JOURNAL OF CATALYSIS **177,** 164–174 (1998)
ARTICLE NO. CA982098

Properties of Modified Zirconia Used as Friedel–Crafts–Acylation Catalysts

V. Quaschning, J. Deutsch, P. Druska, H.-J. Niclas, and E. Kemnitz[1]

Humboldt-Universität zu Berlin, Hessische Strasse 1-2, D-10115 Berlin, Germany; Institut für Angewandte Chemie Adlershof,
Rudower Chaussee 5, D-12484 Berlin, Germany

Received January 22, 1998; revised March 17, 1998; accepted March 17, 1998

Both precipitated and aerogel synthesized zirconia were modified employing gaseous and solid compounds, respectively, as well as concentrated mineral acids. The sulfur and phosphorous-containing samples were characterized by nitrogen adsorption, X-ray diffraction, FTIR pyridine adsorption, ammonia TPD, and 1-butene isomerization. Modification of zirconia samples results in enhanced Brønsted acidity and catalytic activity. Especially ammonium sulfate and sulfite generate strong acidic centers at the surface in high concentrations. As was shown on the basis of XPS measurements the final calcination step in air converts the sulfite into surface sulfate, resulting finally in the same, or at least very similar, surface states of both differently treated samples. Some few degrees enhanced catalytic activities were obtained using sulfated zirconia aerogels. Applied to the benzoylation of anisole, a slurry of these catalytically active zirconia samples yields similar high conversion degrees as nonafluorobutanesulfonic acid known as an excellent catalyst for this reaction in homogeneous solution. There is evidence to assume that the benzoylation reaction under the conditions used occurs exclusively at Brønsted acid sites but not at Lewis sites. A hypothetical path for the action of a sulfated zirconia surface in the catalytic step is proposed.

Key Words: **modified zirconia; aerogel; acylation catalyst; Brønsted acidity.**

INTRODUCTION

Increasingly demanding environmental pressure and the resulting drive towards clean technologies force us to develop ecologically friendly alternatives. There are at least two different ways, to synthesize alternative products or to find quite new clean synthesis routes to the same product. A considerable part of synthesis processes in the chemical industries is based on acid catalyzed reactions. Commonly, these reactions are classified in Lewis and Brønsted catalyzed ones. For both kinds there are numberless examples using homogeneous reaction conditions. These include Friedel–Crafts reactions, where Lewis (1) or Brønsted acids (2, 3) are used in stochiometric or even excess amounts to achieve satisfactory reaction rates and yields. Homogeneous catalysts form strong complexes with reaction products that must be destroyed by hydrolysis. Workup procedures result in the loss of catalyst, acidic wastes, and corrosion problems. An improved procedure was demonstrated by Effenberger *et al.* using only catalytic amounts of trifluoromethanesulfonic acid (4) and nonafluorobutanesulfonic acid (5) under homogeneous conditions.

Just the use of solid catalysts, instead of the above-mentioned ones, offers some additional technical advantages besides the already discussed environmental factors. Solid acids are not corrosive and can be handled and separated easily from the liquid reaction mixtures. There are some attempts to replace the above-mentioned Lewis or mineral acids by solid acids like acidic zeolites in electrophilic aromatic substitutions (6).

Recently, some general aspects of the use of solid acids in environmentally clean technologies have been published by Clark and Macquarrie (7). Therefore, only the use of sulfated zirconia as a heterogeneous catalyst may be reflected here. Already in 1979 Arata *et al.* (8, 9) realized the enhanced acidity of solid zirconia treated with diluted sulfuric acid and then calcined at elevated temperatures. For many years, those sulfated zirconia were considered as solid super acids. Today, it seems to be doubtless that sulfated zirconia reveal high acidity, but they are not super acids (10–12). Many publications appeared during the past reflecting the wide interest in applicable solid acids and especially documenting the pronounced role of sulfated zirconia (13–17). We started to investigate the use of sulfated zirconia, employing several sulfating reagents for the formation of isooctanes which are of some interest as additives for gasoline (18).

This paper deals with modified zirconia catalysts used for acylation reactions which are of some technical importance.

EXPERIMENTAL

Sample Preparation

Standard procedure. I. *Preparation of zirconia oxides.* Zirconia oxide was prepared by adding aqueous ammonia to an aqueous solution of $ZrOCl_2$ until a pH of 8 was achieved. The solid was filtered, washed several times, and

---

[1] To whom correspondence should be addressed.

dried at 110°C for 15 h (**ZR/1**). A sample of this oxide was calcined at 500°C in air (**ZR/c1**). Additionally, a ZrO_2 sample was prepared by hydrolyzing $Zr(i\text{-}OPr)_4$, followed by drying and final calcination at 550°C (**ZR/c2**).

II. *Synthesis of modified zirconia.* The sulfation of zirconia was performed

- by kneading $ZrO_2 \cdot \times H_2O$ (sample ZR/1) thoroughly with solid $(NH_4)_2SO_4$ (**ZR/amSO$_4$**) or solid $(NH_4)_2SO_3$ (**ZR/amSO$_3$**) or by kneading anhydrous ZrO_2 (sample ZR/c2) with $(NH_4)_2SO_4$ (**ZR/c-amSO$_4$**), respectively. The three samples were calcined at 500°C in air for 1 h.
- by passing an air flow, saturated with $SOCl_2$ (**ZR/SOCl$_2$**) or SF_4 (**ZR/SF$_4$**), respectively, for 2 h at 150°C. A subsequent air flow was used to remove physisorbed gaseous products.

In some cases the catalysts were investigated in relation to a commercially available sulfated zirconia catalyst of the MEL group (MEL XZO682/01, Magnesium Elektron Ltd.), hereafter noted as **ZR/com**.

Sol–gel procedure. Zirconia aerogels were prepared following the standard procedure described by Ward and Ko (13). In a glovebox $Zr(n\text{-}OPr)_4$ (70 wt% in propanol) was diluted in a mixture of propanol and nitric acid. The water–alcohol mixture, prepared in a second beaker, was added to the alkoxide–alcohol–acid solution and stirred until gelation occurred. After an aging period of about 30 min the gel was put into an autoclave. The aerogels were prepared by heating these mixtures up to 300°C and 160 bar and maintaining the supercritical conditions for 1 h. The alcohol and further components were removed by controlled expansion. The whole procedure is described in detail elsewhere (19). After removal of the solvent in the first heat treatment step the aerogel powder was dried under vacuum at 300°C, followed by filling the system with nitrogen. These two steps were repeated several times. The calcination step was performed under flowing air for 2 h at about 500°C for pure and phosphated zirconia and at about 550°C for sulfated zirconia, respectively.

The components $Zr(n\text{-}OPr)_4$/water/propanol/acid were used in an overall molar ratio of 1 : 3.6 : 13.7 : 0.8. Modified aerogels were prepared by replacing the appropriate molar amount of nitric acid by sulfuric or phosphoric acid.

