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Characterization of the Acid Strength of SiO_2–ZrO_2 Mixed Oxides

H. J. M. Bosman,[1] E. C. Kruissink, J. van der Spoel, and F. van den Brink

Industrial Catalysis Section, DSM Research B.V., P.O. Box 18, 6160 MD Geleen, The Netherlands

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The preparation of SiO_2–ZrO_2 mixed oxides and the single oxides SiO_2 and ZrO_2 from H_2SiF_6 and/or H_2ZrF_6 is described. The catalysts are characterized using Hammett colour indicators, temperature programmed desorption of ammonia, XRD, XPS, and infrared spectroscopy. New IR bands and absence of XRD crystallinity show mixing of SiO_2 and ZrO_2 on an atomic scale in the amorphous coprecipitate. However, as could be concluded from the difference between surface concentrations of Zr and Si measured with XPS and the mean bulk concentrations, the ZrO_2 precipitates somewhat more quickly than SiO_2. The acid strength of the SiO_2–ZrO_2 mixed oxides corresponds to an H_0 value between −11.4 and −13.8 (super-acidity). There is a fair correlation between the surface concentration of strong acid sites, determined from NH_3 TPD, and the performance in the acid catalyzed dehydration of cyclohexanol to cyclohexene. In addition to the concentration of acid sites, their acid strength is an important factor determining the performance of the SiO_2–ZrO_2 catalysts in the dehydration of cyclohexanol. The acid strength needed for the dehydration of cyclohexanol corresponds to $H_0 \leq +2.8$. Chemically mixed SiO_2–ZrO_2 oxides contain strong acid sites as opposed to the single oxides SiO_2 and ZrO_2, which contain only weak acid sites. XPS shows an oxygen depletion on the surface of the mixed oxides, which indicates that the strong acid sites are of the Lewis type. © 1994 Academic Press, Inc.

INTRODUCTION

The preparation and characterization of acidic and basic heterogeneous catalysts has been the subject of many studies. It has generally been recognized that both acidic and basic properties of catalysts and catalyst carriers are of great importance for their use in various processes. Therefore it is interesting to search for relationships between the method of preparation of catalysts, their acid/base strength distribution, and their catalytic activity (1). Insight into acidic and/or basic properties of heterogeneous catalysts may be obtained via test reactions and characterization techniques. A combination of these will hopefully lead to relations between catalyst properties and performance and eventually to an insight into the nature of active sites.

It has long been known that certain mixed oxides show much stronger acidic properties than the single oxides of which they are composed. Examples are SiO_2–Al_2O_3, SiO_2–TiO_2, SiO_2–MgO, and SiO_2–ZrO_2. The mechanism of the generation of strong acidity as a result of chemically mixing oxides has been the subject of many studies. Among the mixed oxides mentioned, the SiO_2–Al_2O_3 system has been studied extensively. This is not so much the case for SiO_2–ZrO_2, first studied by Dzis'ko *et al.* (2, 3) and more recently by others (4, 5–10). In view of the rather incomplete knowledge of the SiO_2–ZrO_2 system we selected it for further investigation.

Preparation of mixed SiO_2–ZrO_2 samples is, according to the literature, often performed by hydrolysis of solutions of tetraethylorthosilicate (TEOS) and zirconyl chloride or zirconyl nitrate in ethanol or in ethanol/water mixtures. The hydrolysis conditions used are not always described extensively. When a homogeneously mixed oxide is desired, the use of the starting materials mentioned might pose a problem, because of their difference in reactivity. Addition of caustic soda to zirconyl salts results in fast hydrolysis and condensation–polymerization, starting already at pH values as low as 1–2 (11). The rate of silica precipitation from TEOS is strongly pH dependent, since both hydrolysis and condensation–polymerization are catalyzed by acids and bases. Also, concentrations of TEOS and water have a significant influence on the kinetics of these reactions. For many conditions, in particular for intermediate pH values, the rate of silica precipitation will be considerably lower than the rate of zirconia precipitation from zirconyl salts.

In our work we use a totally different method. Following the idea that fluorozirconate ions might be less reactive than zirconyl ions, we investigated the precipitation of zirconia from H_2ZrF_6 solution, and compared this to the precipitation of silica from H_2SiF_6 solution (see Results and Discussion). Indeed H_2ZrF_6 appears less reactive than zirconyl nitrate (as follows from the significantly higher pH of 4.2 where precipitation starts). Moreover, reactivities of H_2SiF_6 and H_2ZrF_6 are not very different. Thus the use of mixed H_2SiF_6 and H_2ZrF_6 solutions for the preparation of mixed SiO_2–ZrO_2 oxides seems very suitable.

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[1] To whom correspondence should be addressed.

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In this study we describe the preparation of SiO_2–ZrO_2 mixed oxide catalysts with varying Si/Zr ratios from H_2SiF_6 and H_2ZrF_6. The catalysts thus prepared are characterized using adsorption of basic colour indicators, NH_3 TPD, BET measurements, diffuse reflectance infrared spectroscopy (DRIFTS), XRD, and XPS. Their catalytic properties are studied in the dehydration of cyclohexanol, a well known test reaction for acid catalysts (12–14). A relationship between the acid amount determined by NH_3 TPD and activity in the test reaction is established. An insight into the nature of the acid sites can be obtained using XPS. Finally, the applicability of the models of Tanabe *et al.* (15) and Kung (16) on the generation of acidity in mixed oxides to our SiO_2–ZrO_2 catalyst is discussed.

EXPERIMENTAL

Preparation of Catalysts

Mixed and single oxides are prepared from aqueous solutions of H_2SiF_6 and/or H_2ZrF_6. A very pure, aqueous H_2SiF_6 solution, with a concentration of 3.0 wt% Si (resulting in 64 g of dry SiO_2 per kg solution) is prepared from a 40 wt% H_2SiF_6 solution obtained from Kemira Fertilizers (Pernis, The Netherlands, the former UKF Pernis). This is achieved using concentrated H_2SO_4 to set free SiF_4 and HF gas at 393–423 K. The gases are subsequently readsorbed in very pure water (demineralized water is purified using a Millipore system, resulting in a specific resistance > 18 Mohm · cm). Silica precipitated from this pure H_2SiF_6 solution contains typically < 1 ppm Fe, <1 ppm Ca, and <1 ppm Na as measured by atomic absorption spectroscopy, whereas silica precipitated from the unpurified H_2SiF_6 solution normally contains about 300–600 ppm Ca, about 40 ppm Fe, and about 20 ppm Na.

In preliminary experiments zirconium-containing solutions were obtained by dissolving (hydrous) zirconia in aqueous HF solution. Zirconium is most probably present as H_2ZrF_6 in such solutions (17). In the preparation of the samples discussed in this paper, an alternative procedure is followed consisting of mixing aqueous solutions of zirconyl nitrate and HF.

The following chemicals, all of *pro analysis* quality, are used:

—Zirconyl nitrate [$ZrO(NO_3)_2 \cdot xH_2O$] [14985-18-3] (Ventron).

—HF [7664-39-3] (Merck, 40 wt% aqueous solution).

—Ammonia [7664-41-7] (Baker, 25 wt% aqueous solution).

Mixed oxides SiO_2–ZrO_2 and the single oxides SiO_2 and ZrO_2 are prepared by (co-)precipitation at a constant pH of 9.0, at 300 K. To this end a thermostated, double-walled glass reactor is used with a volume of 1 dm^3 (height = 0.16 m, diameter = 0.09 m), provided with baffles and turbine stirrer. Before preparation, 500 ml of water is introduced into the reactor. Then two solutions, with a volume of 250 ml each, one containing H_2SiF_6 and H_2ZrF_6 and the other containing NH_3 made up from a 25 wt% stock solution, are pumped simultaneously into the reactor. The Si- and/or Zr-containing solution is made up from the pure H_2SiF_6 solution mentioned above, zirconyl nitrate, 40 wt% HF solution, and water in such proportions to obtain the desired ratio of SiO_2 to ZrO_2, and a concentration of SiO_2–ZrO_2 solids in the final suspension of about 20 g/dm^3. Some samples were prepared under more dilute conditions, but these samples were not investigated as catalysts. The addition of the solutions takes about half an hour. The pH is kept constant by adjusting the flow rate of the basic solution. The reaction mixture is vigorously stirred, at a rate of 260 rpm.

