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Catalytic Activity of Bulk and Supported Sulfated Zirconia

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Summary

To assess whether Lewis acid sites are present on zirconium sulfate, we prepared water-free bulk zirconium sulfate. Furthermore, a water-free silica-supported zirconium sulfate catalyst was prepared by deposition-precipitation of zirconia on silica and subsequent gas-phase reaction with SO_3 . The activity of these catalysts was compared with that of two conventionally prepared sulfated zirconia catalysts.

The different catalysts were extensively characterized. XPS indicated that the conventionally prepared sulfated zirconia catalysts contained sulfuric acid. The activity of the catalysts was determined with the gas-phase *trans*-alkylation of diethylbenzene with benzene and the solvent-free liquid-phase addition of acetic acid to camphene.

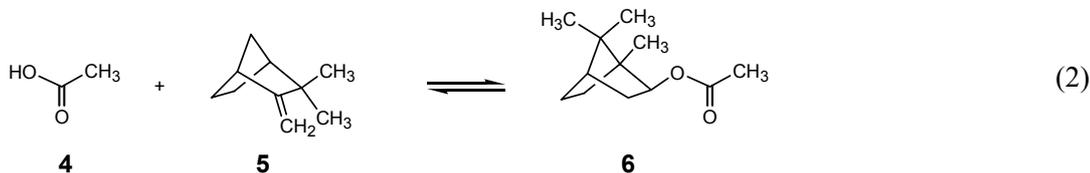
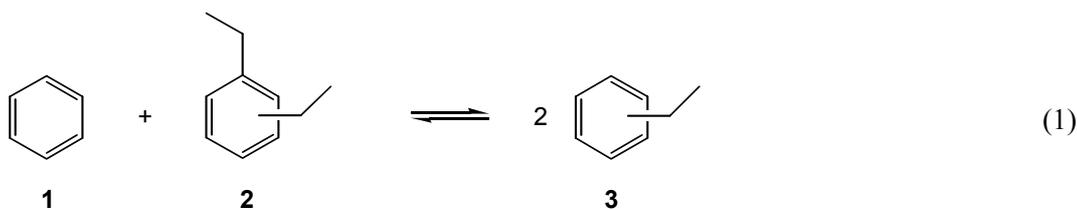
Both water-free zirconium sulfate catalysts did not exhibit a significant activity; Lewis acid sites are therefore not active in these sulfated zirconia catalysts. Upon exposure to water vapor the initially water-free catalysts were active. The stability of the conventional sulfated zirconia catalysts appeared to be determined in the gas-phase by the volatilization of sulfuric acid. As a result, a highly porous catalyst was more effective than a catalyst based on zirconia of a relatively low porosity. With liquid-phase reactions extraction of sulfuric acid proceeds leading to an acid liquid, which is catalytically active also after separation of the solid catalyst from the reaction mixture.

1. Introduction

The presence of catalytically active Lewis acid sites in sulfated zirconia catalysts is much debated [1-5]. The conventional preparation of sulfated zirconia catalysts involves reaction of freshly precipitated zirconium hydroxide with diluted sulfuric acid or impregnation of zirconium hydroxide with sulfuric acid or ammonium sulfate [6,7]. The final solid acid catalyst results by calcination at a temperature of 723 to 873 K. Provided thermodynamic equilibrium has been reached, all water and free sulfuric acid should have evaporated upon calcination at 673 to 873 K and only chemically bonded sulfate groups remain [8]. Above 890 K, bulk anhydrous $\text{Zr}(\text{SO}_4)_2$ decomposes [1]. When uptake of water by the calcined catalyst is prevented or after loading of the catalyst in the reactor physisorbed water is removed by thermal treatment, only Lewis acid sites are present. Since it is difficult either to prevent the uptake of water vapor or to remove adsorbed water completely, it is difficult to attribute the acid activity of sulfated zirconia catalysts unambiguously to Lewis acid sites.