Sample Characterization

Crystallographic identification of the samples was performed using X-ray powder diffraction with CuKα radiation (XRD 7, Rich. Seifert & Co., Freiberg). The specific surface areas were measured using nitrogen adsorption at 77 K by the standard BET method (ASAP 2000 system, Micromeritics). The sulfur, phosphor, and chlorine contents were determined by elemental analysis. The fluoride contents were measured according to the Seel method (20).

The surface analytical studies were performed by an ESCALAB 220 iXL spectrometer (Fisons Instruments) consisting of two vacuum chambers: the analyser and the fast entry air lock/preparation chamber. The powdered samples were fixed on a carbon tape (carbon conductive tape, Pelco International) at the top of the sample holder and transferred into the UHV. The X-ray source was monochromatic focused AlKα radiation (1486.6 eV) with an input power of 150 W. The emerging charge of the sample was equalised with the installed charge compensation. The final peak position was determined using the C 1s peak (shifted to 285.0 eV) corresponding absorbed carbon species. The XPS-measurements were performed at a constant pass energy of 25 eV. The ESCALAB was calibrated routinely with the appropriated XPS lines of Au, Ag, and Cu, as given in Ref. (21).

For determining the nature of the acid sites (LZ, Lewis acid sites; BZ, Brønsted acid sites) all samples were characterized by FTIR photoacoustic spectroscopy with chemisorbed pyridine. In detail, about 70 mg of the sample were pretreated under nitrogen (35 ml/min) at 150°C; 30 μl of pyridine were adsorbed after 15 min at this temperature. Each sample was flushed with nitrogen for another 15 min to remove physisorbed pyridine. Spectra of the sample (pyridine-loaded sample and the unloaded sample, background) were taken at room temperature over a range of 4000–400 cm^{-1}, using a MTEC-cell and FTIR system 2000, Perkin Elmer. All spectra were normalized, setting the almost strongest peak in the zirconia system at 530–630 cm^{-1} to 100% transmission and multiplying the whole spectrum by this factor. To compare the amount of acid sites of the different samples we determined the intensity of the bands at about 1450 cm^{-1} (LZ) and 1490 cm^{-1} (LZ + BZ) of the normalized spectra. If there are no BZ at the surface the intensity of the 1490 cm^{-1} vibration is one-third of that of the 1450 cm^{-1} band. Therefore the experimentally determined height of the 1490-cm^{-1} band was reduced by one-third of the 1450 cm^{-1} band height to get the BZ intensity.

The temperature-programmed desorption (TPD) of ammonia was used to characterize the acid strength distribution of the solids. The desorbed ammonia was absorbed in 0.1 *N* sulfuric acid and than titrated, allowing determination of the overall amount of acid sites of the solids.

In a nickel tube approximately 300 mg of the grained catalyst (0.4–0.5-mm diameter fraction) was pretreated under nitrogen (70 ml/min) up to 500°C. Following the sample was cooled to 120°C and exposed to a stream of nitrogen and ammonia. The physisorbed ammonia was removed over 1 h at 120°C. After cooling down to 80°C the TPD program (10 K/min, up to 600°C) was started. The desorption of ammonia was detected by continuous running IR spectroscopy

(FTIR system 2000, Perkin Elmer). The band at 930 cm^{-1} was used to obtain the ammonia desorption profile. Behind the IR-cell an absorption cell was situated, containing a known amount of sulfuric acid. The amount of desorbed ammonia was determined by a titration with sodium hydroxide to get the quantitative amount of acid sites at the catalysts' surface.

Catalytic Reactions

I. *Double-bond-isomerization of 1-butene as probe reaction.* Butene isomerization was performed in a downward-flow, fixed-bed glass-reactor. Approximately 250 mg of the grained catalyst (0.4–0.5-mm diameter fraction) was pretreated under nitrogen (10 ml/min) for 20 min at 100°C. At this temperature the sample was exposed to the feed stream mixture of nitrogen (10 ml/min) and 1-butene (0.6 ml/min). A residence time of 1.2 s was set up. The composition of the product stream at the exit of the reactor, consisting of 1-butene and E/Z-2-butene, was determined by a Shimadzu gas chromatograph GC-14A with a flame-ionization detector (column: Di-*n*-propylsulfon on 0.2–0.4-mm Poralith, I.D. 2.4 mm, length, 4 m) after 3, 6, 9, . . . min, time-on-stream. Conversion is given as the conversion into the product 2-butene.

II. *Benzoylation of anisole.* The reaction between anisole and benzoic anhydride or benzoyl chloride was carried out in liquid phase in a round-bottom 50-ml 3-necked flask, provided with a magnetic stirrer, a thermometer, and a reflux condenser with a $CaCl_2$-tube. For each reaction a mixture of 12 ml of anisole, 0.00265 mol of the acylation agent, 0.2 g of the catalyst, and 0.1 g of *n*-tetradecane added as an internal standard for the GC-detection was used. The temperature was kept at 140°C. After a reaction time of 7 h the analysis of the products was performed gaschromatographically, using a HP 5890 A with a flame-ionization detector (column: Rtx 1, methylsilicon, Restec corp., I.D. 0.25 mm, length, 30 m). Conversion is given as the conversion into the products, *p*- and *o*-methoxybenzophenone.

For comparison, typical solid Lewis acids like β-AlF_3 (22) and calcined γ-Al_2O_3 were included into the measurements of the acylation activity.

RESULTS

Bulk Properties of the Zirconia Samples

Tables 1 and 2 summarize the notations and some characteristics of the catalysts prepared by standard and aerogel synthesis.

Standard preparation. It was verified that a drastic decrease in the specific surface area occurred after calcination of pure $Zr(OH)_4$ at about 773 K (340 → 40 m^2/g) due to the crystallization process. Exclusively the monoclinic crystallized ZrO_2 was detected. The sulfate and sulfite treatment of amorphous $Zr(OH)_4$ reduced the decrease in the specific surface area (150 m^2/g) and led to the tetragonal crystallized phases, whereas the sulfate treatment of monoclinic ZrO_2 no longer showed this effect on crystallization and the surface area. A modification with gases at comparatively low temperatures resulted in some amorphous material with a large surface area in the case of $SOCl_2$ and a small surface area in the case of SF_4, respectively. The sulfur content was about 1% (gaseous modification) to 4% (solid sulfate treatment). An enrichment of sulfur and fluorine at the surface was detected by comparison between elemental analysis (bulk) and XPS-measurements (surface).