The solids are filtered and washed with water, using a Buchner funnel. Preliminary experiments showed that, after using 5 dm^3 of water, the pH of the filtrate has passed a maximum of about 9.5 to 10 and attains a value of 9.0. A larger quantity of washing water results only in a very slow further decrease of the pH of the filtrate. For this reason a standard amount of 5 dm^3 water is used. After washing, the solids are dried at 373 K under vacuum for 16 h and calcined in air at the desired temperature (573 K or 773 K, heating rate 1 K/min) in a Carbolite GPF-2 calcination furnace. The catalysts are coded Si_xZr_y, in which x and y give the amount (in weight percent) of SiO_2 and ZrO_2, respectively.

One mechanically mixed SiO_2–ZrO_2 oxide (SiO_2–ZrO_2 50/50 coded $Si_{50}Zr_{50}^*$, prepared by intense mixing of the single oxides in a mortar at room temperature) is also incorporated in the characterization study.

BET Surface Area and Pore Volume

The total (BET) surface area of a catalyst is determined from physical adsorption of N_2 at $T = 78$ K, by applying the BET equation on the part of the adsorption isotherm with $0.05 \leq p/p_0 \leq 0.35$, measured in a Micromeritics Digisorb 2600 apparatus. From the complete adsorption and desorption experiment a pore volume distribution and total pore volume can be derived by applying the Kelvin equation at $p/p_0 = 0.99$.

Acid Strength Determination with Basic Indicators

Acid strength measurements of the SiO_2–ZrO_2 catalysts are performed on samples which are calcined in air at 573 K for 50 h. A small portion of the catalyst (~0.1 g) is transferred directly from the calcination furnace to a tube and immediately contacted with water-free isooctane (dried on mol sieve 4A). About 2 ml of the indicator solution (containing ~0.2 mg of indicator) is added to the suspension. The colour of the indicator on the catalyst surface appears within a few seconds, and is noted.

The following basic indicators are used (1, 18):

—α-naphthyl red (4-phenylazo-1-naphthylamine, Aldrich), $pK_a = +4.0$.

—4-aminoazobenzene (4-phenylazoaniline [60-09-3], Aldrich, 98 wt%), $pK_a = +2.8$.

—Crystal Violet [548-62-9] (Aldrich), $pK_a = +0.8$.

—dicinnamalacetone [622-21-9] (Aldrich, 98 wt%), $pK_a = -3.0$.

—anthraquinone [84-65-1] (Aldrich, 97 wt%), $pK_a = -8.2$.

—4-nitrotoluene [99-99-0] (Aldrich, 99 wt%), $pK_a = -11.4$.

—2,4-dinitrotoluene [121-14-2] (Aldrich, 97 wt%), $pK_a = -13.8$.

Ammonia TPD Measurements

Ammonia TPD measurements are performed in a thermobalance (Perkin–Elmer TGS-2). The calcined catalyst samples are recalcined *in situ* at 573 or 773 K in N_2 (flow: 5 liters/h) until constant weight. After cooling in the N_2 flow, NH_3 is adsorbed on the catalyst for 15 min at a temperature of 333 K in a 5 Nl/h flow of 2.5% NH_3 in N_2. The sample is then purged with N_2 for 5 min after which the temperature of the catalyst is raised at 10 K/min up to the calcination temperature. The weight loss of the catalyst sample due to the desorption of NH_3 from the catalyst is measured as a function of temperature. A TPD profile is obtained by plotting the first derivative of the weight loss with respect to temperature.

XRD Measurements

The dried single and mixed oxides are studied by X-ray diffraction, employing a Philips PW 1730 diffractometer equipped with a Cu anode and a nickel filter. The diffractograms are recorded using the Cu$K\alpha$ line ($\lambda = 1.5418$ Å) at $3° < 2\theta < 60°$.

XPS Measurements

X-ray photoelectron spectra of the oxides are recorded on a Leybold MAX 200 apparatus using Mg$K\alpha$ radiation (13 kV, 20 mA) at a pressure of 10^{-9} mbar. Quantitative analysis (19) is carried out using calculated sensitivity factors (correction for photo-ionization cross section (20), spectrometer transmission and electron escape depth).

Infrared Measurements

The infrared spectra are recorded on a Bruker IFS 85 FTIR spectrophotometer equipped with a DTGS detector. A special reaction chamber (Harrick, type HVC-DR2) for *in situ* treatment of the catalysts in combination with a diffuse reflectance attachment (a so-called praying mantis, Harrick, type DRA-2CO) is used. The sample holder can contain about 50 mg of sample and can be heated to temperatures of 973 K (sample temperature is lower). The cell is equipped with KBr windows transparent at wavenumbers down to 310 cm^{-1}. A spectrum is recorded by taking 100 scans at a resolution of 4 cm^{-1}. Samples are made by preparing a 1 : 100 dilution of the catalysts in KBr.

Test Reaction

The experimental set-up for testing the acid catalysts consists of a glass reactor (height = 0.34 m, diameter = 0.017 m) which is filled with 50 mg of catalyst (particle size 0.5 to 1.0 mm) mixed with 1450 mg inert glass beads (particle size 0.5 mm). The reactor can be heated to the desired reaction pretreatment temperature with an electrical furnace (Heraeus oven type RCK 3/30). Pure cyclohexanol ([108-93-0], Janssen Chimica, 99 wt%) is fed to the reactor using a micro-flow pump (Gilson, type 302). The cyclohexanol flow is mixed with N_2 before entering the reactor tube. The feed used in this work consisted of 0.0287 liter cyclohexanol/h and 7.2 Nl N_2/h giving LHSV = 0.575 liter cyclohexanol/g catalyst/h (W/F = 0.18 g h mol^{-1}). The product stream is cooled after the reactor is collected and analyzed gas chromatographically using a 25-m CP-Sil-5 CB on WCOT fused silica column, N_2 as carrier gas and an FID detector.

RESULTS AND DISCUSSION

Precipitation of Catalysts

A H_2ZrF_6 solution can be prepared by dissolving hydrous zirconia in an aqueous HF solution (17). We found that, when ammonia is added to the acid solution and the pH is recorded, small white "flocs" are observed starting at a pH value of 4.2. When the pH is raised further an increasingly turbid, white suspension is obtained. The precipitation is similar to that of SiO_2 from a H_2SiF_6 solution. From H_2SiF_6 solutions of approximately the same concentration, formation of white flocs occurs at a slightly higher pH of about 5. This similarity suggests that mixed H_2SiF_6–H_2ZrF_6 solutions could be a good starting material for the preparation of mixed SiO_2–ZrO_2 oxides.

In the experiments mentioned above we prepared H_2ZrF_6 from hydrous zirconia which is precipitated by addition of ammonia to zirconyl nitrate. We found that an acid obtained by direct mixing of solutions of zirconyl nitrate and HF produces the same titration curve upon addition of ammonia as the H_2ZrF_6 solution mentioned above. Also, the resulting product shows roughly the same properties (BET). Thus, in preparing the mixed oxides, we use a H_2ZrF_6 solution prepared from zirconyl nitrate and HF.

The precipitate appears easily filtrable for concentrations of solids in the final suspension of >8 g/liter; for lower concentrations a very gelatinous product is obtained which is difficult to separate and wash. Such precipitates also show, after drying and calcining, much higher BET surface areas. Probably these observations can be explained by considering the influence of the fluoride concentration, corresponding to the solids concentration, on coagulation kinetics. The concentration of solids mentioned above corresponds to a fluoride concentration of 0.6 *M*. For silica particles (diameter of about 15 nm), Allen and Matijevic (21) found a critical coagulation concentration (c.c.c.) of 0.8 *M* NaCl at pH = 8.7. The c.c.c. is the electrolyte concentration for which coagulation is just observable after a specified time, being 1 h for the particular case cited here; above this concentration the rate of coagulation increases strongly with electrolyte concentration. We performed similar measurements using NH_4F, and found a c.c.c. of 0.6 *M* for the same pH and time. No data are available on the coagulation kinetics of mixed SiO_2–ZrO_2 oxides, but the trends will be similar. Thus for NH_4F concentrations >0.6 *M* the rate of coagulation will be significantly higher than for concentrations below this value, resulting in much larger particles and better filtrability. After calcination at 573 or 773 K in air all catalysts are obtained as white solids.