In view of the fact that complete removal of water vapor cannot be readily achieved, we prepared water-free bulk and silica-supported zirconium sulfate. The bulk anhydrous $\text{Zr}(\text{SO}_4)_2$ was obtained by reaction of zirconium tetrachloride with oleum [1]. The silica-supported zirconium sulfate resulted from deposition-precipitation of zirconium hydroxide on silica, calcination at 723 K and subsequent reaction with gaseous sulfur trioxide. The catalytic activity of the sulfated zirconia's was measured in the gas-phase *trans*-alkylation of benzene (**1**) with diethylbenzene (**2**) to ethylbenzene (**3**, reaction 1) [8,9] and the liquid-phase hydroacyloxy-addition reaction of acetic acid (**4**) and camphene (**5**) to isobornyl acetate (**6**, reaction 2) [8,10]. With the *trans*-alkylation we used an amorphous silica-alumina catalyst as a reference.

For comparison purposes we prepared and investigated also two different sulfated zirconia catalysts prepared conventionally [6,7]. One catalyst was prepared by reaction of 0.5 M H_2SO_4 with freshly precipitated zirconium hydroxide and calcination at 773 K [$\text{H}_2\text{SO}_4/\text{ZrO}_2(\text{prec.})$], the other in a similar way but with calcined zirconia [$\text{H}_2\text{SO}_4/\text{ZrO}_2(\text{Gimex})$] [8]. It is interesting that it has been concluded from their infrared spectra that addition of water vapor leads to formation of sulfuric acid [5]. As the volatility of sulfuric acid and its constituents is higher than that of metal sulfates, the transport of water and sulfur oxides out of the porous structure of the zirconia is important.



The difficult transport of strongly adsorbing molecules out of a porous system may give an explanation for the result mentioned in the literature that the reaction of zirconium hydroxide with sulfuric acid leads to a fairly active catalyst, whereas reaction of calcined zirconia with sulfuric acid providing the same sulfur content did not result in an active catalyst [11]. Accordingly, the removal of the constituents of sulfuric acid out of calcined zirconia will proceed much more smoothly than that out of zirconium hydroxide. The activity of catalysts prepared from zirconium hydroxide thus may be due to water and sulfuric acid remaining in the catalyst providing Brønsted acid sites. The sulfated zirconia catalyst based on non-porous calcined zirconia [$\text{H}_2\text{SO}_4/\text{ZrO}_2$ (Gimex)], on the other hand, will lose readily most of its sulfuric acid during thermal treatment.

Furthermore, we investigated the effect of water on the activity of the above-mentioned sulfated zirconia catalysts and the observed activities were compared. We have extensively characterized the different catalysts by XPS, physical adsorption, analytical electron microscopy, and thermogravimetry.

2. Experimental

2.1. Catalyst preparation

The water-free bulk zirconium sulfate $\text{Zr}(\text{SO}_4)_2$ was prepared by treatment of ZrCl_4 with oleum as published earlier [1].

The preparation of the silica-supported, water-free sulfated zirconia catalyst started with the deposition-precipitation of zirconia on silica. In a reaction vessel (2 L) equipped with a pH-meter, thermometer, baffles and a stirrer (1000 rpm), 13.5 g (0.225 mol) SiO_2 [Aerosil OX50 (Degussa-Hüls), $50 \text{ m}^2/\text{g}$] was suspended in 750 mL water. Under stirring, both 4.0 M HCl and 4.0 M NH_3 were separately *injected* via narrow tubes (i.d. 1.0 mm) ending below the level of the liquid using two Gilson Minipuls III peristaltic pumps. Whereas the 4.0 M HCl was injected at 0.25 mL/min, the injection of the 4.0 M NH_3 solution was automatically regulated to maintain a pH of 4.5. When a constant pH of 4.5 was reached, the 4.0 M HCl was replaced by a 4.0 M HCl (250 mL) solution containing 3.92 g (12.2 mmol) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. After addition of these solutions at a pH of 4.5, the pH was raised to 6.5 with the 4.0 M NH_3 solution. The wet residue was re-suspended three times in water (300 mL) for one day followed by filtration in order to remove remaining NH_4Cl impurities. The final residue was dried at 393 K for one day and subsequently sieved; the 500-850 μm fraction was isolated. Calcination was performed under carefully controlled conditions using a quartz fixed bed reactor (i.d. 10 mm) equipped with a K-type thermocouple. The 500-850 μm sieve fraction was calcined at 723 K for 10 h (heating/cooling rate: 5 K/min) in a dry air flow (50 mL/min). On top of the sieve fraction, glass beads (d 1.0 mm) were placed to achieve effective preheating of the air.