TABLE 1

Preparation Conditions and Sample Characteristics of Modified Zirconia Samples

Sample	Modifying agent	Temperature (°C)	X-ray detected phases	Specific surface area (m^2/g)	S-content bulk/ surface (wt%)	X-content bulk/ surface (wt%)
ZR/1	—	110	Amorphous	341	—	—
ZR/c1	—	500	Monoclinic, some tetragonal ZrO_2	40.5	—	—
ZR/c2	—	550	Monoclinic ZrO_2	38.9	—	—
ZR/amSO_4	$(NH_4)_2SO_4$ solid	500	Tetragonal ZrO_2	139	4.2 surface: 9.0	—
ZR/amSO_3	$(NH_4)_2SO_3$ solid	500	Tetragonal ZrO_2	157	3.4 surface: 4.7	—
ZR/c-amSO_4	$(NH_4)_2SO_4$ solid	500	Monoclinic ZrO_2	28.9	2.5 surface: n.d.	—
ZR/$SOCl_2$	$SOCl_2$ gaseous	150	Amorphous	367	1.7 surface: 2.4	Cl: 7.5 surface: n.d.
ZR/SF_4	SF_4 gaseous	150	Amorphous	40.4	0.9 surface: 1.2	F: 23 surface: 31

Note. n.d., not determined.

TABLE 2

Preparation Conditions and Sample Characteristics of the Aerogel Samples before and after the Calcination Step

Sample	Modifying agent	Temperature (°C)	X-ray detected phases[a]	Specific surface area (m^2/g)	Contents of CHN	S (wt%)	P
A	—	300	Tetragonal ZrO_2	232	7.5	—	—
A/SO_4	H_2SO_4	300	Tetragonal ZrO_2	346	7.6	3.8	—
A/PO_4	H_3PO_4	300	Tetragonal ZrO_2	306	6.7	—	0.6
A/c	—	500	Tetragonal, some monoclinic ZrO_2	134	<1.2	—	—
A/c-SO_4	H_2SO_4	550	Tetragonal ZrO_2	138	<1.2	1.6	—
A/c-PO_4	H_3PO_4	500	Tetragonal ZrO_2	267	<1.2	—	1.6

[a] All aerogel samples are not crystalline but show broad and low-intensity reflexes.

Aerogel samples. All starting aerogel samples are materials with very large specific surface area. They are not crystalline but show broad and low-intensity reflexes in the diffraction pattern. The calcination at about 500°C—in order to reduce the content of organic compounds—also leads to a decrease in the specific surface area. But even after calcination the pure zirconia aerogel has quite a high BET area of 140 m^2/g, in comparison to the results of the standard preparation. The specific surface area of the calcined sulfated aerogel is also—despite the 50-K higher temperature—in the same range as that obtained by a standard preparation of sulfated zirconia. The phosphated zirconia aerogel exhibits a high BET area of 267 m^2/g after the calcination at 500°C. Again, at this temperature the pure zirconia aerogel already contained monoclinic crystallized components, whereas the modified aerogels crystallized only in the tetragonal form.

Acidic Properties

Two methods were used to characterize the acidic properties of the samples: FTIR photoacoustic spectroscopy was carried out in order to distinguish between Lewis and Brønsted acid sites. The temperature-programmed desorption (TPD) of ammonia was used to characterize the acid strength distribution of the solids and, furthermore, to obtain the quantitative amount of acid sites in the specified temperature range.

The FTIR photoacoustic spectra of pyridine, chemisorbed at the solid surfaces, are shown in Fig. 1. The quantitative results are listed in Table 3. The surface of unmodified zirconia (ZR/1, ZR/c1, ZR/c2, A/c) contains only Lewis acid sites. The sulfur treatment results in the formation of Brønsted acid sites for all other samples. The biggest quantity of Brønsted acidity can be achieved as a result of modification using SF_4 (ZR/SF_4). Furthermore, there is no significant wavenumber shift for the pyridine adsorbate complexes. Consequently, the strength of the acid sites of all samples is comparable (cf. also TPD profiles).

Two characteristic profiles of the ammonia TPD spectra are given in Fig. 2. The spectra are normalized allowing a direct comparison of the investigated samples by comparing the areas under the curves which are proportional to the concentration of acid sites (given in millimoles of ammonia per gram of sample). A typical TPD profile for an unmodified zirconia, like for the sample ZR/c2, has only

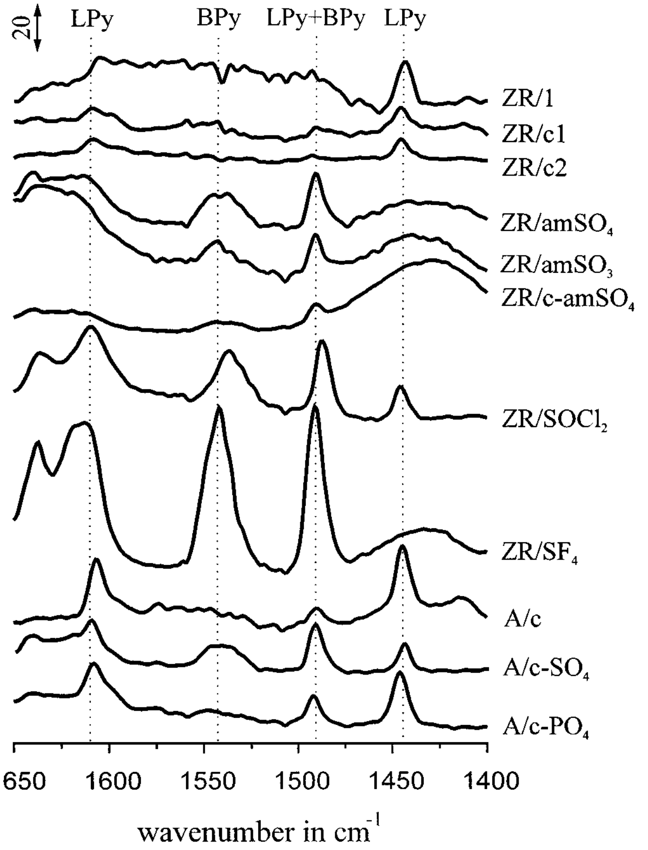


FIG. 1. Normalized FTIR photoacoustic spectra of pyridine chemisorbed at zirconia surfaces (70 mg catalyst weight, 30 μl pyridine adsorption at 150°C, flow system).

TABLE 3

Quantitative Results of the FTIR Photoacoustic Spectroscopy of Pyridine Adsorbat Complexes and of the Ammonia-TPD

Sample	Preparation temperature (°C)	Specific surface area (m^2/g)	FTIR-PAS		NH$_3$-TPD concentration/ density of acid sites	
			LZ (1450 cm^{-1})[a]	BZ (1490 cm^{-1})[a]	(mmol/g)	(μmol/m^2)
ZR/1	110	341	17.5 (high)	0.0 (low)	0.28	0.82
ZR/c1	500	40.5	8.5 (medium)	0.0 (low)	0.28	6.91
ZR/c2	550	38.9	9.0 (medium)	0.0 (low)	0.16	4.11
ZR/amSO$_4$	500	139	0.0 (low)	14.0 (high)	0.30	2.16
ZR/amSO$_3$	500	157	0.0 (low)	12.0 (high)	0.33	2.10
ZR/c-amSO$_4$	500	28.9	0.0 (low)	5.5 (small)	0.09	3.11
ZR/SOCl$_2$	150	367	13.0 (high)	24.5 (high)	n.d.	n.d.
ZR/SF$_4$	150	40.4	0.0 (low)	64.0 (very high)	n.d.	n.d.
A/c	500	134	27.5 (high)	0.0 (low)	0.38	2.84
A/c-SO$_4$	550	138	9.5 (medium)	13.0 (high)	0.32	2.32
A/c-PO$_4$	500	267	20.5 (high)	4.0 (small)	0.52	1.95

Note. n.d., not determined, ammonia-TPD measurements were not possible.