BET Surface Area and Pore Volume

Table 1 gives the BET specific surface areas and pore volumes of the catalysts calcined at 573 and 773 K. The Si_0Zr_{100} sample has a very low BET surface area of 12–22 m^2/g. In the literature BET surface areas of 14 to 120 m^2/g are reported for ZrO_2 (1, 4, 10, 22) depending on the precipitation procedure. The BET surface areas of the mixed oxides and pure SiO_2 are roughly in the same range of 118–154 m^2/g for the catalysts calcined at 573 K but they show lower values of 103–131 m^2/g if calcined at 773 K. The $Si_{50}Zr_{50}$ sample is an exception to this rule and shows a significantly lower surface area. We will demonstrate below that chemical and catalytic properties of this sample are deviating, too.

Acid Strength Measurements Using Basic Indicators

Table 2 lists colours of the basic indicators on the SiO_2–ZrO_2 catalyst surfaces. From the table it is clear that not all the colour changes observed are in agreement with the changes reported by Walling (23) or Tanabe *et al.* (1). The observation of a colour on the surface of a catalyst cannot be completely objective. Some indicators give more intense colours, e.g., Methyl Red showing a purple colour on the acid sites of SiO_2–ZrO_2 mixed oxides instead of the red colour indicated by Walling (23). The orange colour of Methyl Red on SiO_2 probably indicates that a small amount of acid sites of $H_0 < +4.0$ are present, but aminoazobenzene ($pK_a = +2.8$) shows its basic colour. Furthermore, 4-nitrotoluene shows a change of colour from white to pink when comparing the $Si_{100}Zr_0$ and $Si_{87}Zr_{13}$ catalyst. It is presumed that the colour of 4-nitrotoluene on the acid sites of SiO_2–ZrO_2 mixed oxides is pink instead of yellow as reported by Tanabe *et al.* (1).

TABLE 1

Texture Data of the Synthesized SiO_2–ZrO_2 Catalysts

Catalyst code	BET-surface (573 K) (m^2/g)	BET-surface (773 K) (m^2/g)	Pore volume (573 K) (ml/g)
$Si_{100}Zr_0$	120	105	0.515
$Si_{87}Zr_{13}$	154	117	
$Si_{75}Zr_{25}$	119	131	0.438
$Si_{50}Zr_{50}$	69	42	0.320
$Si_{25}Zr_{75}$	118	103	
Si_0Zr_{100}	22	12	0.093

Note. Pretreatment temperatures are given between brackets. Pore volumes are given at $p/p_0 = 0.99$.

When observing the colours of Methyl Red adsorbed on different catalysts it is clear that acidity is generated by chemically incorporating ZrO_2 in a SiO_2 matrix. Pure SiO_2 has no acid sites with a strength of +2.8 or stronger, but pure ZrO_2 contains some weak acid sites as indicated by the dark red colour of adsorbed Methyl Red. Aminoazobenzene colours orange on ZrO_2 indicating a small amount of acid sites having $H_0 \leq +2.8$, but Crystal Violet ($pK_a = 0.8$) is adsorbed in its basic form. Anthraquinone shows its acid colour when adsorbed on all the mixed oxides. This indicates acid sites with a strength ≤ -8.2. Presumably the acid sites on our SiO_2–ZrO_2 mixed oxides even have a strength ≤ -11.4 if the colour of 4-nitrotoluene adsorbed on strong acid sites is pink.

The highest acid strength reported for pure ZrO_2 is $H_0 = +1.5$ (1, 24), whereas for SiO_2 an acid strength of $\sim +7.1$ to $+3.3$ (1, 24) is given, depending on the precipitation procedure. Our results on the pure oxides are in line with these reported acid strengths. For SiO_2–ZrO_2 mixed oxides the highest acid strength reported is -8.2 (2). We have found that the strength of the acid sites of our mixed oxides may even be as high as $-11.4 < H_0 < -13.8$. This may be due to the different precipitation procedures. As we will demonstrate, this low H_0 value most probably does not result from residual fluorine in the catalysts but from the intrinsic properties of our SiO_2–ZrO_2 mixed oxides.

Ammonia TPD Experiments

In Figs. 1 and 2 the ammonia TPD profiles (first derivative of weight loss with respect to temperature) are given

TABLE 2

Acid Strength Determination of the Various SiO_2–ZrO_2 Catalysts Measured by Adsorption of Basic Indicators

Indicator	pK_a	Colour according to Refs. (1, 23)		Colour on catalyst					
		Acid	Basic	$Si_{100}Zr_0$	$Si_{87}Zr_{13}$	$Si_{75}Zr_{25}$	$Si_{50}Zr_{50}$	$Si_{25}Zr_{75}$	Si_0Zr_{100}
Methyl Red	+4.0	Red	Yellow	Orange	Purple	Purple	Purple	Purple	D. red
Aminoazobenzene	+2.8	Red	Yellow	Yellow	Red	Red	Red	Red	Orange
Crystal Violet	+0.8	Yellow	Blue	White	Yellow	Yellow	L. yell	White	White
Dicinnamalacetone	−3.0	Red	Yellow	Yellow	Orange	Red	Orange	Orange	Yellow
Anthraquinone	−8.2	Yellow	Colourless	White	Yellow	L. yell	L. yell	L. yell	White
4-Nitrotoluene	−11.4	Yellow	Colourless	White	Pink	Pink	Pink	Pink	White
2,4-Dinitrotoluene	−13.8	Yellow	Colourless	White	White	White	White	White	White

for the series of catalysts calcined at 573 and at 773 K, respectively. From Figs. 1 and 2 it can be seen that all catalysts contain both weakly and more strongly bound ammonia. The peak at $T < \sim 450$ K is due to physically adsorbed and/or weakly chemisorbed ammonia, whereas the peak at $T > \sim 450$ K is assigned to strongly chemisorbed ammonia. For all mixed oxides the maximum of this peak is found at ~520–550 K with the exception of the $Si_{50}Zr_{50}$ sample, which has a maximum at ~670 K as can be seen in Fig. 2.

Table 3 gives the amount of strong acid sites (i.e., the amount of NH_3 adsorbed on the catalysts at 450 K in the TPD) on the various catalysts calcined at 573 K. Pure SiO_2 contains hardly any strong acid sites. ZrO_2 contains 0.06 mmol/g of strong acid sites, which is in accordance with measurements of Shibita *et al.* (24), who reported 0.06 mmol/g acid sites having an $H_0 \leq +1.5$ and 0.28 mmol/g for acid sites having an $H_0 \leq +4.0$. The strong acid site density, however, is higher on our ZrO_2. Shibita *et al.* reported a density of strong acid sites of 0.5 per nm^2 and our ZrO_2 contains 1.6 strong acid site per nm^2. The mixed SiO_2–ZrO_2 catalysts prepared in our study contain 3.1–5.0 strong acid sites per nm^2 or 0.44–0.99 mmol/g. Dzis'ko *et al.* (2, 3) reported that their SiO_2–ZrO_2 catalysts contain at most 0.78 acid sites per nm^2, a much lower density than the catalysts prepared in our study.

XRD Measurements

Figure 3 shows the X-ray diffraction patterns of the mixed oxides and of SiO_2. All these samples are X-ray amorphous. In contrast the ZrO_2 sample is crystalline (Fig. 4a). The XRD pattern matches that of the monoclinic mineral baddeleyite (ZrO_2). The mechanically mixed oxide ($Si_{50}Zr^*_{50}$) shows a superposition of reflections of the crystalline ZrO_2 and a broad reflection of amorphous SiO_2 (Fig. 4b).

