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Microcalorimetric and Catalytic Studies on Sulfated Zirconia Catalysts of Different Preparations

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Sulfated and metal ion-promoted sulfated zirconia were synthesized by freeze-drying as well as by conventional and aerogel synthesis. The acidity of the samples was studied by means of microcalorimetry; the catalytic performance of the samples was evaluated in the reaction between benzoic anhydride and anisole at 50°C and RT. Supercritical drying and freeze-drying gave access to sulfated zirconia with large pore diameters and pore volumes. As a result, high conversions in the Friedel–Crafts acylation were observed; a further increase in activity was achieved by metal ion promotion. The results of the benzoylation reaction were related to data from microcalorimetric experiments. The adsorption was performed not only with ammonia and pyridine in the gas phase, but also with a mixture of pyridine in anisole, much more consistent with the catalysis conditions. Only from the latter experiments, the higher catalytic performance of cryogel and aerogel samples was confirmed. Therefore, using such liquid mixtures might be a suitable method to distinguish between good acylation catalysts and less active samples. © 2001 Academic Press

Key Words: **sulfated zirconia; microcalorimetry; catalysis; freeze-drying; cryogel; aerogel; benzoylation.**

1. INTRODUCTION

Sulfated zirconia (SZ) and metal ion-promoted SZ have attracted considerable interest (1–11). They are recognized as very strong acids and possess all the advantages of heterogeneous catalysts. These oxidic materials can be employed in the skeletal isomerization of light paraffins as well as in other acid-catalyzed reactions like alkylation (12), nitration (13), acylation (14, 15), or selective catalytic reduction of NO with propane (16, 17). Friedel–Crafts acylation, for example, is commonly catalyzed by $AlCl_3$, but SZ and promoted SZ can be used with success, too. In hydrocarbon chemistry, especially iron and manganese-promoted SZ (FMSZ) is known for having catalytic activities 2–3 times higher than those of unpromoted SZ. The enhancement in activity was ascribed not to a higher acidity but to redox effects of the metallic dopants. However, this point is still under discussion (18–22).

The properties of SZ can be influenced by a variety of parameters, such as the nature of the zirconium precursor, the level of sulfate coverage, the conditions of introducing sulfate (and metal promotors), and the calcination temperature. The classical route proceeds via precipitation of zirconium hydroxide, followed by sulfation and calcination. An alternative procedure employs the sol–gel method. The ability to control the network structure by the choice of solvent and precursor, the homogeneity at a molecular level, low-temperature synthesis, and one-step processes are some of the advantages of sol–gel chemistry (23). Drying of the gel can be achieved by an increase in temperature (formation of xerogels), by supercritical drying (aerogels), or by freeze-drying (cryogels). Both aerogels (4, 24–26) and cryogels possess favourable textural characteristics, but examples of freeze-dried samples are limited in literature hitherto.

The heterogeneity of a solid material's surface and the question of accessibility of acid sites (structural relations) cause difficulties in the determination of acidity. Typically, the interaction of the solid acid with basic probe molecules is measured by spectroscopic, thermoanalytical, or indicator techniques; and NMR or IR shifts, desorption temperatures, or the heats of adsorption are employed for the determination of the acid strength (27–33). But dependencies of the activity on the acidity may not always be valid as claimed by Farcasiu and Hancu (34) or Vartuli *et al.* (35). There is a lack of correlation between the observed catalytic activities and the acid strength, especially if the reactants and the probe molecules are very different in nature. Obviously, for a correlation with a catalytic reaction in liquid phase like an acylation, a probe molecule similar to the reactants should be employed. But in the case of microcalorimetry, for instance, the adsorption of ammonia or pyridine is still frequently used (35–38). Recently, Ferino *et al.* investigated sol–gel zirconia catalysts, testing the acidity and basicity by

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adsorption of NH_3 and CO_2 (39). Heats of ammonia adsorption on SZ catalysts, their relation to catalytic activities, and the deactivation after selective poisoning of the acid sites with NH_3 were investigated by Yaluris *et al.* (40). Drago and Kob reported a combined calorimetry–adsorption method using pyridine as probe molecule for modified zirconia samples (41). In contrast to most other studies, the latter experiments were performed in the liquid phase.