[a] Classification of the intensities in the FTIR spectra: 0 · · · 2, low; 2 · · · 6, small; 6 · · · 12, medium; 12 · · · 30, high; >30, very high.

one maximum at a temperature of about 240°C. The profile of the sulfated zirconia sample, e.g. ZR/c-amSO$_4$, is more differentiated, exhibiting two maxima at temperatures of about 220 and 340°C. The amount of desorbed ammonia and, hence, the total number of acid sites is not higher but comparable for both the sulfated and the unmodified sample (cf. Table 3). However, there is a distinct difference in the distribution of the acid strength. In relation to the ZR/c2 sample the sulfated sample ZR/c-amSO$_4$ clearly provides a higher concentration of stronger acid sites (cf. Fig. 2). This fact is demonstrated by the larger area under the desorption curve in the range between 450 and 550°C.

It was not possible to get the desorption profiles and the quantitative amount of desorbed ammonia of the samples ZR/SOCl$_2$ and ZR/SF$_4$. These two samples were prepared by a low temperature modification with SOCl$_2$ or SF$_4$. The original gases as well as their hydrolysis and decomposition products were released during the progress of the temperature program of the ammonia desorption. A reaction between the gases and ammonia was observed (probably the formation of ammonium halides). Therefore, it was impossible to determine the acidity of these samples on basis of TPD measurements. However, all other samples were investigated by NH$_3$-TPD and provided ammonia desorption profiles which were classified in one of these two modes. All sulfated and the sulfited zirconia (ZR/amSO$_4$, ZR/amSO$_3$, ZR/c-amSO$_4$, A/c-SO$_4$) were similar and showed a two-maxima-type of TPD-profile with a higher concentration of stronger acid sites. The other samples, unmodified ZR/1, ZR/c1, ZR/c2, and A/c and the phosphated aerogel A/c-PO$_4$, gave desorption profiles containing only one maximum and more weaker acid sites.

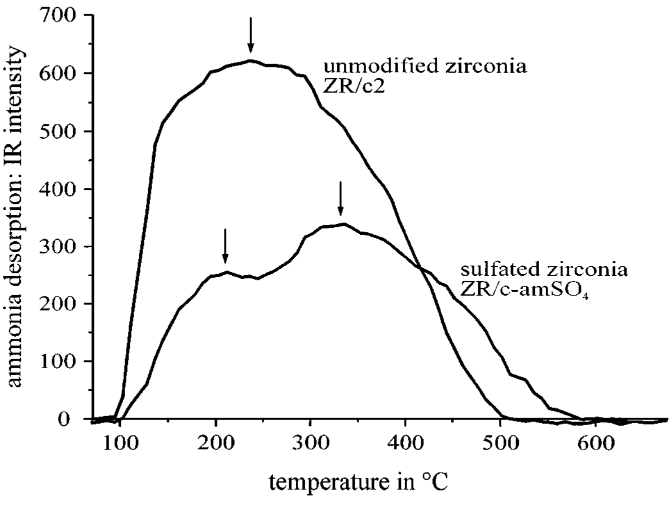


FIG. 2. Normalized ammonia TPD profiles of unmodified and sulfated zirconia.

The results of the ammonia-TPD of all zirconia samples—the concentration of acid sites and their density—are summarized in Table 3. Comparing the quantitative results of the ammonia-TPD, the concentration of acid sites is approximately 0.3 mmol/g for each modified and unmodified sample. Only the ZR/c2 and the resulting ZR/c-amSO$_4$ sample possess a lower concentration, due to a lower specific surface area. All aerogel samples reveal higher concentrations of acid sites and a larger surface area. For that reason, the normalized concentration of acid sites of the catalysts are given as specific concentrations. The samples exhibit a mean concentration of acid sites between 2 and 3 μmol/m^2. Lower values were found for the starting material ZR/1, probably caused by its extremely high surface area. Higher values of the acid site concentration were found for the calcined zirconia ZR/c1 and ZR/c2 with a

TABLE 4

Catalytic Activity of the Zirconia Samples

Sample	Butene isomerization (conversion into 2-butene in %)	Reaction between anisole and: Benzoyl chloride (conversion into ketones in %)	Reaction between anisole and: Benzoic anhydride (conversion into ketones in %)
ZR/1	0	0	0
ZR/c1	0	0	0
ZR/c2	0	0	0
ZR/amSO$_4$	66	76	80
ZR/amSO$_3$	90	62	33
ZR/c-amSO$_4$	82	49	20
ZR/SOCl$_2$	18	1	1
ZR/SF$_4$	56	12	17
A/c	0	0	0
A/c-SO$_4$	93	86	95
A/c-PO$_4$	0.7	7	0
ZR/com	n.d.	57	65
β-AlF$_3$	0	0	0
γ-Al$_2$O$_3$	n.d.	2	n.d.

Note. Isomerization of 1-butene to E-/Z-2-butene (T = 100°C, residence time = 1.2 s) and benzoylation of anisole after 7 h at T = 140°C. n.d., not determined.

quite low specific surface area. Obviously, the creation of high surface material does not result in a proportionally enhanced number of acid sites at the surface.

Catalytic Properties

Two reactions were used to evaluate the catalytic activity of the modified and unmodified zirconia samples: the isomerization of 1-butene to E/Z-2-butene and the benzoylation of anisole to 4- and 2-methoxybenzophenone. The double-bond isomerization of 1-butene depends on the presence of Brønsted acid sites. At relatively low temperatures (100°C) E/Z-2-butene is the only product. This test reaction was consequently used in order to characterize the Brønsted acidity. The reaction between benzoyl chloride or benzoic anhydride with anisole is of some applicational interest. Friedel–Crafts reactions are commonly considered to be Lewis acid catalyzed reactions, but principally they can occur at Brønsted sites (H_2SO_4, CF_3SO_3H), too (3–6).