The maximum of the reflection due to SiO_2 is at $2\theta \sim 22°$ ($d = 3.9$ Å). A second peak next to the SiO_2 reflection appears if the ZrO_2 content in the mixed oxide increases. This indicates that a second amorphous, probably ZrO_2-rich phase is present in the precipitate. At high ZrO_2 contents there is no separate band of amorphous SiO_2 visible. The absence of sharp lines in the ZrO_2-rich mixed

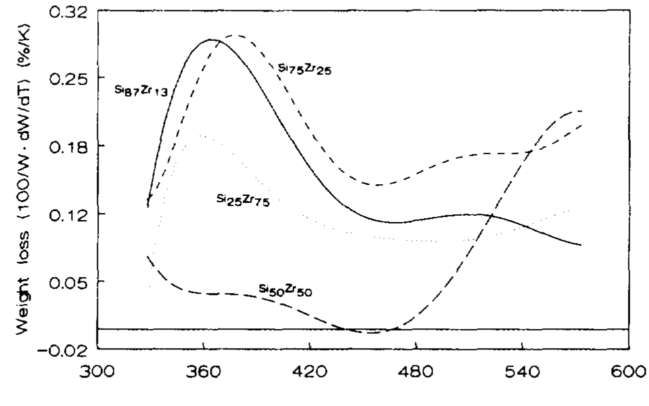

FIG. 1. Ammonia TPD profile of SiO_2–ZrO_2 mixed oxides calcined at 573 K.

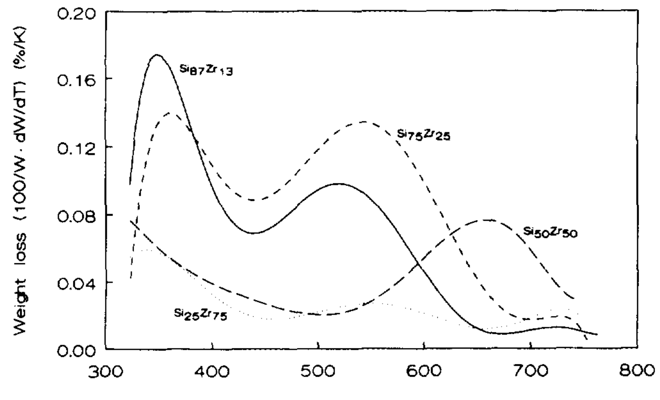

FIG. 2. Ammonia TPD profile of SiO_2–ZrO_2 mixed oxides calcined at 773 K.

TABLE 3

The Concentration of Strong Acid Sites on the SiO_2–ZrO_2 Mixed Oxides Calcined at 573 K (as Determined from the Amount of NH_3 Desorbing at Temperatures >473 K in the TPD)

Catalyst	Amt. NH_3 desorbed (mmol/g)	Concentration of sites (NH_3 molecules/nm^2)
$Si_{100}Zr_0$	0.078	0.39
$Si_{87}Zr_{13}$	0.79	3.06
$Si_{75}Zr_{25}$	0.99	4.97
$Si_{50}Zr_{50}$	0.44	3.85
$Si_{25}Zr_{75}$	0.63	3.18
Si_0Zr_{100}	0.059	1.61

oxide ($Si_{25}Zr_{75}$) indicates that no crystalline (ZrO_2) domains larger than 30–40 Å are present. The presence of more than one broad amorphous band indicates that there is no perfect (random) mixing and that Si/Zr ratios vary locally throughout the oxide. A new weak band at 2*θ* ~ 50° (*d* ~ 1.8 Å) shows up in mixed oxides with a ZrO_2 content larger than 50 wt%. The $Si_{50}Zr_{50}$ sample shows a small sharp peak at 2*θ* = 31°, for which we do not yet have an explanation.

XPS Measurements

XPS is used to determine the surface concentrations of Zr, Si, O, F, N, and C of the catalysts (calcined at 773

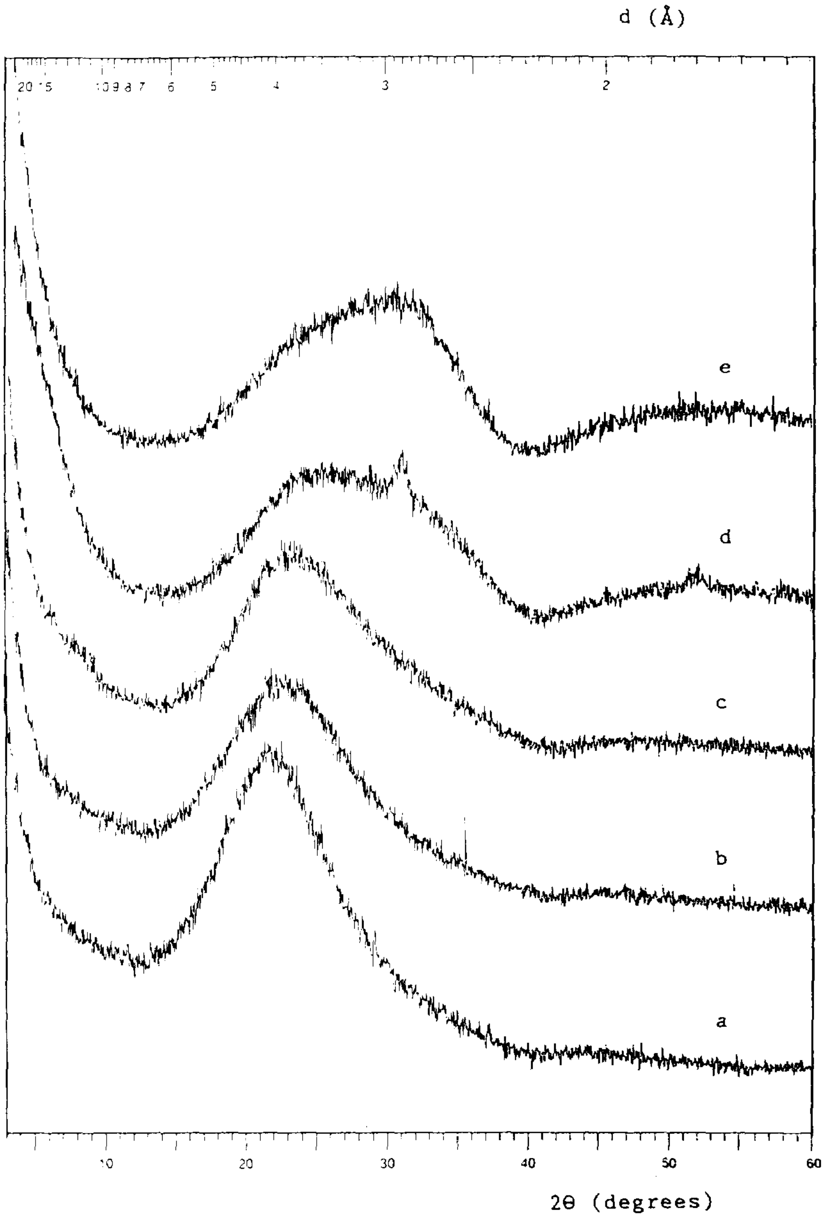

FIG. 3. X-ray diffraction patterns of SiO_2–ZrO_2 chemically mixed oxides and SiO_2. (a) $Si_{100}Zr_0$; (b) $Si_{87}Zr_{13}$; (c) $Si_{75}Zr_{25}$; (d) $Si_{50}Zr_{50}$; (e) $Si_{25}Zr_{75}$.