The next step involved the sulfation of the small zirconia particles. For the oxidation of SO_2 to SO_3 a layer of a finely powdered 2 wt% Pt/ SiO_2 catalyst was installed at half-height of the glass bead layer. Helium was used to maintain a gas flow of 50 mL/min. The temperature

was raised to 675 K at 5 K/min. Subsequently 5 vol.% of SO₂ and 5 vol.% of O₂ were added to the helium flow, which was maintained for 5.5 h. Via a heat-traced tube (423 K) the gas-flow leaving the reactor was passed through a stirred suspension of Ca(OH)₂ in water. Next, the temperature was lowered to 573 K and the SO₂ and O₂ were switched off, after which the temperature was decreased to room temperature at 5 K/min.

A literature procedure was used for the preparation of calcined H₂SO₄-impregnated ZrO₂ catalysts [6,7]. Two different ZrO₂ sources were used.

(1) Precipitated ZrO₂: 20.23 g (62.8 mmol) ZrOCl₂·8H₂O was dissolved in water (160 mL) and 25 wt% NH₃ was added dropwise under vigorous stirring until pH = 8. Next, the NH₄Cl was removed re-suspending the wet residue by four times in water (300 mL) for one day followed by filtration. The ZrO₂ residue was dried at 433 K for 16 h.

(2) Commercial ZrO₂ (Gimex B.V., The Netherlands, surface area 60 m²/g, monoclinic).

Sulfation of both zirconia's was performed by stirring 4.0 g (32.46 mmol) of each zirconia sample with 20 mL 0.5 M H₂SO₄ for 3 h and drying at 433 K for 16 h (no filtration). Sieve fractions (500-850 μm) were calcined in a flow of dry air (50 mL/min) at 773 K for 3 h (heating/cooling rate: 10 K/min). The catalysts were isolated from the reactor as well as stored under dry air prior to analysis and application.

2.2. Catalyst characterization

XPS analysis was performed on a Vacuum Generators (Fisons Instruments) MT-500 with a non-monochromatic Al X-ray source (Kα 1486.6 keV) and a CLAM-2 hemispherical analyzer for electron detection. The samples were supported on carbon adhesive tape. Spectra were corrected for charging using the Si(2p) peak and scaled on the Si(2s) peak. For the determination of the binding energies a background correction was applied.

Thermostabilities were determined by analyzing the relative loss of weight in a dry N₂ flow (50 mL/min) as a function of temperature and time with a PC-controlled Perkin-Elmer TGS-2 TGA apparatus, autobalance AR-2. Temperature program: 1 h at 323 K, heating rate 10 K/min to 1123 K followed by 15 min at 1123 K. Samples of *ca.* 3.5 mg were used.

Transmission electron microscopy was performed with a Philips EM420 and a Philips CM200 equipped with a field-emission gun and an EDAX detector for elemental analysis. Ground and ultrasonically dispersed (in dry *n*-hexane) samples were brought on copper grids covered by a thin polymer film on which carbon was deposited.

SEM analysis was performed with a Philips XL 30 FEG equipped with an EDAX detector for elemental analysis. The samples were supported on carbon adhesive tape and covered with a carbon layer by vapor-deposition.