The results of the double-bond isomerization of 1-butene are given in Table 4. Regarding this reaction, unmodified zirconia is catalytically inactive. This fact does not depend on the preparation conditions like the calcination temperature or the procedure of synthesis (aerogel synthesis providing high specific surface area samples). The phosphate modified zirconia aerogel is also catalytically inactive. In contrast, all of the sulfur containing samples catalyze the isomerization of butene. Best results were obtained using the sulfated zirconia samples: the sulfated aerogel A/c-SO$_4$, the ammonium sulfite (ZR/amSO$_3$), and ammonium sulfate treated samples (ZR/amSO$_4$ and ZR/c-amSO$_4$). But even the SF$_4$ modified zirconia was a good catalyst for this reaction due to its very large amount of Brønsted sites detected by FTIR spectroscopy.

All catalyst samples were also tested in the benzoylation of anisole. The conversion degrees of the reaction between benzoyl chloride or benzoic anhydride and anisole forming *p*- and *o*-methoxybenzophenone are shown in Table 4. The commercial catalyst ZR/com and the solid Lewis acids β-AlF$_3$ and γ-Al$_2$O$_3$ were also included for comparison. Again all pure zirconia samples (ZR/1, ZR/c1, ZR/c2, and A/c) were catalytically inactive regarding the acylation reaction. Only little activity was observed using the phosphated zirconia aerogel A/c-PO$_4$ (in case of the acyl chloride) as well as the samples ZR/SOCl$_2$ and ZR/SF$_4$. Best results were obtained using the sulfated zirconia aerogel. The sulfated and the sulfited zirconia were also very good catalysts, depending somehow on the kind of the acylating agent. The ZR/com sample showed a conversion of about 60% under the conditions used. Finally, some of our samples have the same or a better catalytic activity regarding the benzoylation of anisole than the commercially available catalyst.

AlF$_3$ and Al$_2$O$_3$ were hardly or not able to catalyze the Friedel–Crafts acylation under the same conditions. Both comparative samples exhibit only Lewis acidity.

The dependency of the conversion degree of the acylation reaction on the time and on the reaction temperature was investigated for some representative zirconia samples. Figure 3 illustrates the conversion degree in dependence on the time of reaction employing the ZR/com sample and the

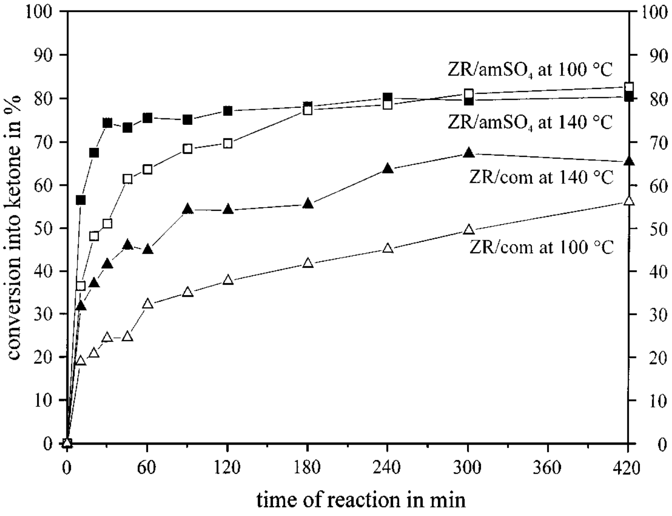


FIG. 3. Reaction between anisole and bezoic anhydride on ammonium sulfate modified zirconia ZR/amSO$_4$ in relation to Zr/com catalyst: dependency of the conversion degree on the reaction time at two different temperatures.

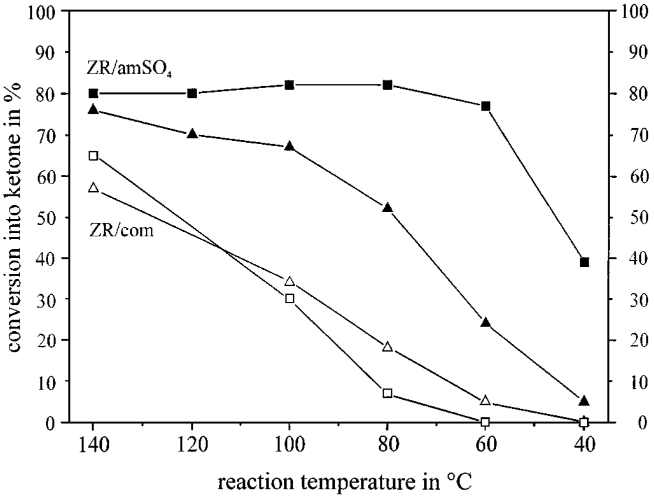


FIG. 4. Benzoylation of anisole on ammonium sulfate modified zirconia ZR/amSO_4 in relation to Zr/com catalyst: dependency of the conversion degree on the temperature after 7 h reaction time, using benzoic anhydride (■ and □) and benzoyl chloride (▲ and △) and anisole as reagents.

ammonium sulfate modified zirconia ZR/amSO_4. The reaction between benzoic anhydride, commonly considered to be less reactive in relation to benzoyl chloride, and anisole was carried out at 100 and 140°C, respectively. ZR/amSO_4 results in a higher yield of ketones at both temperatures than the ZR/com catalyst. High conversion degrees were already achieved for the ZR/amSO_4 sample after 2 (140°C) or 3 h (100°C) reaction time. Using the ZR/com catalyst, at least 4 h at 140°C were necessary to get similar yields of the ketone.

The ZR/amSO_4 catalyst is also able to catalyze the benzoylation of anisole at lower temperatures. Figure 4 shows the conversion results in dependence on the reaction temperature after 7 h. It is remarkable that, particularly when using the acid anhydride in the reaction, the conversion degree is still very high at 60°C only. For example, the ZR/com catalyst yields, even at 80°C, only about 18% using benzoyl chloride and only 7% if the anhydride is used for the acylation reaction. Therefore, the ketone yields are constantly higher for the ZR/amSO_4 catalyst than in the case of the ZR/com catalyst.

DISCUSSION

Surface and Bulk Properties of the Zirconia Samples

Due to the variety of modification reagents zirconia samples with quite different properties were synthesized and tested. Two preparation methods (standard and aerogel synthesis) and the different modification reagents influence not only the bulk properties but also the acidity of the samples and, therefore, their applicability as solid acid catalysts.

As expected, pure zirconia crystallizes in the monoclinic modification, exhibiting a comparatively low BET surface area (cf. Table 1). On the contrary, modifying $Zr(OH)_4$ with solid ammonium sulfate or sulfite results in the tetragonal crystallized modification with a larger surface area. Probably, the presence of sulfate or related compounds prevents the zirconia from an undisturbed crystallization and from a decrease of the specific surface area. The modification with gaseous reagents like $SOCl_2$ or SF_4 at 150°C leads to the formation of amorphous materials.