In a recent study (42), we have investigated the application of freeze-drying for the synthesis of promoted and unpromoted SZ. Freeze-dried samples showed high activity in Friedel–Crafts acylation; higher catalytic activities were always observed for the metal ion-promoted catalysts, especially the iron-promoted catalysts. The investigations were extended now to check the behaviour of the catalysts in the reaction of anisole and benzoic anhydride. The influence of metal ion promotion on the catalytic properties was studied under milder conditions and for shorter reaction times. In the present work we also relate the results of the acylation reaction to microcalorimetric data. The adsorption was performed not only with ammonia and pyridine in the gas phase, but also with a mixture of pyridine in anisole, which is more consistent with the reaction conditions. The results will be compared to those of conventionally prepared SZ and aerogels, made by supercritical drying.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Freeze-dried zirconia samples were prepared according to (42). Briefly, equal volumes of 0.4 M $ZrOCl_2 \cdot 8H_2O$ solution and *tert*-butanol were mixed and added dropwise to a solution of aqueous ammonia at a pH of 10. The precipitate was washed several times with a butanol–water mixture (1 : 1) until free of chloride. The hydroxide gel was then placed in the freeze-dryer and liquid nitrogen was used to freeze it. Solvent sublimation and drying of the sample lasted about 24 h, until finally a pressure of 0.04 mbar was achieved. The dried zirconium hydroxide was impregnated with solutions of 0.6 M $(NH_4)_2SO_4$, 0.3 M $Fe(NO_3)_3 \cdot 9H_2O$, and 0.3 M $Mn(NO_3)_2 \cdot 4H_2O$, respectively. The amounts were chosen according to 10 wt% SO_4^{2-}, 1.5 wt% Fe, and 0.5 wt% Mn. After sulfation and metal ion promotion, the samples were dried at 110°C. For activation, the material was calcined in flowing air at 650°C for 3 h.

For comparison, a conventionally synthesized sample and two aerogel samples were prepared according to the literature (26). Briefly, the standard SZ was made by kneading a precipitated $ZrO_2 \cdot xH_2O$ with solid $(NH_4)_2SO_4$, followed by calcination in air. The aerogels were synthesized from $Zr(OPr)_4$ in propanol, by adding nitric acid (without/with sulfuric acid) to the hydrolysing solution. Supercritical drying was carried out at 280°C and 150 bar, and the raw aerogel was calcined in flowing air.

TABLE 1

Characterization of the Calcined SZ Samples, Prepared by Freeze-Drying, Conventional Preparation, and Aerogel Synthesis

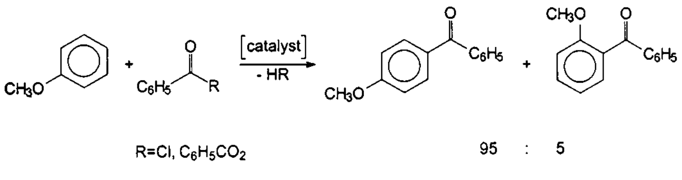
	S (wt%)	S_{BET} (m^2/g)	$V_{p,des}$ (cm^3/g)	d_{max} (Å)
F-SZ	1.65	132	0.54	140
F-FSZ	1.83	128	0.52	180
F-MSZ	1.73	127	0.55	180
F-FMSZ	1.90	141	0.58	180
S-SZ	3.44	139	0.16	40
A-SZ	1.27	138	0.52	200
A-Z	—	134	0.50	210

The calcined samples were labeled as follows. The first letter indicates the synthesis route: F = freeze drying, A = aerogel synthesis, S = standard/conventional synthesis. The following letters refer to the elements: Z = zirconia, S = sulfate, F = iron, M = manganese. For instance, sample F-FSZ denotes the freeze-dried iron-promoted, sulfated zirconia.

The catalysts were characterized by elemental analysis, low-temperature nitrogen adsorption (ASAP 2010, Micromeritics), X-ray diffraction (XRD 7, Rich. Seifert & Co., Freiberg), and FTIR photoacoustic spectroscopy with pyridine (FTIR system 2000, MTEC cell, Perkin Elmer) (26). Results are given in Table 1.

2.2. Catalytic Probe Reaction

The acylation reaction (cf. Scheme 1) was carried out in the liquid phase using 2.65 mmol of benzoic anhydride, 12 ml of anisole, and 0.1 g of tetradecane (internal standard for GC). The stirred reaction mixture was heated to the desired temperature and 200 mg of the freshly calcined catalyst was added. To carry out the acylations at RT, it was necessary to initially increase the temperature of the reaction mixture to 35°C (10 min). When the color of the slurry became yellow and the "start of catalytic action" was indicated by thin-layer chromatography, heating was stopped. After the mixture was allowed to cool to RT (22°C), the reaction continued for the rest of the reaction time at this temperature.