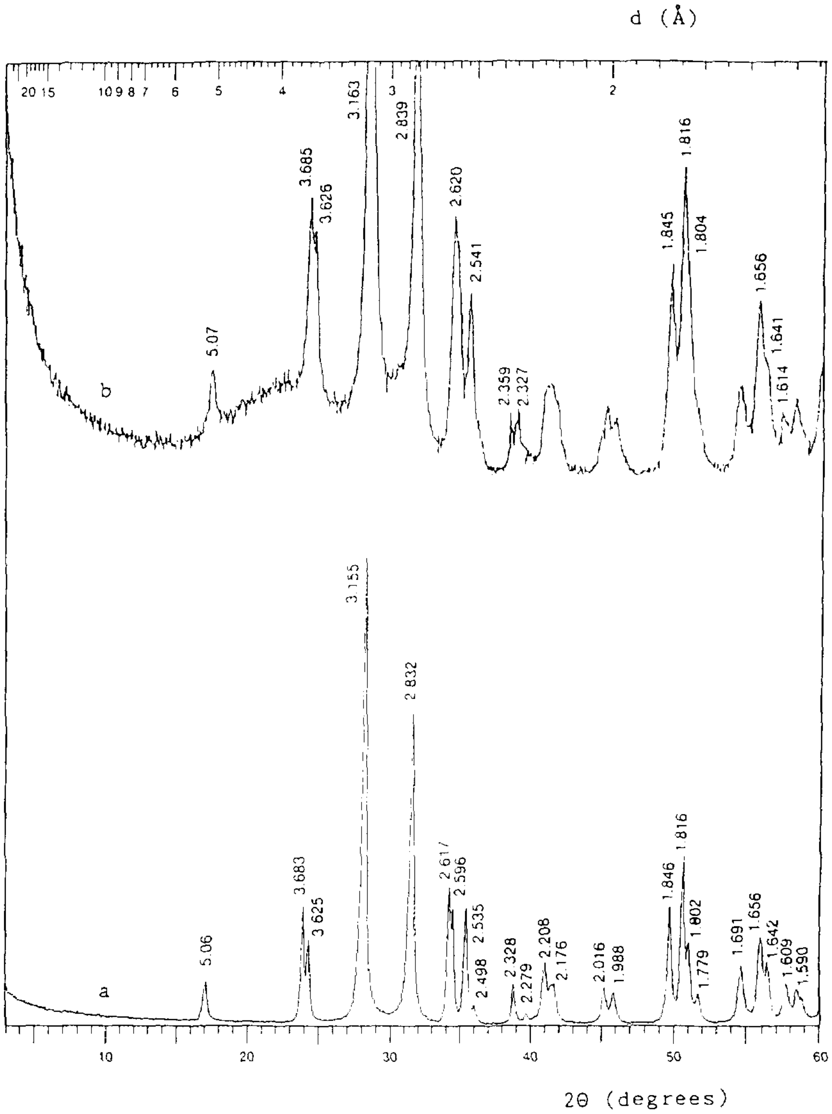

FIG. 4. X-ray diffraction patterns of ZrO_2 and one mechanically mixed oxide. (a) Si_0Zr_{100}; (b) $Si_{50}Zr^*_{50}$.

K). The $Si_{25}Zr_{75}$ sample was also studied before calcination but after drying at 373 K. Figure 5 gives a typical XPS spectrum (of $Si_{25}Zr_{75}$ calcined at 773 K) together with assignments of lines. Table 4 gives quantitative results of the measurements (relative accuracy ±10%).

Comparing the binding energies to those measured by Slinkin *et al.* (5) we find a satisfactory agreement. Setting the C(1*s*) line to 284.6 eV we obtain the following binding energies for the lines measured in the mixed oxides and used for quantification: 183.3–183.5 eV for Zr(3*d* 5/2), 103.3–103.5 eV for Si(2*p*), and 532.4–532.9 eV for O(1*s*). The F(1*s*) signal has a binding energy of approximately 686 eV.

The surface concentration of fluorine is very low (1 at.%). From bulk elemental analysis we learned that the bulk content of fluorine is 0.3 wt% (which equals 0.4–1.4 at.% F, depending on the Si/Zr ratio). Combining the two results leads to the conclusion that the fluorine is evenly distributed throughout the catalysts. The surface content is roughly 0.3–0.4 F per nm^2 (depending on the Si/Zr ratio). The strong acid site density for the mixed oxides is 3–5 per nm^2 (Table 3). The experiments with the Hammett indicators on single SiO_2 and ZrO_2 prepared from H_2SiF_6 and H_2ZrF_6, respectively, show that the acid strengths are comparable to literature values for materials prepared from other sources. Apparently the residual fluorine does not influence the acidity of the single oxides significantly. Therefore we believe that the high values of the acid strength measured on the mixed oxides prepared from mixtures of the fluorides are not caused by residual fluorine but are an intrinsic property of the catalysts.

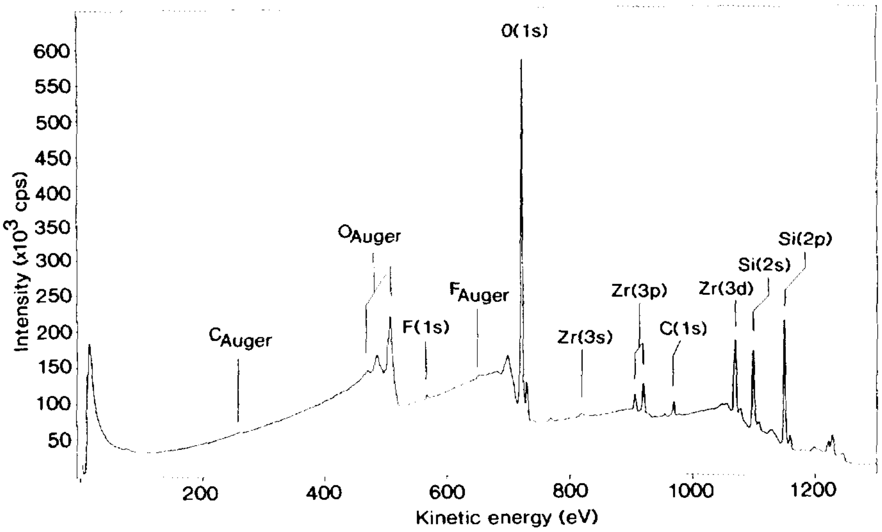

FIG. 5. XPS spectrum of $Si_{75}Zr_{25}$ calcined at 773 K together with band assignments. Spectrum recorded with Mg$K\alpha$ (1253.6 eV).

From the Zr/Si bulk and surface ratios it follows that SiO_2 precipitates more slowly than ZrO_2; the surface is enriched in Si. From an XPS measurement of the uncalcined $Si_{75}Zr_{25}$ compared to the calcined catalyst it becomes clear that calcination does not alter the surface concentrations of Si, Zr, and O to a large extent. The Zr/Si ratio is the same for both samples within the experimental error. Therefore the surface enrichment of Si is mainly due to differences in precipitation rates. This effect is also reported by Slinkin *et al.* (5), who also used XPS. They found that the surface Zr concentration is some 40% below the bulk concentration for catalysts containing up to 15 wt% ZrO_2 prepared from TEOS and $ZrO(NO_3)_2$. We found that the surface Zr concentration is 50–60% of the bulk concentration for catalysts containing up to 50 wt% ZrO_2. The $Si_{25}Zr_{75}$ sample is very poor in Zr on its surface. Here the surface Zr concentration is only 15% of the bulk Zr concentration. Consequently, we must conclude that our precipitation method does not lead to a completely homogeneous distribution of Si and Zr, as we had hoped.

The bulk oxygen concentration in all mixed and single oxides is 66.7 at.% (atomic ratio O/(Si + Zr) equals 2). From the XPS measurements we learn that SiO_2 has a surface oxygen concentration of 69 at.%, in agreement with the bulk concentration. All mixed oxides, however, show a depletion of oxygen at the surface. The average ratio O/(Si + Zr) amounts to 1.5, even for the dried, uncalcined sample. This depletion of oxygen at the surface may well be an indication for strong Lewis acidity of the mixed oxides. The ZrO_2 sample also shows an oxygen depletion at the surface. The O/Zr ratio measured is 1.4, which also indicates Lewis acidity on ZrO_2. From the

TABLE 4

Surface Concentrations of Zr, Si, O, F, N and C of the Various SiO_2–ZrO_2 Catalysts Calcined at 773 K and the Uncalcined $Si_{75}Zr_{25}$ Catalyst as Determined Using XPS (Relative Accuracy 10%)

	Concentration (at.%)						Atomic ratio Zr/Si	
Catalyst	Zr	Si	O	F	C	N	Bulk	Surface
$Si_{100}Zr_0$	0	29 (31)	66 (69)	0.9	4.6	—	0	0
$Si_{87}Zr_{13}$	1.3 (1.5)	35 (40)	52 (59)	0.8	11	—	0.07	0.04
$Si_{75}Zr_{25}$ u	3.1 (3.6)	29 (34)	53 (62)	3.4	9.1	3.3	0.16	0.11
$Si_{75}Zr_{25}$	3.1 (3.4)	34 (37)	55 (60)	0.6	7.3	—	0.16	0.10
$Si_{50}Zr_{50}$	6.8 (8.1)	27 (32)	50 (60)	0.8	17	—	0.49	0.26
$Si_{25}Zr_{75}$	6.1 (6.9)	28 (31)	55 (62)	0.8	9.8	—	1.46	0.22
Si_0Zr_{100}	23 (41)	0.8[a]	33 (59)	1.5	42	—	∞	—

Note. The relative concentrations of Zr, Si en O leaving out F, N and C are given in brackets. u uncalcined sample.