Similar results were obtained with the aerogel phases. All samples are less crystalline (tetragonal zirconia) and exhibit a large specific surface area after the first thermal treatment at 300°C. Again, the pure zirconia aerogel contains some monoclinic components after the calcination step, whereas the modification prevents it from a transformation, as was already found by Ward and Ko (13), who investigated extensively the dependencies of aerogel properties on several synthesis parameters. Even after calcination pure zirconia aerogel exhibits a quite large BET surface area of about 140 m^2/g as opposed to ZR/c1 and ZR/c2 which show only about 40 m^2/g. The specific surface areas of the calcined sulfated aerogels are, despite the 50 K higher temperature, in the same range as those for the modified zirconia samples ZR/amSO_4 and ZR/amSO_3 (140 m^2/g). The phosphated zirconia aerogel reveals a very high BET surface area of 267 m^2/g after a calcination at 500°C.

It is remarkable that the samples ZR/amSO_4 and ZR/amSO_3 exhibit very similar properties. Their powder diffraction patterns are equal and also the sulfur contents and BET surface areas, respectively, are the same. Identical FTIR spectra and similar results for the ammonia desorption were obtained. The catalytic activities are comparable, too. These two samples were modified using solid ammonium salts: the sulfate in the case of ZR/amSO_4 and the sulfite in the case of ZR/amSO_3. We suppose the reason for these similarities is an oxidation of the sulfite (S^{IV}) resulting in the formation of surface sulfate (S^{VI}). This is very probable under the conditions used for the sample preparation (calcination at high temperatures in presence of air). Evaluation of the XPS measurements gave some interesting effects (Fig. 5). Irrespective of their preparation with $SOCl_2$ (ZR/$SOCl_2$), SO_3^{2-} (ZR/amSO_3), and SO_4^{2-} (ZR/amSO_4), the sulfur signal shows a peak position of S^{VI}; that means an oxidation of a lower valent sulfur species. In contrast, a modification with SF_4 (ZR/SF_4) did not reveal any change of the binding energy of sulfur, showing clearly that no oxidation happened under these conditions.

The $(NH_4)_2SO_3$-modified sample ZR/amSO_3 shows a significant shift of its XPS Zr 3d signal to higher binding energies, in comparison with the signal of unmodified ZrO_2. The same experimental results were achieved using $SOCl_2$ and SF_4, respectively, as modifying agents. In contrast, the

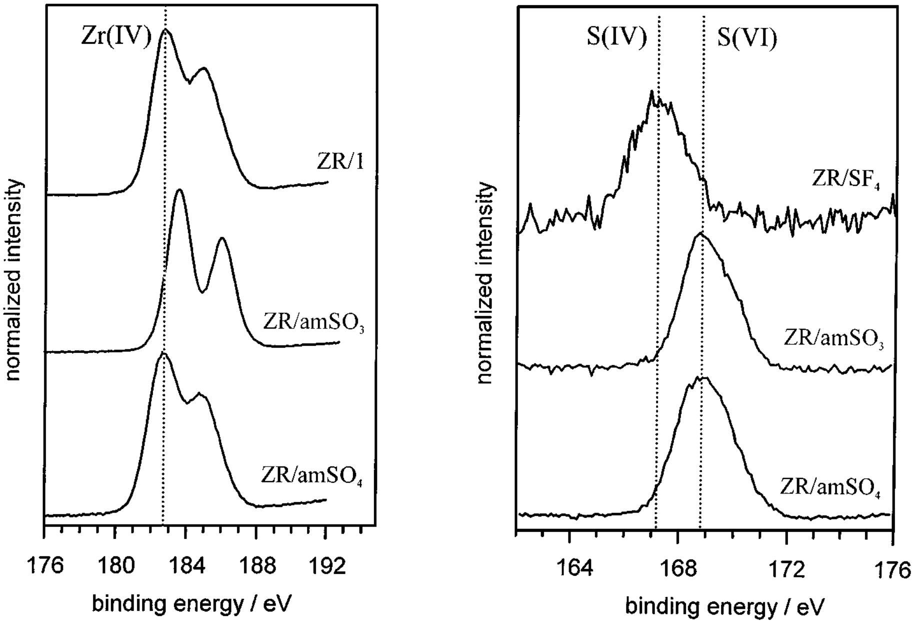


FIG. 5. Selected XP spectra of pure and surface modified zirconia catalysts, given in arbitrary units: left, Zr 3d signal; right, S 2p signal. Dotted lines give the peak positions of typical Zr(IV), S(IV), and S(VI) compounds, respectively.

$(NH_4)_2SO_4$-modified sample has the same peak position like unmodified zirconia. The peak shift to higher binding energies is an indication for a lower electron density at the surface zirconium atoms, tantamount to a higher acidity at the surface.

The FTIR photoacoustic spectra of the pyridine adsorbate complexes (cf. Fig. 1) of the modified samples ZR/$SOCl_2$ and ZR/SF_4 show a very large amount of Brønsted acid sites. Unfortunately, a distinct determination of the acid strength by ammonia TPD was impossible due to their preparation at 150°C only. During heating the release of hydrogen halides (HX) was observed. It is not entirely clear whether adsorbed HX is already present at the surface, formed by the reaction of SF_4 and $SOCl_2$ with surface hydroxyl groups during the treatment, or if it will be formed as a result of hydrolysis of Zr–X bonds during calcination. Water for hydrolysis can be originated either by desorption or from surface hydroxyl groups. Therefore, both adsorbed HX and surface OH groups cause a high concentration of Brønsted acid sites.

Whereas HCl is commonly more weakly adsorbed at surface sites, HF should result in stronger bonded surface complexes being consequently able to contribute to the surface Brønsted acidity of these samples. However, it represents only a weak Brønsted acid. Even the lower catalytic activity of these samples in the butene isomerization (ZR/SF_4, about 56%) and in the acylation reaction (only about 15%) is obvious on this basis because adsorbed HF should exhibit a lower acidity than sulfate species on the surface, although the overall concentration of Brønsted acid sites is very large.

A Correlation between Brønsted Acid Sites and the Catalytic Activity

Figure 6 illustrates the dependencies of the observed conversion degrees of the isomerization of 1-butene on the kind and the amount of acid sites of the solids. The sample ZR/SF_4 is not plotted in this figure because of its very high overall Brønsted acidity mainly influenced by adsorbed HF, as discussed above. For comparison, the data for this sample are: LZ, 0; BZ, 64; conversion of 1-butene, 56%.