SCHEME 1

2.3. Microcalorimetric Studies

Microcalorimetric measurements were performed, both in the gas phase and the liquid phase.

1. Gas-phase adsorption: ammonia/pyridine. Microcalorimetric data were determined using a heat flow calorimeter of the Tian-Calvet type (C 80, Setaram), connected to a volumetric glass line with on-line injection system for pulsing the reactive gases. Ammonia (purity >99.9%) was injected from a storage vessel; a glass flask containing pyridine outgassed under vacuum was used for the adsorption of pyridine. After every pulse, the equilibrium pressure was measured with a differential pressure gauge (Barocel, Datametrics). Both the calorimetric and volumetric data (pressure, adsorbed volume, heats of adsorption, differential and integral enthalpies) were stored and analyzed by microcomputer. Before the adsorption experiments, about 70–80 mg of the respective sample was degassed under vacuum overnight at 400°C. In order to limit diffusion phenomena, an adsorption temperature of 150°C was chosen. The first adsorption cycle was finished at a final equilibrium pressure of 0.6 Torr. The system was then evacuated. After the desorption peak had appeared, a secondary adsorption cycle was performed at the same temperature. In all cases, the level of irreversible adsorption is practically constant above 0.2 Torr. Thus, at this pressure the amounts of irreversibly and totally adsorbed base were determined from the difference between adsorption and readsorption and from the adsorption cycle, respectively.

2. Liquid-phase adsorption: pyridine in anisole. Liquid-phase experiments were performed using a Titrys calorimeter (Setaram); the calorimetric data were analyzed by microcomputer. The samples (∼200 mg) were pretreated under vacuum overnight at 400°C and then sealed in ampoules. At 70°C the mixture of pyridine in anisole (0.0307 mol/l) was injected stepwise every 2 h. Each dose consisted of 0.2 ml and was introduced with an injection rate of 0.05 ml/min. A separate study under the same experimental conditions was performed in a quartz UV–vis cell and the absorbance of pyridine at 251 nm was measured with a Perkin-Elmer UV–vis spectrophotometer. These absorbances were used to calculate the concentrations of pyridine in solution at equilibrium. The amount adsorbed by the solid is given by the difference between the amount in solution at equilibrium and the amount added.

3. RESULTS

3.1. Catalytic Activity

In a former study (42), the reaction of benzoyl chloride with anisole was performed for 3 h at 60°C on freeze-dried zirconia catalysts. High conversion degrees were achieved especially in the case of iron-promoted samples. First, the problem of leaching was studied with respect to benzoyl chloride as benzoylating agent. The effect of Fe was investigated using (i) F-FSZ, (ii) a mixture of F-SZ and Fe_2O_3, and (iii) pure Fe_2O_3. With all iron-containing samples, the analysis of the reaction mixture confirmed our expectation that leaching processes occured with benzoyl chloride. A small amount of iron (5–10 ppm in the 1.5 wt% promoted sample) was leached out from the catalyst. The concentration of iron in the reaction mixture increased with the percentage of loading. When iron oxide was present as (co-)catalyst, complete conversion was observed. Thus, the enhancement in activity might be due to the formation of $FeCl_3$ in the reaction mixture.

TABLE 2

Reaction between Benzoic Anhydride and Anisole on Modified SZ under Different Reaction Conditions

	Yields of both 4- and 2-methoxybenzophenone			
	50°C, 3 h	22°C, 1 h	22°C, 3 h	Leaching test[b]
F-SZ	86	21	31	30
F-FSZ	90[a]	37	51	50
F-MSZ	90[a]	29	43	45
F-FMSZ	88[a]	37	52	52
S-SZ	63	14	21	—
A-SZ	93[a]	41	54	—

[a] Complete conversion of benzoic anhydride.

[b] After 3 h reaction time at 22°C, the catalysts were filtered off and the reaction mixture was analyzed again 2 weeks later.

