Preparation of zirconium oxide on silica and characterization by X-ray photoelectron spectroscopy, secondary ion mass spectrometry, temperature programmed oxidation and infra-red spectroscopy

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Preparation of zirconium oxide on silica and characterization by X-ray photoelectron spectroscopy, secondary ion mass spectrometry, temperature programmed oxidation and infra-red spectroscopy

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Abstract

Well dispersed $\text{ZrO}_2/\text{SiO}_2$ catalysts with a satisfactory thermal stability have been prepared by reaction between zirconium ethoxide dissolved in ethanol and hydroxyl groups of the silica support, followed by calcination in air at temperatures up to 700°C . Characterization of the catalysts in intermediate stages of the preparation by secondary-ion mass spectrometry (SIMS), infra-red spectroscopy (IR) and temperature-programmed oxidation (TPO) gives a detailed picture of the formation of the ZrO_2 from the ethoxide precursor. Intensity ratios of the zirconium and silicon X-ray photoelectron spectroscopy (XPS) signals have been used to estimate the dispersion of the catalysts and to investigate their thermal stability. The results obtained on the ethoxide-derived catalysts are compared with those on $\text{ZrO}_2/\text{SiO}_2$ catalysts prepared by incipient wetness impregnation from an aqueous solution of zirconium nitrate. The work illustrates how useful the combination of XPS, SIMS, IR and TPO is for investigating the genesis of catalysts.

Keywords: zirconium oxide/silica, catalyst preparation (precipitation), surface characterization, catalyst characterization (IR, SIMS, TPO, XPS).

INTRODUCTION

Zirconium oxide is a versatile catalyst which exhibits activity for a number of reactions, including hydrogenation [1], dehydrogenation, cracking, and the formation of alkenes from alcohols [2]. According to Tanabe and co-workers [3 and refs. therein, 4], ZrO_2 surfaces possess both acidic and basic, as well as reducing and oxidizing properties.

Zirconium oxide is also of interest as a catalyst support. Highly dispersed zirconium oxide on silica appears particularly attractive because it combines the chemical properties of ZrO_2 with the favourable mechanical stability of a

SiO₂ support [5,6]. The preparation of highly dispersed silica-supported zirconia forms the subject of this paper.

The simplest way to prepare ZrO₂/SiO₂ catalysts is by impregnating the silica until incipient wetness with an aqueous solution of zirconium nitrate, followed by calcination in air. As the results presented in this paper show, this procedure leads to large ZrO₂ particles which leave most of the silica uncovered. However, a method in which the silica is contacted with a solution of zirconium ethoxide and acetic acid in ethanol, yields after calcination in air a well dispersed and thermally stable ZrO₂, which covers the silica to a much greater extent.

The aim of this paper is to compare the two preparation methods by characterizing the catalysts in intermediate stages of the preparation with a combination of four techniques: X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), infra-red spectroscopy (IR) and temperature-programmed oxidation (TPO).

EXPERIMENTAL

Catalyst preparation

The exchange preparation was carried out by adding 2 g of zirconium ethoxide (97%, Aldrich), 1 ml of concentrated acetic acid, and 5 g of silica (Grace 322, surface area = 250 m²/g) to 70 ml of ethanol at room temperature. The mixture was stirred overnight and filtered afterwards. Next the filtrate was dried at 25°C. The loading of this catalyst, determined by comparing the weight of this catalyst after calcination at 680°C with that of the untreated silica after calcination at 680°C, was 16 ± 0.5 wt.-% of ZrO₂. This catalyst was used for thermal stability studies with XPS. A second ethoxide-derived catalyst was made with an approximately five-fold diluted solution and had a loading of about 9 ± 1.5 wt.-% ZrO₂. This catalyst was used for SIMS, IR and TPO analysis.