2.3. Gas-phase *trans*-alkylation of benzene (**1**) and diethylbenzene(**2**)

The gas-phase *trans*-alkylation reaction was performed in an automated micro-flow apparatus containing a quartz fixed-bed reactor (i.d. 10 mm) at 10⁵ Pa [16 vol% benzene (**1**, *p.a.*, dried on molsieve), 3.2 vol% diethylbenzene (**2**, consisting of 25% ortho, 73% meta, 2% para isomers, dried on molsieve), N₂ balance (50 mL/min), WHSV = 1.5 h⁻¹] with 2.0 mL of the tube reactor filled with catalyst particles (500-850 μm sieve fraction, typically 1.4 g). Two separate saturators were connected to the inlet of the reactor for the supply of **1** and **2**. The partial vapor pressure of **1** and **2** was controlled by adjusting the temperature of the saturator-condensers and the N₂ flow rate. After equilibration for 30 min at the applied reaction temperatures (473 K and 673 K, heating rate 10 K/min) within a dry N₂ flow (50 mL/min), benzene (**1**) and diethylbenzene (**2**) were passed through the reactor. To prevent condensation of both reactants and products prior to GC analysis [Hewlett Packard 5710 A, column: CP-sil 5CB capillary liquid-phase siloxane polymer (100% methyl) 25 m × 0.25 mm, 323 K, carrier gas: N₂, FID, sample-loop volume: 1.01 μL], tubes were heat-traced (398 K). FID sensitivity factors and retention times were determined using ethene (99.5 %, dried over molsieve) and standard solutions of **1**, **2**, and ethylbenzene (**3**, 99%) in methanol (*p.a.*). The conversion of **2** was measured as a function of time [8].

2.4. Liquid-phase hydro-acyloxy-addition of acetic acid (4) to camphene(5)

A mixture of glacial acetic acid (4 *p.a.*, 0.70 mol), camphene (5 95%, 0.70 mol) and acetic anhydride (*p.a.*, 9.05 mmol) was mechanically stirred (1500 rpm) overnight at 328 K under a N₂ atmosphere. Subsequently, 2.5 g of catalyst was quickly suspended in the reaction mixture. The composition of the soluble fraction of the reaction mixture was analyzed by capillary GC as a function of reaction time; samples were prepared as follows: 1.00 mL of the reaction mixture was added to water (25.00 mL) followed by an extraction with *n*-heptane (25.00 mL). 1.00 mL of the *n*-heptane fraction was diluted with *n*-heptane to 25.00 mL in a volumetric flask. 1.0 μL of the diluted solution was injected into the GC [Varian 3400, column: DB-5 capillary liquid-phase siloxane polymer (5% phenyl, 95% methyl), 30 m × 0.323 mm, temperature program: 5 min at 333 K, 10 K/min to 553 K, 10 min, carrier gas: N₂, FID]. In the case of hydro-acyloxy-addition reactions performed in the presence of water, 320 μL (17.78 mmol) H₂O was added instead of acetic anhydride. To establish whether leaching occurs, the insoluble catalyst particles were removed from the reaction mixture by filtration with a double-ended glass filter under a dry N₂ atmosphere (before equilibrium had established), whereas the composition of the reaction mixture was further measured as a function of time. Since no solid residue remained after evaporation of the reaction mixture to dryness *in vacuo*, removal of the solid particles was complete.

3. Results and discussion

3.1. Catalyst characterization

The chemical composition of the different catalysts investigated are collected in Table 1. Also the sulfur contents calculated for complete conversion to Zr(SO₄)₂ are indicated. The experimental sulfur contents are lower than the calculated values. The reaction of the silica-supported zirconia with gaseous sulfur trioxide is therefore not complete and the reaction of zirconium hydroxide and zirconia with sulfuric acid involves only a limited fraction of the zirconia. As to be expected, the specific surface area of the catalyst prepared from zirconium hydroxide is much larger than that of the other catalysts. The catalyst based on calcined zirconia exhibited the X-ray diffraction pattern of zirconia and the catalyst based on zirconium hydroxide showed broadened reflection of zirconia. The bulk water-free zirconium sulfate did not display an X-ray diffraction pattern; after exposure to ambient air (relative humidity 50 to 60%) for two weeks the sharp X-ray diffraction pattern of Zr(SO₄)₂·4H₂O appeared [1].

Table 1. Quantitative analysis of elements by ICP-AES and Flash-combustion GC for the 10 wt% ZrO₂/SiO₂ subjected to gaseous SO₃ and for the conventional H₂SO₄/ZrO₂ catalysts. Residual atom (%): oxygen.