Consequently, the experiments were extended to the application of benzoic anhydride, where no iron chloride can be formed. The results of the catalytic tests at 50°C and at RT are presented in Table 2. Unmodified zirconia does not catalyze the formation of methoxybenzophenone, and also at a temperature of 140°C no reaction was observed here. A conversion of 63% of benzoic anhydride was reached after 3 h of reaction time at 50°C in the case of conventionally prepared S-SZ. Still higher values were observed for the other modified samples. The reaction even could be carried out at RT. Under these mild conditions, 20 to 50% conversion into the ketone was observed after 1 and 3 h reaction time, respectively. The catalytic activity of SZ increased markedly after promotion with metal ions. Enhancement by one-third was generated by manganese impregnation (21 → 29%). Treatment with iron was found to be even more effective (21 → 37%). There was no synergistic or additive effect from multiple metal doping. In any case, a selectivity as high as 90–100% for the ketone was observed; small amounts of benzoic acid were formed as the only by-product in the indicated experiments.

After 3 h reaction time at RT, the catalysts were filtered off and the reaction mixture was analyzed again 2 weeks later. If leaching had occurred, a further increase in conversion should have been the result. After 2 weeks, no iron was detected in the reaction mixture and no further increase in conversion was observed. Thus, the problem of leaching and homogeneous instead of complete heterogeneous catalysis did not occur with benzoic anhydride.

3.2. *Microcalorimetric Measurements*

The adsorption of basic probe molecules was used to characterize both number and strength of surface acid sites on calcined SZ catalysts. Ammonia and pyridine, respectively, were chosen since they differ in proton affinity in the gas phase (846 and 912 kJ/mol for ammonia and pyridine, respectively (32)) and molecule diameter (0.26 and 0.53 nm, respectively).

The curves of the differential heat of ammonia adsorption on selected zirconia samples are illustrated in Fig. 1. The two aerogels (pure and sulfated zirconia) as well as the cryogel (promoted sulfated zirconia) behave very similarly. The initial heats of adsorption are in the range of 200 kJ/mol. In contrast, the sample S-SZ exhibits a lower initial heat value of approximately 140 kJ/mol only. Interestingly, no difference between pure and sulfated zirconia samples was found in the case of ammonia adsorption, irrespective of their different profiles from ammonia TPD and the differences in Brønsted and Lewis acidity.

The strength of the acid sites of all samples was found to be rather heterogeneous: with increasing volume of adsorbed ammonia the adsorption heat decreases continuously. Therefore, a figure showing the acid site distribution is less informative in this case and will not be shown here.

The amounts of irreversibly and totally adsorbed ammonia were determined from the two isotherms at 0.2 Torr, cf. Fig. 2a. In the region of very low pressure, the total quantity of NH_3 adsorption (first cycle isotherm) increases very quickly with increasing pressure, indicated by an almost vertical slope of the initial isotherm part. This is due to the presence of a large number of acid sites strongly interacting with ammonia. As shown in Fig. 2b, this behaviour is similar for all the samples.

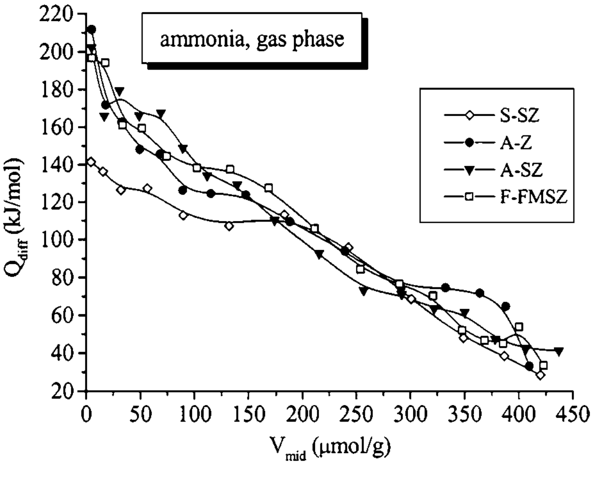


FIG. 1. Differential heat of ammonia adsorption at 150°C as a function of the ammonia uptake for zirconia samples prepared by standard preparation, aerogel synthesis, and freeze-drying.

