetic probes, rather than other acid-strength scales, is more appropriate when comparing the acid strength of different materials.

CONCLUSION

The study of acid activity of WO_x/ZrO_2 solid acid catalysts as a function of preparation method indicated several key findings. Preparing WO_x/ZrO_2 catalyst by the simultaneous co-precipitation of tungsten with the formation of hydrous zirconia yielded a catalyst with a higher strong acid site density as compared to WO_x/ZrO_2 catalysts prepared by impregnation. The calorimetry results are consistent with catalytic data on this point. W/Zr-Cop and Fe/W/Zr-Cop catalysts contained more strongly acidic sites than the catalyst prepared via impregnation (W/Zr-IM). The addition of small amounts of iron (Fe/W/Zr-Cop) to the tungsten/zirconia catalyst increases the acid site strength and produces a more active paraffin isomerization catalyst. The calorimetry data indicates that the acid site strength of the tungsten/zirconia materials is similar to or slightly higher than that found in zeolites or sulfated zirconia and is comparable to sulfuric acid. However, in the case of pentane isomerization, the W/Zr catalysts are about four orders of magnitude more active than zeolitic acid sites based on turnover frequency. We conclude that comparisons of catalytic activity between materials based entirely on acid strength may not be valid and that kinetic probes would be more appropriate.

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