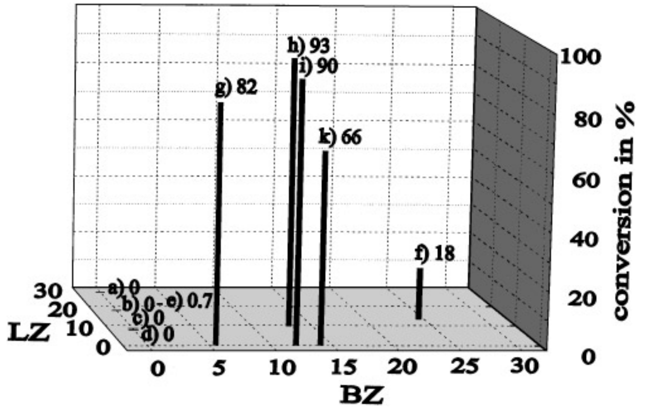


FIG. 6. Conversion degrees for the butene isomerization in a Lewis versus Brønsted acidity presentation. The conversion degrees are reflected by the height of the columns, whereas the acidic properties define the position of zirconia samples: (a) A/c; (b) ZR/1; (c) ZR/c2; (d) ZR/c1; (e) A/c-PO_4; (f) ZR/$SOCl_2$; (g) ZR/c-amSO_4; (h) A/c-SO_4; (i) ZR/amSO_3; (k) ZR/amSO_4.

All samples which have only Lewis acid sites are unable to catalyze the isomerization reaction (points on the left-hand side of Fig. 6). As expected, all samples with Brønsted acid sites are good catalysts for the butene isomerization (columns on the right-hand side), as was also reported by Ward and Ko (14, 15). On this basis it is possible now to summarize all zirconia samples in three groups:

Group A. Samples with little or no Brønsted acidity, catalytically inactive:

all unmodified zirconia samples: ZR/1, ZR/c1, ZR/c2
the unmodified and the phosphated aerogels: A/c and A/c-PO_4;

Group B. Samples with a medium concentration of Brønsted acidity, catalytically very active:

the sulfated and sulfited zirconia samples: ZR/amSO_4, ZR/amSO_3, ZR/c-amSO_4
the sulfated aerogel: A/c-SO_4;

Group C. Samples with a very high concentration of Brønsted acidity due to adsorbed HX, only medium catalytic activity:

SF_4- and $SOCl_2$-modified zirconia samples: ZR/SF_4, ZR/$SOCl_2$. These two samples are amorphous at 150°C; HX molecules are adsorbed at the surface, generating the large amount of Brønsted acidity in the FTIR spectra. The calcination leads in the case of the ZR/SF_4 sample, for instance, to a ZrO_xF_y phase. Consequently, the samples ZR/SF_4 and ZR/$SOCl_2$ can be considered to belong to a different category of materials.

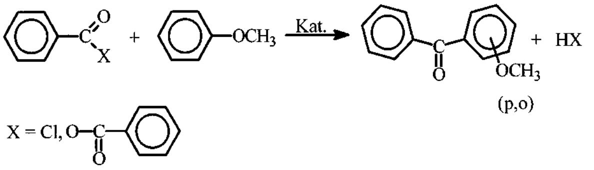
The kind of crystallization of zirconia is not so important for this classification. Whereas most of the monoclinic zirconia samples are to be found in group A, there is also one monoclinic sulfated zirconia (ZR/c-amSO_4) in group B. The tetragonal crystallized sample A/c-PO_4 is not arranged in group B of the catalytically very active samples but in group A. That means that the priority impact of (sulfate) modification is not the formation of a tetragonal crystallized zirconia bulk. The formation of strong acidic surface sites is the most important impact of the sulfation process.

Although sample ZR/c-amSO_4 possess a small amount of Brønsted sites—on the basis of photoacoustic spectroscopy—it belongs to the catalytically very active samples. This can be explained by its comparatively small surface area (about 29 m^2) and the limited sensitivity of photoacoustic spectroscopy being obviously not sufficient enough to detect this small absolute amount of acid sites. However, the TPD-profile clearly indicates the strong acidity of the surface of this sample.

The TPD measurements should also be interpreted in categories of these groups with distinct differences in the ammonia desorption profiles. Comparing the normalized profiles of the samples from groups A and B there are two main differences (cf. Fig. 2). The ammonia desorption profiles of all catalytically active samples of the second group exhibit two maxima. For the inactive samples of group A, there is only one maximum being broader and located with the peak maximum at slightly lower temperatures. Additionally, the profiles are not differentiated evidently. More important, in relation to group A samples more ammonia is desorbed at higher temperatures (about 500°C) from those catalysts which belong to group B. Therefore, the catalytically active samples possess a higher number of strong acid sites in comparison with the unmodified nonactive samples. Generally, it was impossible to carry out TPD measurements on samples of group C.

The Benzoylation of Anisole

The reaction between anisole and benzoic anhydride or benzoyl chloride was investigated (Eq. [1]).



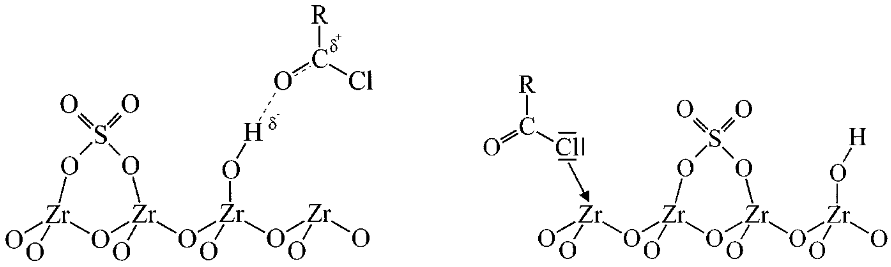
[1]

The conversion degrees obtained in the acylation reaction are widely spread. In contrast to Patil *et al.* (23), all pure zirconia samples are catalytically inactive with respect to the acylation reaction. Using the phosphated zirconia aerogel, as well as the $SOCl_2$- and SF_4-modified zirconia samples, only low activity was observed. The ammonium sulfite (ZR/amSO_3) and sulfate (ZR/c-amSO_4) modified zirconia samples possess a medium catalytic activity. The conversion raised to about 80%, employing the sulfated samples A/c-SO_4 and ZR/amSO_4 as catalysts: The sulfated zirconia aerogel was the best catalyst due to its high concentration of strong Brønsted acid sites combined with a large BET area. The modification of $Zr(OH)_4$ with solid ammonium sulfate resulted also in a very effective catalyst sample.

Applied to the benzoylation of anisole, some of the investigated samples have the same or better catalytic activity than the ZR/com catalyst, showing only conversion degrees of about 60%. Even in comparison with ZR/com, also, considerably higher conversion degrees were achieved using the ZR/amSO_4 sample at lower temperatures and shorter reaction times (due to faster kinetics).

The test reaction used is classified as Friedel–Crafts acylation. Two possible mechanisms of activation are presented in Scheme 1. The benzoic compound may be activated on both Brønsted and Lewis acid sites.