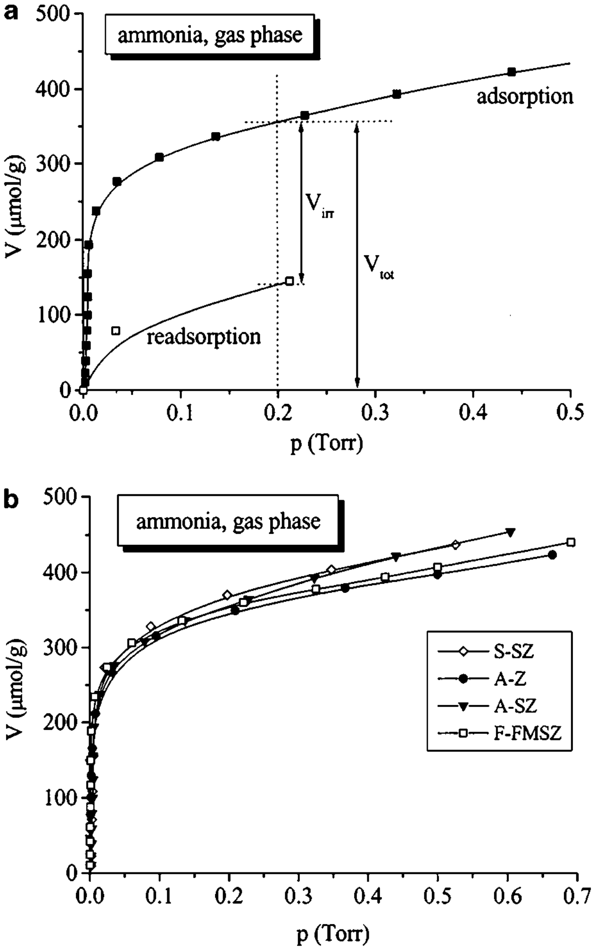


FIG. 2. Ammonia adsorption isotherm at 150°C. (a) Determination of the amount of totally and irreversibly adsorbed ammonia, respectively, from two successive sorption cycles on the sulphated zirconia aerogel A-SZ. (b) Comparison of the adsorption isotherms of differently synthesized zirconia samples.

Quantitative results of NH_3 adsorption are summarized in Table 3. For all samples about 350 to 370 μmol/g of totally adsorbed ammonia were determined. Since S_{BET} is comparable for all zirconia samples, there are no differences in the surface area normalized values, too (2.5–2.7 μmol/m^2).

TABLE 3

Total and Irreversible Adsorption of Ammonia at $p = 0.2$ Torr and $\theta = 150^\circ$C

Catalyst	S_{BET} (m^2/g)	V_{tot} (μmol/g)	V_{irr} (μmol/g)	V_{tot} (μmol/m^2)	V_{irr} (μmol/m^2)	V_{irr}/V_{tot}
S-SZ	139	370.2	245.4	2.66	1.76	0.66
A-Z	134	346.6	190.8	2.59	1.42	0.55
A-SZ	138	355.4	215.4	2.58	1.56	0.61
F-FMSZ	141	354.1	230.1	2.51	1.63	0.65

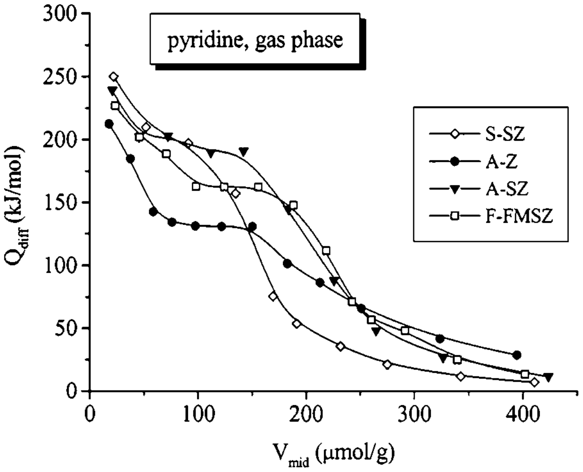


FIG. 3. Differential heat of pyridine adsorption at 150°C as a function of the pyridine uptake for zirconia samples prepared by standard preparation, aerogel synthesis, and freeze-drying.

TABLE 4

Total and Irreversible Adsorption of Pyridine at $p = 0.2$ Torr and $\theta = 150^\circ$C

Catalyst	S_{BET} (m^2/g)	V_{tot} (μmol/g)	V_{irr} (μmol/g)	V_{tot} (μmol/m^2)	V_{irr} (μmol/m^2)	V_{irr}/V_{tot}
S-SZ	139	251.2	198.5	1.81	1.43	0.79
A-Z	134	288.0	190.0	2.15	1.42	0.66
A-SZ	138	298.7	233.2	2.16	1.69	0.78
F-FMSZ	141	297.0	226.0	2.11	1.60	0.76

Reversible adsorption involves weak interactions (<50 kJ/mol), which is ascribed mainly to physisorption and is catalytically not relevant. For the determination of the relevant acid site concentration, the irreversibly adsorbed ammonia should be taken into account. Unmodified zirconia slightly differs from the other three samples in the portion of irreversibly adsorbed ammonia, which amounts to 0.55 in contrast to 0.61–0.66. Thus, the amount of strongly bonded ammonia is higher in the case of sulfated than in the case of pure zirconia samples.