Sample	Element	Atom (%)		BET area (m ² /g)
		Calc. (100% sulfated)	ICP-AES / Flash-combustion GC	
SO ₃ /ZrO ₂ /SiO ₂	S	3.0	1.7	50
	Zr	1.5	1.3	
	Si	27.6	23.7	
H ₂ SO ₄ /ZrO ₂ (prec.)	S	7.3	4.0	217
	Zr	23.9	23.9	
H ₂ SO ₄ /ZrO ₂ (Gimex)	S	7.3	1.8	50
	Zr	23.9	24.2	

Deposition-precipitation of zirconium hydroxide on silica at a constant pH level of 4.5 leads to very finely divided zirconia. Fig. 1 shows an electron micrograph of the resulting catalyst precursor. Tiny zirconia particles have been deposited onto the non-porous silica spheres.

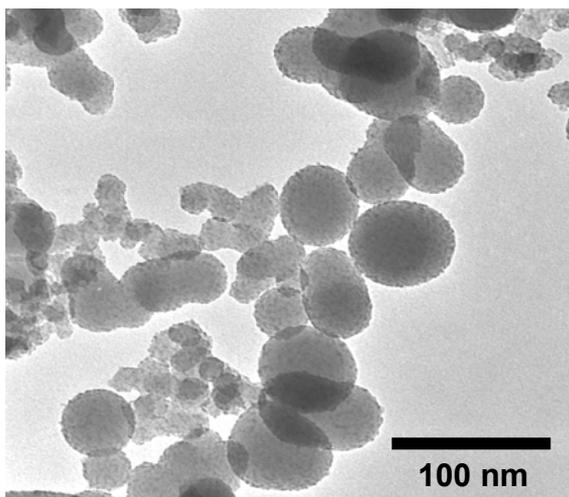


Fig. 1. Transmission electron micrograph of 10 wt.% ZrO₂/SiO₂ prepared by pH-static deposition-precipitation onto silica [8]. Large light-gray spheres: silica support (Aerosil OX50, Degussa-Hüls) Dark dots: zirconia.

Thermogravimetry indicated a continuous weight loss of the sulfated silica supported zirconia of only about 3 %. The thermogravimetric data on the catalysts prepared by reaction of zirconia with sulfuric acid were more informative (see also ref. [12]). When the temperature was raised with 10 K/min, the catalyst prepared by reaction with calcined zirconia showed a much more smooth weight loss, which set on already at about 350 K. Apparently, it is much more difficult to remove the constituents of sulfuric acid out of the much more porous structure of the zirconium hydroxide.

The bulk anhydrous Zr(SO₄)₂ catalyst exhibited a ratio of the areas of the S(2p) and the Zr(3d_{5/2,3/2}) peak of 0.50. Employing XPS atomic sensitivity factors of S(2p) = 0.54 and Zr(3d_{5/2,3/2}) = 2.1, the S/Zr atomic ratio is 2.0, which agrees with the bulk chemical composition. The energy of the S(2p) peak of the silica-supported zirconia after treatment with sulfur trioxide was at 170.0 eV, which agrees nicely with that exhibited by anhydrous bulk zirconium sulfate, which was at 170.3 eV [1]. Bulk anhydrous zirconium sulfate has the Zr(3d_{5/2,3/2}) peak at 185.6 eV and zirconia at 183.3 eV. The partial conversion of the supported zirconia into zirconium sulfate is not only evident from the chemical analysis, but also from the energy of the Zr(3d_{5/2,3/2}) peak, which was at 184.1 eV. Together with the broadening of the peak, which was 0.3 eV, the sulfur-to-zirconium peak ratio being 0.25 instead of 0.5 as measured with the bulk zirconium sulfate, indicates the incomplete reaction of the tiny zirconia particles. It is significant that the zirconia catalysts prepared by reaction of sulfuric acid with zirconium hydroxide exhibit a S(2p) binding energy of 169.3 eV, which is nearly identical to that of liquid H₂SO₄ (169.4 eV [13]). The Zr(3d_{5/2,3/2}) peak of the catalysts is broadened and is positioned at an energy lower than that measured for bulk anhydrous zirconium sulfate. The XPS results therefore point to the presence of sulfuric acid adsorbed on a zirconia surface that has reacted at most to a limited extent to the sulfate.