High catalytic activity in the acylation reaction was observed for the samples that show high conversion degrees in the butene isomerization reaction, too. Therefore, it can be concluded that both reactions, the isomerization of 1-butene as a test reaction for Brønsted acidity and the



SCHEME 1. Proposed model for the catalytic action of a sulfated zirconia surface (activation at both Brønsted and Lewis acid sites). The surface sulfate was drawn in simplified terms as chelating bidentate sulfate only.

acylation, take place on the same kind of acid sites of the zirconia samples used. This clearly indicates the dominating impact of Brønsted acid sites for the benzoylation of anisole using modified zirconia as a heterogeneous catalyst. If the isomerization of 1-butene and the Friedel–Crafts acylation proceed at the same kind of acid sites of similar strength, both conversion lines should be proportional. Figure 7 illustrates the relation between the conversions of these two reactions. The dashed line (not calculated) was drawn as an optical assistance. A good correlation was found for the conversion degrees of both catalyzed reactions, as a result of obviously similar activation at the catalyst surface.

Therefore, the mechanism of the acylation is supposed as follows: The activation occurs on Lewis or Brønsted acid sites when typical Lewis acids, e.g. $AlCl_3$, or Brønsted acids, e.g. CF_3SO_3H, are employed as catalysts in the homogeneous phase. However, using solid acids (heterogeneous catalysts) like modified solid zirconia the reaction proceeds at Brønsted acid surface sites.

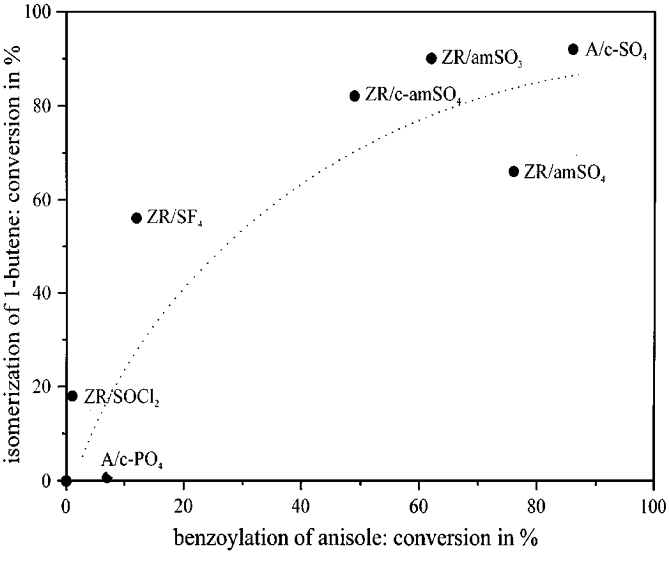


FIG. 7. Dependencies of the conversion degrees of 1-butene isomerization and benzoylation of anisole by benzoyl chloride on different zirconia samples. Zero percent conversion for both reactions: ZR/1, ZR/c1, ZR/c2, and A/c.

The gaschromatographically detected para to ortho ratio of the product isomers is about 94 : 6 for all catalytically active samples investigated here. The same result for the benzoylation reaction was observed in the commonly performed homogeneous catalysis (6).

CONCLUSIONS

Comparing different modifying reagents it can be stated that zirconia kneaded with solid ammonium sulfate or ammonium sulfite generates very high Brønsted acidity at the zirconia surface after a certain calcination procedure. An increased acidity can be achieved using aerogel techniques for the synthesis of sulfated zirconia. Here, a comparatively large BET surface area, combined with a high concentration of Brønsted acid sites has been obtained, resulting in an even slightly higher active phase. All these three sulfated samples yield comparatively high conversion degrees in the employed benzoylation reaction of anisole. Generally, the conversion degrees of the benzoylation exhibits a good correlation for all catalysts investigated with the used probe reaction, the double-bond isomerization of 1-butene. Under the conditions used the above-described benzoylation reaction occurs exclusively on Brønsted acid sites. In contrast, solid Lewis acids showed little or no conversion of the benzoylation agents into the desired aromatic ketones under the applied conditions.

ACKNOWLEDGMENTS

E. Kemnitz and V. Quaschning thank the Verein der Chemischen Industrie (VCI), the Fond der Chemischen Industrie (FCI), and the Bundesministerium für Bildung, Wissenschaft, Forschung, und Technologie (BMBF) for financial support. Assistance in aerogel synthesis by Dr. Tomaz Skapin from the Josef-Stefan-Institute, Ljubljana, is gratefully acknowledged.

REFERENCES

1. Leigh, W. J., Arnold, D. R., Humphreys, R. W. R., and Wong, P. C., *Can. J. Chem.* **58**, 2537 (1980).
2. Popp, F. D., and McEwen, W. E., *Chem. Rev.* **58**, 321 (1958).
3. Merz, G., *Synthesis* 612 (1972).

4. Effenberger, F., and Epple, G., *Angew. Chem.* **84**, 295 (1972).
5. Effenberger, F., Sohn, E., and Epple, G., *Chem. Ber.* **116**, 1195 (1983).
6. Paul, V., Sudalai, A., Daniel, T., and Srinivasan, K. V., *Tetrahedron Lett.* **35**, 2601 (1994).
7. Clark, J. H., and Macquarrie, D. J., *Chem. Soc. Rev.* **25**, 303 (1996).
8. Hino, M., Kobayashi, S., and Arata, K., *J. Am. Chem. Soc.* **101**, 6439 (1979).
9. Hino, M., and Arata, K., *J. Chem. Soc., Chem. Commun.* 851 (1980).
10. Song, X., and Sayari, A., Sulfated Zirconia-Based Strong Solid-Acid Catalysts: Recent Progress: *Catal. Rev.-Sci. Eng.* **38**, 329 (1996).
11. Corma, A., *Current Opinion in Solid State & Material Science* **2**, 63 (1997).
12. Schneider, M., and Baiker, A., Aerogels in Catalysis: *Catal. Rev.-Sci. Eng.* **37**, 515 (1995).
13. Ward, D. A., and Ko, E. I., *J. Catal.* **150**, 18 (1994).
14. Ward, D. A., and Ko, E. I., *Chem. Mater.* **5**, 956 (1993).
15. Ward, D. A., and Ko, E. I., *J. Catal.* **157**, 321 (1995).
16. Morterra, C., Cerrato, G., Pinna, F., and Signoretto, M., *J. Catal.* **157**, 109 (1995).
17. Clearfield, A., Serrette, G. P. D., and Khazi-Syed, A. H., *Catal. Today* **20**, 295 (1994).
18. Hess, A., and Kemnitz, E., *Appl. Catal.* **149**, 373 (1997).
19. Skapin, T., *J. Mater. Chem.* **5**, 1215 (1995).
20. Seel, F., *Angew. Chem.* **76**, 532 (1964).
21. Anthony, M. T., and Seah, M. P., *Surf. Interface Anal.* **6**, 95 (1984).
22. Hess, A., and Kemnitz, E., *J. Catal.* **149**, 449 (1994).
23. Patil, M. L., Jnaneshwara, G. K., Sabde, D. P., Dongare, M. K., Sudalai, A., and Deshpande, V. H., *Tetrahedron Lett.* **38**, 2137 (1997).