[a] Signal from contamination with a grease containing silicon. *Si(2p)* binding energy = 101.6 eV instead of ~103.4 eV for the other samples.

literature it is indeed known that acid sites on ZrO_2 are mainly of Lewis type (1).

All samples contain some carbon on the surface, which is commonly observed in XPS spectra of samples which are pretreated *ex situ* and transferred to the XPS machine in air. The Si signal on pure ZrO_2 is an artefact probably arising from slight contamination with a grease containing silicon (binding energy Si(2*p*) = 101.6 eV as compared to 103.4 eV for mixed oxides and SiO_2).

Infrared Measurements

The characteristic cation–oxygen stretch and cation–oxygen–cation bending vibrations of (mixed) oxides are known to be in the 700–1200 cm^{-1} region of the infrared spectrum. For instance Makarov *et al.* (3) used this spectral region to determine the level of mixing of their SiO_2–ZrO_2 mixed oxides. In this spectral region SiO_2 has absorption bands (Si–O–Si) at 1170, 1100, and 810 cm^{-1}, whereas ZrO_2 has only one absorption band (Zr–O–Zr) at 735 cm^{-1}. Mechanical mixtures will give spectra that can be derived by linear combination of the spectra of the components. This is confirmed in our study of the $Si_{50}Zr^*_{50}$ sample (not shown). Spectra of SiO_2–ZrO_2 samples obtained by coprecipitation (chemical mixing) differ essentially from the spectra of pure or mechanically mixed oxides in the absence of characteristic absorption bands of the single oxides and in the appearance of new bands.

In Fig. 6 spectra in the 1400–400 cm^{-1} region of the mixed oxides are compared with SiO_2. Figure 7 gives the spectra of the single oxides SiO_2 and ZrO_2. The spectrum of pure SiO_2 resembles those reported in the literature (3, 9, 25, 26). Bands at ~1180 (shoulder), 1100 (strong), 810 (medium), and 470 (strong) cm^{-1} are found. The ZrO_2 spectrum shows absorptions at 780 (medium), 610 (strong), 500 (shoulder), and 450 (medium) cm^{-1}. Two bands (at 610 and 500 cm^{-1}) are roughly the same as reported in the literature (9, 26). The 780 cm^{-1} band has not been observed before. A band at 735 cm^{-1} is reported for ZrO_2 in this region (3, 9, 26).

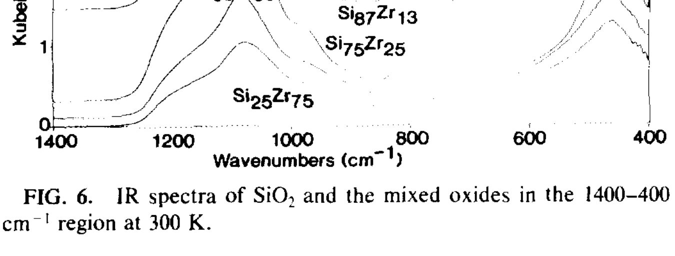

FIG. 6. IR spectra of SiO_2 and the mixed oxides in the 1400–400 cm^{-1} region at 300 K.

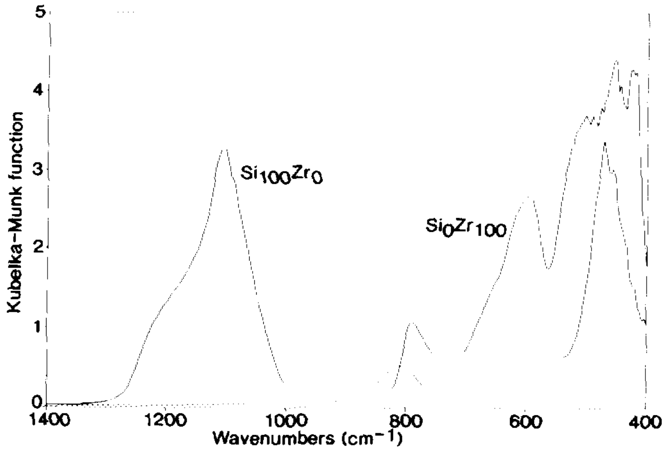

FIG. 7. IR spectra of SiO_2 and ZrO_2 in the 1400–400 cm^{-1} region at 300 K.

Differences in the preparation procedure, however, may influence the position of these lattice vibrations. In the SiO_2-rich mixed oxides (more than 50 wt.% SiO_2) the band at 810 cm^{-1} is visible, indicating the presence of SiO_2 entities in the mixed oxide. For catalysts containing 50 and 75 wt.% ZrO_2 (33 and 60 mol% ZrO_2) this band is very small or hardly visible. This observation is in agreement with measurements of Makarov *et al.* (3). This band is probably a Si–O–Si symmetric stretch (lattice vibration) which disappears below a certain Si–O–Si chain length. It is striking that no typical ZrO_2 bands can be seen in any spectrum of the mixed oxides, which may again be due to the fact that there are no long Zr–O–Zr chains. The absorption band at 1100 cm^{-1} for pure SiO_2 shifts to increasingly lower frequencies as the amount of ZrO_2 in the mixed oxide increases. For the $Si_{25}Zr_{75}$ sample the maximum of this band is at 1070 cm^{-1}. This band is tentatively assigned to an asymmetric Si–O–Si stretch perturbed by the presence of Zr in its environment (e.g., shorter Si–O–Si– chain length). An alternative explanation could be the occurrence of Si–O–Zr stretching bands close to the 1100 cm^{-1} band. In the region 900–1000 cm^{-1} new absorption bands appear (at ~980 and ~910 cm^{-1}), of which the integrated absorbance relative to the band at 1100–1070 cm^{-1} increases as the ZrO_2 content of the mixed oxide increases. The 980 cm^{-1} band can be ascribed to a Si–O· ·Zr stretching (3, 9, 25, 27). Also, the 910 cm^{-1} band has been observed before in SiO_2–ZrO_2 samples (27).

Test Reaction

The dehydration of cyclohexanol to cyclohexene over acid catalysts has been the subject of a number of studies (1, 12–14). Depending on catalyst properties and reaction conditions (higher temperature, higher contact times), skeletal isomerization of the product cyclohexene may also occur (12) yielding methylcyclopentene. The dehydration of cyclohexanol is a suitable test reaction for characterization of, e.g., zeolite acidity (13, 14). From preliminary experiments in our study it was concluded that the test reaction is kinetically controlled. Apparent activation energies are determined to be 75 kJ/mol for temperatures between 523 and 623 K (zero order kinetics). This high value is comparable to values reported by Karge *et al.* (13, 14), who measured 67–74 kJ/mol.

Figure 8, giving the conversion vs time plots for tests on mixed oxides, shows that the SiO_2–ZrO_2 catalysts deactivate. The deactivation is probably due to acid-catalyzed coke formation, but also H_2O produced may lower the conversion (13, 14). At a reaction temperature of 573 K the main product is cyclohexene (selectivity > 98%, some methyl cyclopentene is formed).

In Fig. 9 the average conversion of cyclohexanol and in Fig. 10 the normalized conversion of cyclohexanol (mol/m^2/h), both between 3 and 5 h of reaction, are plotted against the amount of ZrO_2 (wt.%) in the catalysts. From the figures it is obvious that incorporation of both Zr in a SiO_2 matrix and Si in a ZrO_2 matrix leads to a catalyst having a higher activity in the acid-catalyzed dehydration of cyclohexanol. The optimum in activity is around 50 wt.% ZrO_2.

Figure 11 shows the relation between the normalized average conversion of cyclohexanol between 3 and 5 h of reaction and the strong acid site density on the catalyst. As a measure of the strong acid site density the ammonia content in the NH_3 TPD at T = 473 K is taken (catalyst pretreated at 573 K). From the figure it can be seen that there is a good correlation between the concentration of strong acid sites and the catalytic performance (activity) in the test reaction.

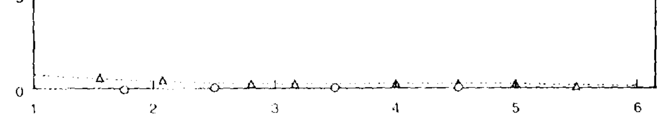

FIG. 8. Dehydration of cyclohexanol: conversion as a function of reaction time at a reaction temperature of 573 K. (○) $Si_{100}Zr_0$; (▼) $Si_{87}Zr_{13}$; (□) $Si_{75}Zr_{25}$; (+) $Si_{50}Zr_{50}$; (◇) $Si_{25}Zr_{75}$; (△) Si_0Zr_{100}.