Figure 3 illustrates the differential heats of pyridine adsorption on the samples. The curve shapes somewhat differ from the corresponding ammonia adsorption in Fig. 1. The initial heats of adsorption are in the range of 210–250 kJ/mol. S-SZ exhibits a continuous decrease in the strength of the acid sites with increasing volume of adsorbed pyridine. In contrast, the aerogel and cryogel samples possess plateaus of constant heat of adsorption. The strongest interaction (190 kJ/mol) can be observed with the sample A-SZ, followed by 165 kJ/mol for F-FMSZ. The unmodified aerogel A-Z exhibits the plateau at about 135 kJ/mol, only. In accordance with the literature, introducing sulfate on the zirconia samples results in a stronger interaction with pyridine.

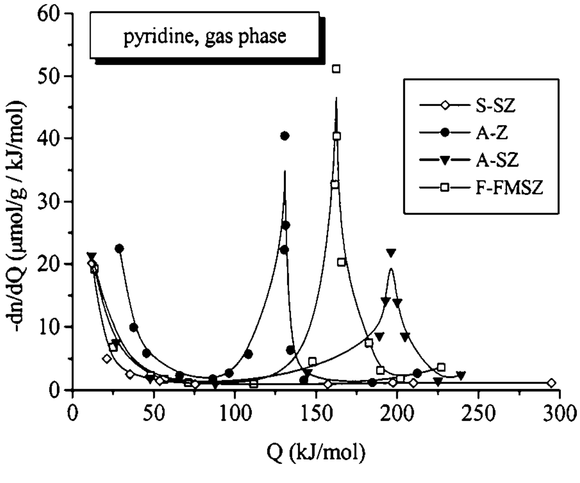


FIG. 4. Acid strength distribution of pyridine adsorption onto differently synthesized zirconia samples at 150°C.

Plateaus in the Q_{diff} vs V_{mid} plots (Fig. 3) correspond to maxima in the spectra graphs $-dn/dQ$ vs Q which is even more clearly illustrated in Fig. 4. The acid site distribution of the pyridine adsorption is heterogeneous in the case of the sample S-SZ. Therefore, no maximum was received for this sample. In contrast, the aerogel A-SZ, the freeze-dried sample F-FMSZ, and the unmodified aerogel A-Z possessed maxima at about 190, 165, and 130 kJ/mol, respectively.

As mentioned above, the isotherms of adsorption and readsorption (not shown here) were used to determine the number of totally and irreversibly adsorbed pyridine at 0.2 Torr, as shown in Table 4. The amount of totally adsorbed pyridine was approximately 290–300 μmol/g (2.1–2.2 μmol/m^2) for all the cryogel and aerogel samples, whereas the conventionally prepared S-SZ exhibited only 250 μmol/g (1.8 μmol/m^2). Comparing the amount of irreversibly adsorbed pyridine, unmodified zirconia showed again the lowest value: The surface density of acid sites relevant for catalysis is about 66% of the total sites occupied by pyridine whereas it is about 77% for the three other samples.

TABLE 5

Comparison of the Amount of Totally and Irreversible Adsorbed Base: Ammonia vs Pyridine

Catalyst	d_{max} (Å)	$V_{tot\,ammonia}/V_{tot\,pyridine}$	$V_{irr\,ammonia}/V_{irr\,pyridine}$
S-SZ	40	1.47	1.24
A-Z	210	1.20	1.00
A-SZ	200	1.19	0.92
F-FMSZ	180	1.19	1.02

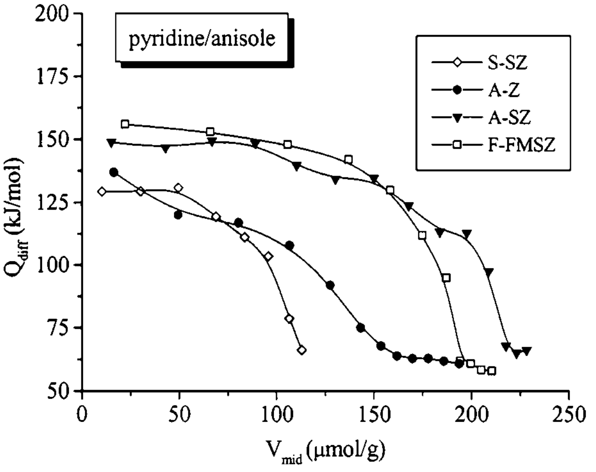


FIG. 5. Differential heat of liquid-phase pyridine adsorption as a function of the pyridine uptake for differently synthesized zirconia samples . The experiment was performed at 70°C using a mixture of pyridine and anisole.