3.2. Gas-phase *trans*-alkylation

The anhydrous bulk zirconium sulfate preparation did not display any activity in the *trans*-alkylation of benzene (**1**) and diethylbenzene (**2**) to ethylbenzene (**3**). At 473 K the silica-supported, gas-phase sulfated zirconia showed a very small activity, which rapidly dropped to a negligible level (Fig. 2). The conclusion is that Lewis acid sites are not active with sulfated zirconia catalysts. The low activity of the silica-supported catalyst is due to adsorption of some water leading to Brønsted acid sites. Desorption of water at 473 K leads to the decrease in activity with time. Pre-hydration of the supported catalyst brings about a slightly higher activity as apparent from Fig. 2; the activity drops again due to the loss of water.

Fig. 3 represents the catalytic activity of the two catalysts prepared by reaction with liquid sulfuric acid. The activity has been measured at 473 and at 673 K. In agreement with the result mentioned in ref. [10] that calcined zirconia does not exhibit activity upon reaction with sulfuric acid and calcination, the activity of the H₂SO₄/ZrO₂(Gimex) catalyst at 473 K is low.

The activity rapidly decreases with time on stream. At 673 K the catalyst did not show any activity. The catalyst prepared by reaction of precipitated zirconium hydroxide with sulfuric acid and calcination [$\text{H}_2\text{SO}_4/\text{ZrO}_2(\text{prec.})$], on the other hand, exhibited a significantly high conversion, which did not drop with time on stream. At 673 K, however, the latter catalyst also showed a very low activity. Since an activity decreasing with temperature is unusual, we compared the behavior of the sulfated zirconia catalysts with that of an amorphous silica-alumina catalyst.

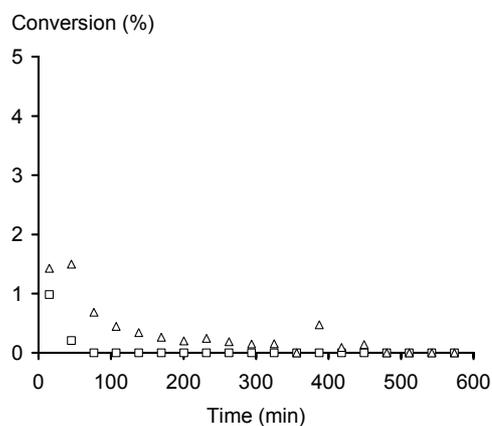


Fig. 2. Conversion of **2** in the *trans*-alkylation of benzene (**1**) and diethylbenzene (**2**) at 473 K on $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$ catalyst; □ before hydration and Δ after hydration (2 h, 2 % H_2O , 50 mL/min).

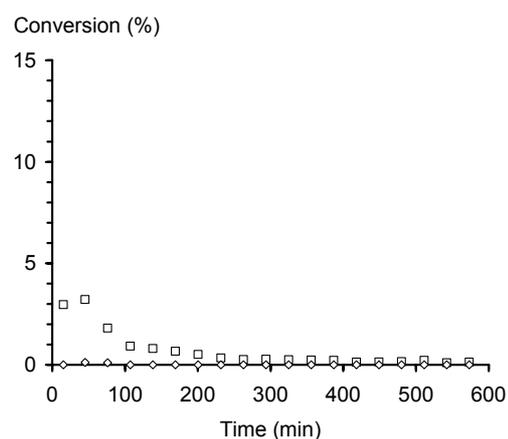
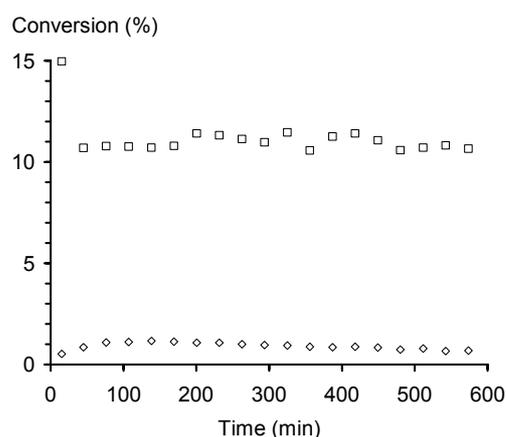