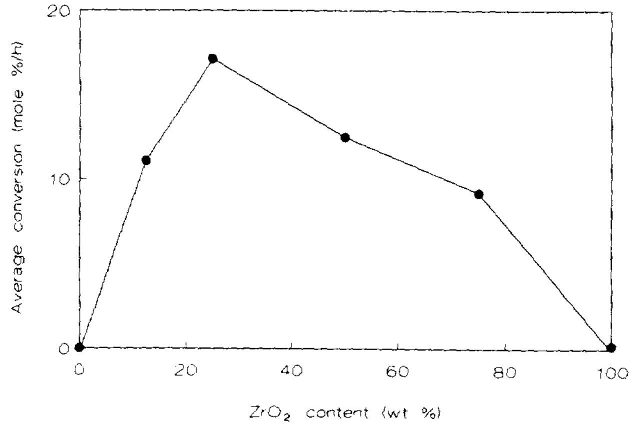

FIG. 9. Average conversion (mol%/h) between 3 and 5 h reaction as a function of the ZrO_2 content (wt.%).

From Fig. 11 it is clear that the $Si_{50}Zr_{50}$ sample shows a different behaviour than the other mixed oxides. From the NH_3 TPD we learned that ammonia binds more strongly to this sample, meaning that the acid strength is higher. This higher acid strength probably causes the higher activity per site (TOF) in the acid-catalyzed dehydration. For this reason, when seeking a relationship between acid amount of the catalysts and their performance in the test reaction, we decided to leave out this sample.

Our results are in fair agreement with the results of Dzis'ko *et al.* (2), who found a maximum number of acid sites on their SiO_2–ZrO_2 catalysts of 0.0013 meq/g for catalysts containing 15 to 57 mol% of ZrO_2 (25 to 70 wt.%). Furthermore, a correlation between the number of acid sites and the activity in the dehydration of isopropyl alcohol is found. In our experiments the width of the region of Zr contents of mixed oxides, which have maximum activity in the dehydration of cyclohexanol, is much smaller. It can be seen in Fig. 10 that, when the $Si_{50}Zr_{50}$ sample is left out, the maximum in activity is around 25 wt.% ZrO_2. Certainly no broad maximum in activity as

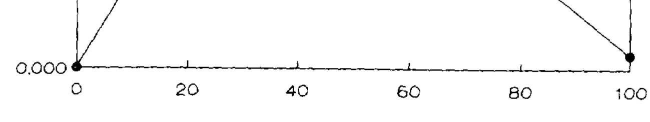

FIG. 10. Normalized average conversion (mol/m^2/h) between 3 and 5 h reaction as a function of the ZrO_2 content (wt.%).

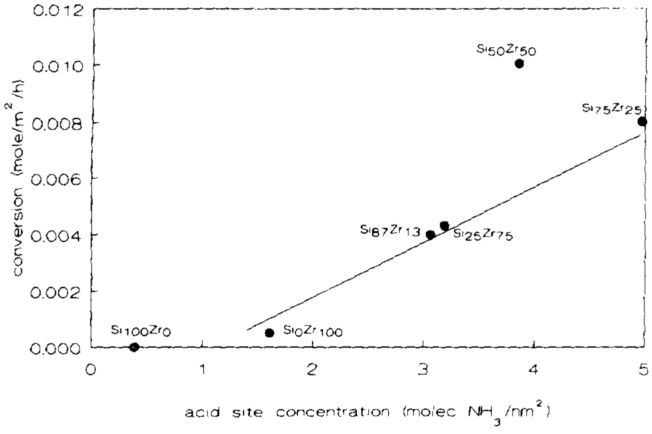

FIG. 11. Normalized average cyclohexanol conversion between 3 and 5 h of reaction (mol/m^2/h) as a function of the acid site concentration (determined from NH_3 content at T = 473 K in the NH_3 TPD).

a function of composition of the catalyst can be seen in our plots. More work is in progress to accurately determine the optimum concentration of ZrO_2 with regard to activity in the acid-catalyzed dehydration.

Soled and McVicker (4) used 2-methylpent-2-ene isomerization as a test reaction for a series of SiO_2–ZrO_2 catalysts and found that catalysts containing 20–28 mol% ZrO_2 (34–89 wt.%) have the maximum activity in the isomerization. Here, too, a broad range in catalyst composition shows a maximum activity in the test reaction.

It is known that pure SiO_2 is inactive in the dehydration of alcohols (2), which is confirmed by our study. α-Naphthyl Red shows an orange colour when adsorbed on pure SiO_2, probably indicating that a very small amount of sites having $H_0 \leq 4.0$ are present. Aminoazobenzene, however, is adsorbed in its basic form. From NH_3 TPD measurements it is also clear that pure SiO_2 contains only surface hydroxyl groups with a very low acid strength since adsorbed NH_3 desorbs at low temperatures. Pure ZrO_2 exhibits some activity in the dehydration of cyclohexanol, and Methyl Red clearly shows its acid colour (dark red) when adsorbed on pure ZrO_2. Aminoazobenzene shows an orange colour when adsorbed on pure ZrO_2, indicating the presence of some acid sites with $H_0 \leq +2.8$. Crystal Violet is adsorbed in its basic form. It is assumed, therefore, that the acid sites of our mixed oxides should have an acid strength corresponding to at least $H_0 \leq +2.8$ to be active in the dehydration of cyclohexanol.

General Discussion

From the literature it is known that the presence of small amounts of ZrO_2 in a SiO_2 matrix results in an increased number of strong acid sites (2, 3). In accordance with this we find that our mixed SiO_2–ZrO_2 catalysts have a lower H_0 than the single oxides, which follows both from our experiments with basic indicator molecules and from our NH_3 TPD measurements. In addition, the increased activity in the acid-catalyzed dehydration of cyclohexanol of the mixed oxides vs the single oxides is indicative of the generation of strong acidity in the SiO_2–ZrO_2 catalysts. From XRD and IR experiments it becomes clear that new Si–O–Zr bonds are formed in the mixed SiO_2–ZrO_2 oxides, which may give them different properties compared to the single oxides. It is known that especially surface acid properties may be influenced. XPS showed an oxygen depletion on mixed SiO_2–ZrO_2 oxides, even on uncalcined samples, indicating Lewis acidity. The mixed oxides studied have Zr/Si bulk ratios ranging from 0.07 to 1.46. The surface Zr/Si ratios, however, range from 0.04 to 0.26, which means that all samples should be considered SiO_2-rich mixed oxides with respect to (surface) acid properties.

It is interesting now to compare the outcome of our characterization study with qualitative models postulated in the literature on the generation and nature of acid sites in mixed oxides. In particular, two models attract attention, namely those postulated by Tanabe *et al.* (1, 15) and by Kung (16). Both models presume dilute solid solutions of one cation in a matrix of the main oxide. The model of Tanabe *et al.* however, uses local effects of the dopant cation on the host matrix to predict the generation of acidity. Following the hypothesis of Tanabe *et al.* on the generation of acidity of binary metal oxides, incorporating SiO_2 in a ZrO_2 matrix would lead to the formation of Lewis acid sites (charge difference = +2), while incorporating ZrO_2 in a SiO_2 matrix would lead to the formation of Brønsted acid sites (charge difference = −4). Contrary to Tanabe's model, Kung (16) also considers long-range effects. Both the electrostatic potential at the substituting cation site and changes in the matrix necessary to balance stoichiometry are considered. Kung's hypothesis on acidity generation predicts Lewis acidity when incorporating ZrO_2 in a SiO_2 matrix. Since the metal–oxygen stoichiometry is the same in both oxides, cationic substitution can take place with minimal effects on the host matrix. The substituted cation (Zr^{4+}) is predicted to be electrostatically more stable in SiO_2 than in bulk ZrO_2, and is therefore more able to accept electrons (Lewis acidity). We believe that our mixed oxides contain Lewis acid sites because of the observed oxygen depletion on the surface (XPS). Kung's model predicts Lewis acid sites and may therefore be more appropriate to our system.