Ammonia and pyridine are molecules of different sterical demand. Thus, further information can be obtained from a comparison of the amount of these two adsorbed basic molecules, cf. Table 5. The largest differences arise for the sample S-SZ. The adsorption of pyridine is much more hindered in the case of this sample than for the others. Obviously, the reason for this should arise from the texture of the catalyst, namely the smaller pore diameter of 40 Å in contrast to the large structural pores of the aerogel and freeze-dried samples (about 200 Å).

As a characterization method, which is closer to the investigated liquid-phase reaction, the adsorption of pyridine diluted in anisole was performed. Figure. 5 shows the differential heats of adsorption on the samples. The curve shapes are completely different from the results of gas adsorption. For A-SZ and F-FMSZ the adsorption profiles exhibit distinctive plateaus, characteristic for a homogeneous distribution of the strength of acid sites. The heat of pyridine/anisole adsorption is approximately 150 kJ/mol, just slightly higher for the metal ion-promoted sample F-FMSZ. The adsorption curve of the pyridine/anisole mixture on S-SZ exhibits a short plateau in the initial stage with heats of adsorption of 130 kJ/mol. With higher loading, a continuous decrease in the strength of acid sites was monitored. Still lower values of the adsorption heat can be observed in the case of pure aerogel A-Z. The plateau is not very well established and the corresponding differential heat of adsorption is less than 120 kJ/mol. A small amount of stronger acidic sites was detected at the initial heat of 138 kJ/mol.

4. DISCUSSION

Modified zirconia samples were synthesized by freeze-drying as well as by conventional and aerogel synthesis. Supercritical and freeze-drying gave access to sulfated zirconia with large pore diameters and pore volumes. In the case of these samples, somewhat broader XRD reflexes indicate less crystallinity and smaller particle size in contrast to conventionally prepared SZ. Similar specific surface areas and the presence of exclusively tetragonal zirconia are characteristic for all the modified zirconia samples investigated. In accordance with other reports (8, 16, 27, 28), sulfate modification of zirconia also influences the acidity of all the samples prepared via different synthesis routes: Brønsted acidity is generated and the formation of strong acidic sites can be observed by ammonia TPD. The results are similar to other reports and will not be discussed further.

Microcalorimetric experiments were carried out with ammonia, pyridine (both as gases), and a liquid mixture of pyridine and anisole. The information from all these microcalorimetric experiments are quite complementary: ammonia is a small molecule which probes the total of the acid sites. Gas-phase measurements with pyridine can reflect influences of accessibility and diffusion. Pyridine, diluted in anisole, is close to the conditions of the liquid-phase acylation reaction and, thus, the most reliable method for investigating correlations between acidity and activity.

In the case of ammonia, no straight correlation between acidity and catalytic activity was found. For all samples the contribution of heats higher than 80 kJ/mol, as the critical value for ammonia chemisorbed on strongly acidic sites, was similar and very high. Only in the case of unmodified zirconia A-Z, the amount of irreversibly adsorbed base was somewhat lower, compared to the sulfated samples. This observation corresponds well to results from ammonia TPD on pure and sulfated zirconia samples (26, 42). Only in the case of sulfate promotion, NH_3 was desorbed at high temperatures (500°C) from the catalysts, whereas unmodified zirconia was found to have acid sites of medium strength, only. Pyridine adsorption resulted in a splitting of the adsorption curves. Higher adsorption heats were measured for the modified samples, compared to those for pure zirconia aerogel. The strength of acid sites was homogeneous for the freeze-dried and supercritical-dried samples whereas the distribution was heterogeneous for S-SZ. Pyridine adsorption in the liquid phase differs significantly from gas-phase adsorption. If a gaseous probe molecule is adsorbed on a solid sample, there is a contribution of about 10 kcal/mol (42 kJ/mol) from nonspecific dispersion force interactions (41). Therefore, the adsorption of pyridine diluted in anisole gave enthalpies in the range of 120–150 kJ/mol only, compared to gas-phase pyridine. Additionally, the curve shapes are different. The highest values of adsorption enthalpy were determined with the two most active samples A-SZ and F-FMSZ. The evolved heat was only slightly higher in the case of the metal ion-promoted sample. Thus, there is no strong evidence from these microcalorimetric data for a higher acidity of FMSZ compared to SZ.