Fig. 3. Conversion of **2** in the *trans*-alkylation of benzene (**1**) and diethylbenzene (**2**) on $\text{H}_2\text{SO}_4/\text{ZrO}_2(\text{prec.})$ (left-hand side) and on $\text{H}_2\text{SO}_4/\text{ZrO}_2(\text{Gimex})$ (right-hand side) □ 473 K and ◇ 673 K.

Fig. 4 shows the conversion of the silica-alumina catalyst at 473 and 673 K. Fig. 4 also indicates that the amorphous silica-alumina catalyst displays the expected dependence of the temperature; at higher temperature the conversion is higher. The higher activity is partly due to reaction to ethene; at 473 K the selectivity to ethylbenzene (**3**) is 100 %, but 50 % at 673 K.

The anomalous behavior of the sulfated zirconia catalysts is due to the loss of sulfuric acid at elevated temperatures. The catalyst prepared from calcined zirconia loses its sulfuric acid at 673 K and, consequently, is not active at this temperature. As a result, decreasing the temperature of the catalyst to 473 K does not restore the activity. Also the more highly porous catalyst prepared from zirconium hydroxide releases sulfuric acid, but in narrow pores some sulfuric acid is left. The loss of sulfuric acid at 673 K is obviously irreversible. When the catalyst prepared from zirconium hydroxide is, however, kept at 473 K, the transport of water out of the porous structure is thus low that a stable activity is exhibited. Pre-hydration of the bulk anhydrous zirconium sulfate does not provide an active catalyst. That no catalytic activity is induced in this case is due to the fact that bulk anhydrous zirconium sulfate readily reacts to a stable tetrahydrate, *viz.*, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ [1]. As a result the hydrolysis of the sulfate by water vapor is suppressed.

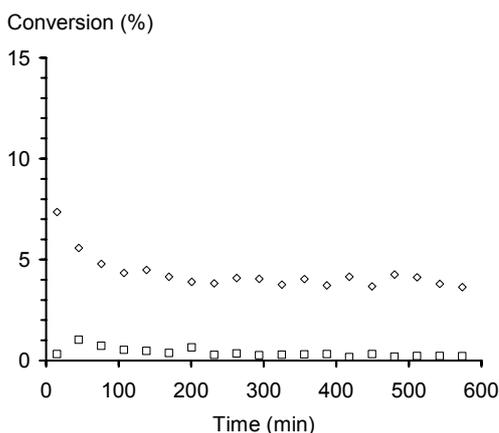


Fig. 4. Conversion of **2** in the *trans*-alkylation of benzene (**1**) and diethylbenzene (**2**) on amorphous silica-alumina. □ 473 K and ◇ 673 K.

3.3. Liquid-phase hydro-acyloxy addition

Neither the anhydrous bulk zirconium sulfate nor the silica-supported, sulfated zirconia were active in the addition of acetic acid (**4**) to camphene (**5**). The lack of activity is due to the fact that addition of acetic anhydride removes water completely from the reactants. Also the liquid-phase reaction thus demonstrates that Lewis acid sites are not active in our catalysts. Addition of water leads to a well measurable activity with both catalysts. Fig. 5 represents the activity of the silica-supported sulfated catalyst after pre-hydration. The activity is considerable, but a homogeneous catalyst, such as, sulfuric acid or BF_3 in acetic acid, is more active raising the conversion to about 70 % in 1500 min. It is interesting that filtration of the catalyst did not stop the reaction. Apparently some sulfuric acid has been formed by reaction with the water, which has been released by the catalyst into the solution.