To compare the activity of SiO_2–ZrO_2 with that of zeolites, data published by Karge *et al.* (13, 14) can be considered. This is difficult, however, because of the strongly differing conditions: activities of the zeolites are measured at 393 K, and for cyclohexanol partial pressures (in helium) up to about 5%. The most active zeolites, viz. BeY, CaY, and the acid form of dealuminated mordenite, showed activities between 2.5 and 3.4 mmol cyclohexanol/g catalyst/h. From the results of Karge *et al.* it can be calculated that the activity could be as high as 3 mol cyclohexanol/g catalyst/h at 573 K using an activation energy of 75 kJ/mol (measured by Karge *et al.* in the temperature range 373–453 K (13, 14), and in our study in the temperature range 523–623 K). Moreover, Karge *et al.* mentioned a titer of 2.88 meq/g for BeY determined in a butylamine titration ($H_0 \leq 3.3$). With this titer a turnover frequency (TOF) of 0.29 s^{-1} can be calculated (again extrapolated to 573 K). Among our SiO_2–ZrO_2 catalysts, the highest activity at 573 K is about 1 mol/g catalyst/h (for $Si_{75}Zr_{25}$), and using NH_3 TPD results a TOF of 0.28 s^{-1} can be calculated. Thus, keeping in mind the uncertainty in the extrapolation, it follows that the activity of the SiO_2–ZrO_2 catalysts is of the same order of magnitude as those of the zeolites Karge *et al.*

CONCLUSIONS

SiO_2–ZrO_2 mixed oxides can be prepared by basic hydrolysis of appropriate mixtures of H_2SiF_6 and H_2ZrF_6. Infrared measurements of the mixed oxides show Si–O–Zr bands in the mixed oxides at 980 and 910 cm^{-1}. Typical bands for ZrO_2 are absent and the positions and/or intensities of typical SiO_2 bands are clearly influenced by the ZrO_2 content. All mixed oxides are X-ray amorphous, whereas the pure ZrO_2 is crystalline. No peaks due to crystalline ZrO_2 can be detected in the chemically mixed material; a mechanically mixed oxide gives an XRD pattern in which both the crystalline ZrO_2 pattern and the amorphous SiO_2 pattern can be recognized.

Adsorption of Hammett indicators shows that the acid strength of surface hydroxyls on SiO_2 prepared from H_2SiF_6 is comparable to the strengths reported on SiO_2 prepared from other sources, the same holding for ZrO_2 prepared from H_2ZrF_6. The mixed SiO_2–ZrO_2 catalysts thus have very high acid strengths (intrinsic property), the H_0 values of which are between -11.4 and -13.8 (super-acidity).

XPS measurements show that SiO_2 precipitates more slowly than ZrO_2; the surface Zr concentration is 30–40% lower than the bulk concentration. Despite the use of fluorides as starting materials the surface fluorine concentration is as low as 1 at.% (0.3–0.4 F per nm^2) and its influence on the acid strength of, e.g., Brønsted acid sites (total concentration of strong acid sites = 3–5 per nm^2) on the surface is negligible. A surface oxygen depletion is observed on the mixed oxides and ZrO_2, indicating Lewis acidity. The model of Kung (16) thus describes the formation of acidity in our SiO_2–ZrO_2 mixed oxides better than the model of Tanabe *et al.* (1, 15).

NH_3 TPD experiments show that at a temperature > 473 K ammonia is still chemisorbed indicating the presence of strong acid sites. A good relationship has been obtained between the strong acid site concentration of the mixed oxides and their activity in the acid-catalyzed dehydration of cyclohexanol to cyclohexene. Also, the strength of the acid sites is of great importance as could be seen from the performance of the $Si_{50}Zr_{50}$ sample. This catalyst adsorbs ammonia more strongly than the other mixed oxides and its activity in the dehydration of cyclohexanol is also higher than all other samples. This sample does not fit into the relationship mentioned above probably because of the differing acidity. From indicator experiments we learned that the acidity needed for the dehydration of cyclohexanol corresponds to $H_0 \leq +2.8$.

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REFERENCES

1. Tanabe, K., Misono, M., Ono, Y., and Hattori, H., *Stud. Surf. Sci. Catal.* **51,** 1 (1989).
2. Dzis'ko, V. A., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," p. 422. Wiley, New York, 1965.
3. Makarov, A. D., Boreskov, G. K., and Dzis'ko, V. A., *Kinet. Katal.* **2,** 84 (1961).
4. Soled, S., and McVicker, G. B., *Catal. Today* **14,** 189 (1992).
5. Slinkin, A. A., Klyachko, A. L., Shpiro, E. S., Kapustin, G. I., Kucherova, T. N., Stakheev, A. Yu., and Ermolov, L. V., *Kinet. Katal.* **32,** 725 (1991).
6. Klyachko, A. L., Brueva, T. R., Kapustin, G. I., Kucherov, A. V., Ermolov, L. V., and Slinkin, A. A., *Kinet. Katal.* **32,** 733 (1991).
7. Slinkin, A. A., Karson, M. S., Dergachev, A. A., Udal'tsova, E. A., and Ermolov, L. V., *Kinet. Katal.* **32,** 934 (1991).
8. Kondratenko, N. E., Barvinok, G. M., Shurov, A. F., and Malygin, N. D., *Izv. Akad. Nauk SSSR, Neorg. Mater.* **27,** 300 (1991).
9. D'yakonov, S. S., Lygin, V. I., Shalumov, B. Z., Shepalin, K. L., Kuznetsov, A. I., Kostina, V. M., and Rastorguev, Y. I., *Izv. Akad. Nauk SSSR, Neorg. Mater.* **20,** 97 (1984).
10. Niwa, M., Katada, N., and Murakami, Y., *J. Catal.* **134,** 340 (1992).
11. Bleier, A., and Cannon, R. M., *in* "Better Ceramics Through Chemistry II: Proceedings of Symposium Held at MRS Spring Meeting, Palo Alto, CA, April 15–18, 1986" (C. J. Brinker *et al.*, Eds.), p. 71, MRS Symposia Proceedings Series, Vol. 73. Materials Research Society, Pittsburgh, PA, 1986.
12. Pines, H., and Haag, W. O., *J. Am. Chem. Soc.* **83,** 2847 (1961).
13. Karge, H. G., Kösters, H., and Wada, Y., *in* "Proceedings of the 6th International Zeolite Conference (Reno 1983)," (Bisio, A. and Olson, D., Eds.), p. 308. Butterworths, Guildford, 1984.
14. Karge, H. G., and Kösters, H., *in* "Preprints, 8th Canadian Symposium on Catalysis (Ontario, 1982)," p. 126.
15. Tanabe, K., Sumiyoshi, T., Shibita, K., Kiyoura, T., and Kitagawa, J., *Bull. Chem. Soc. Jpn.* **47,** 1064 (1974).
16. Kung, H. A., *J. Solid State Chem.* **52,** 191 (1984).

17. Meyer, R. J., "Gmelin's Handbuch der Anorganischen Chemie," Vol. 42, p. 281. Verlag Chemie, Weinheim, 1958.
18. Hammett, L. P., and Deyrup, A. J., *J. Am. Chem. Soc.* **54,** 2721 (1932).
19. Briggs, D., and Seah, M., "Practical Surface Analysis" Vol. 1, Chap. 5. Wiley, Chichester, 1990.
20. Scofield, J. H., *J. Electron Spectrosc. Relat. Phenom.* **8,** 129 (1976).
21. Allen, L. H., and Matijevic, E., *J. Colloid Interface Sci.* **31,** 287 (1969).
22. Hertl, W., *Langmuir* **5,** 96 (1989).
23. Walling, C., *J. Am. Chem. Soc.* **72,** 1164 (1950).
24. Shibita, K., Kiyoura, T., Kitagawa, J., Sumiyoshi, T., and Tanabe, K., *Bull. Chem. Soc. Jpn.* **46,** 2985 (1973).
25. Boccuzzi, F., Coluccia, S., Ghiotti, G., Morterra, C., and Zecchina, A., *J. Phys. Chem.* **82,** 1298 (1978).
26. McDevitt, N. T., and Baun, W. L., *Spectrochim. Acta* **20,** 799 (1964).
27. Thielsch, R., Meiling, W., and Goering, E., *Vacuum* **41,** 1147 (1990).