Comparable results, reporting the redox activity of the promoted sulfated zirconia, were published by several authors (22, 40, 41, 43).

The results from these experiments were related to earlier reports on calorimetric and adsorption studies. No reference data are available for calorimetric investigations on SZ, using a liquid mixture of basic probe molecules in a solvent, which itself is the reactant in the catalyzed liquid-phase reaction. Thus, the data are compared to those from similar studies on zirconia samples, using pyridine in liquid-phase or gas-phase data.

Drago and Kob (41) investigated two kinds of acid sites on SZ by means of cal–ad (combined calorimetry and adsorption). Their experiments were carried out with a slurry of the catalyst in cyclohexane, reacting with a pyridine solution. The analysis of the data resulted in acid strengths of 31.2 kcal/mol (131 kJ/mol) and 25.8 kcal/mol (108 kJ/mol), respectively. This is in quite good agreement with the data reported here. The small difference from our results can be ascribed to a lower adsorption temperature and the general uncertainty of differences in the preparation of the samples.

The acidity values reported by Yaluris *et al.* (40) are very close to our findings. Microcalorimetric studies on SZ were performed at 150°C, using ammonia as probe molecule. The curve shape of the differential heat of adsorption is similar to Fig. 1. Our results demonstrate a difference between the standard S-SZ and the modified cryogel/aerogel samples A-SZ/F-FMSZ; the data of Yaluris *et al.* (MEL-SZ, activated at 588 K) would be between these two groups. The reported distribution of acid sites (30 μmol/g of strong acid sites with differential heats of adsorption in the range of 150–165 kJ/mol and about 40 μmol/g of sites with an intermediate strength of 125–140 kJ/mol) is very close to our acidity values.

Ferino *et al.* (39) investigated the ammonia uptake of pure zirconia sol–gel catalysts at 80°C. An initial heat value of 165 kJ/mol was reported for both xerogel and aerogel. The amounts of irreversibly adsorbed base were 2.1 and 5.9 μmol/m^2, respectively. The aerogel was found to give adsorption heats, which decrease more slowly compared to those of the xerogel. If one takes into account the higher adsorption temperature in our study and differences in the surface area of the catalysts, the results of the sample A-Z (200 kJ/mol and 1.4 μmol/m^2) agree quite satisfactorily.

5. SUMMARY

Freeze-drying is a potential method for synthesizing metal ion-promoted and unpromoted sulfated zirconia. Compared to the standard procedure, these freeze-dried SZ are much more effective in the Friedel–Crafts acylation investigated. Since the surface area of the applied S-SZ is not much lower and the sulfur content is even higher, this catalytic behaviour might be due to the increase in pore volume and pore diameter of the freeze-dried SZ. All these freeze-dried samples exhibit porous structures and surface areas similar to those of aerogel samples created by supercritical drying.

Sulfate modification of zirconia results in strong acidity and the formation of Brønsted acid sites. Thus, the benzoylation of anisole has been successfully carried out with all sulfated samples at a temperature of 50°C using the acid chloride or the anhydride. At room temperature, high yields of methoxybenzophenone were achieved especially in the case of aerogels and freeze-dried samples due to their porosity. The conversion degrees were found to be distinctly higher after metal ion promotion; impregnation with iron was more effective than that with manganese. Leaching did not occur with the metal ion-promoted SZ catalysts when the reaction was performed with benzoic anhydride. Hence, there is a real doping effect.

Suitable conditions of microcalorimetric experiments on the catalysts were investigated. Adsorption of pyridine in the liquid phase resulted in the best correlation to the activity in the regarded Friedel–Crafts acylation. Though a strong interaction of the solid acid's surface with pyridine/anisole does not necessarily correspond to a similar interaction with benzoic anhydride (benzoyl chloride)/anisole with the acidic surface, these liquid-phase adsorption experiments are much closer to the catalytic tests. Thus, they might be a good tool for evaluating the performance of catalysts in this type of reaction.

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