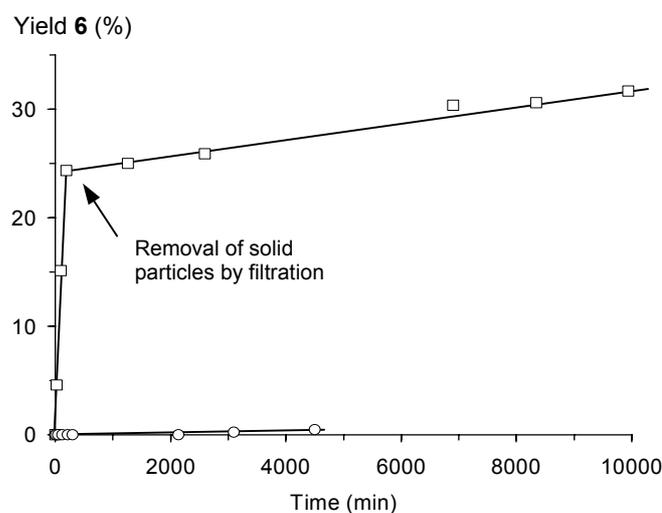


Fig. 5. Course of the reaction to isobornyl acetate (**6**) by the hydro-acyloxy-addition of 0.70 mol acetic acid (**4**) to 0.70 mol camphene (**5**) at 338 K (stirred tank reactor, N_2 atmosphere). ○ 2.5 g $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$ without H_2O and □ 2.5 g $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$ and 320 ml (17.78 mmol) H_2O .

Fig. 6 shows the activities of the sulfated zirconium hydroxide and the sulfated calcined zirconia catalyst. In contrast to the activities displayed in the gas-phase reaction, the calcined zirconia catalyst now shows the higher activity. Since the mass transport in the liquid is much slower, the rate of the reaction is now more strongly transport-limited with the catalyst prepared from the more porous zirconium hydroxide. Upon removal of the solid catalyst by filtration the reaction continues also with these two catalysts.

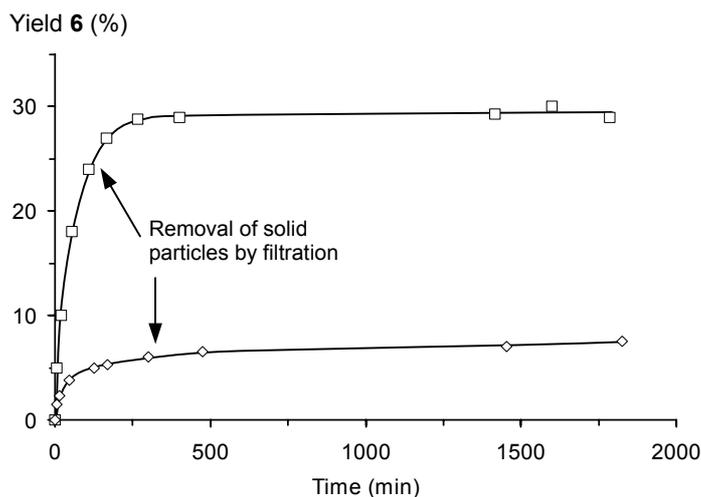


Fig. 6. Course of the reaction to isobornyl acetate (**6**) by the hydro-acyloxy-addition of 0.70 mol glacial acetic acid (**4**) to 0.70 mol camphene (**5**) at 338 K (stirred tank reactor, N₂ atmosphere). □ 2.5 g H₂SO₄/ZrO₂(Gimex) and ◇ 2.5 g H₂SO₄/ZrO₂(prec.).

4. Conclusions

The sulfated zirconia catalysts prepared and investigated in this research do not exhibit activity due to Lewis acid sites both in a gas-phase and in a liquid-phase reaction. The positive effect of water as well as the XPS evidence together with infrared results from the literature suggests that sulfated zirconia catalysts are actually zirconia-supported sulfuric acid catalysts.

The fact that sulfuric acid is the active component leads to a drawback of sulfated zirconia catalysts. In gas-phase reactions at temperatures where the vapor pressure of the constituents of sulfuric acid is considerable, de-activation of the catalyst has to be taken into account. A highly porous structure can significantly slow down the loss of the active constituent of the catalysts. In the liquid-phase dissolution of sulfuric acid can lead to corrosive properties and to contamination of the reaction products. Furthermore deactivation of the catalyst will eventually result.

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