The other ZrO₂/SiO₂ catalysts were made by adding dropwise an aqueous solution of Zr(NO₃)₄·5H₂O (BDH) to the silica until the incipient wetness point was reached. The catalyst was dried at room temperature for twenty-four hours and then at 110°C. The zirconium loading of this sample was 8 wt.-% ZrO₂. Samples with a loading of 16 and 24 wt.-% were made by applying a second and a third impregnation step, as described above. Finally, a fourth nitrate-derived sample with a ZrO₂ loading of 20 wt.-% was made by a one-step incipient wetness impregnation. This sample was used for SIMS, IR and TPO analysis.

A model system was prepared in order to study the zirconia catalysts in XPS without charging complications [7]. The support consisted of a single-crystal silicon wafer covered by a thin (approximately 1 nm) oxide layer. Zirconium was deposited on this wafer by adding the wafer to a solution of zirconium

ethoxide in ethanol–acetic acid, heated to its boiling point. Next the wafer was dried in air at 50°C.

Characterization techniques

XPS spectra were measured with a VG Escalab 200 equipped with a monochromatized Al X-ray source and a five-channel detector. All spectra were collected with the analyser at a pass energy of 50 eV. In order to minimize charging problems, samples were prepared by pressing catalyst powder in indium. Corrections for charging were made by using the Si 2p XPS peak of the silica as an internal reference; all binding energies are reported with respect to the Si 2p peak at 103.4 eV.

SIMS spectra were measured with a Leybold SSM 200. We used a 5 keV Ar⁺ primary ion beam with a current density of 3 $\mu\text{A}/\text{cm}^2$. The samples were pressed into indium pellets. Charge compensation was not employed.

Infrared spectra were recorded with a Hitachi 270-30 dispersive spectrometer with a resolution of 2 cm^{-1} . Samples were prepared by pressing a mixture containing 200 mg of KBr and 1 mg of catalyst into a self supporting wafer.

TPO experiments were carried out with 200 mg of freshly dried catalyst in a reactor which was heated to 500°C at a rate of 3°C/min. We used a 5% oxygen in helium flow of 7.5 ml/min. The gases were analysed with a Leybold mass spectrometer (Quadrupac PGA 100) which could record up to 8 masses quasi-simultaneously.

RESULTS

X-ray photoelectron spectroscopy

As silica-supported zirconia is an insulator, its XPS spectrum is affected by charging. This is illustrated in Fig. 1, where XPS spectra are compared, in the range between 150 and 200 eV, of a $\text{ZrO}_2/\text{SiO}_2$ catalyst and an electrically conducting model system. The spectrum of the real catalyst shows a single broad Si 2s peak at about 166 eV and a poorly resolved Zr 3d doublet with the $3d_{5/2}$ component at about 195 eV. The expected values for Si 2s of SiO_2 and Zr $3d_{5/2}$, however, are about 12 eV lower, 154 and 182.4 eV [8], respectively. Charge shifts observed in the XPS spectra of the other $\text{ZrO}_2/\text{SiO}_2$ samples ranged from 8 to 25 eV, depending on the amount of catalyst powder present on the indium sample holder. Charging was considerably more severe in reference samples of pure zirconium ethoxide, nitrate and oxide, from which XPS spectra could not be obtained at all.

The XPS spectrum of a conducting $\text{ZrO}_2/\text{SiO}_2/\text{Si}$ model catalyst, on the other hand (Fig. 1), exhibits a sharp and well resolved Zr(3d) doublet with a Zr $3d_{5/2}$ binding energy of 183.4 eV, a Si 2s peak for the oxide layer at 155 eV

Fig. 1. XPS spectra in the range of the Si 2s and Zr 3d peaks of a real $\text{ZrO}_2/\text{SiO}_2$ catalyst (top) and of a conducting $\text{ZrO}_2/\text{SiO}_2/\text{Si}(100)$ model catalyst (bottom), showing the effect of electrical charging. The spectrum of the real catalyst exhibits a charge shift of about 11 eV and is severely broadened in comparison to that of the model catalyst. Note that the spectrum of the latter contains two Si 2s peaks, one at about 151 eV for zero-valent silicon from the substrate and the other at about 154.5 eV for Si^{4+} from the 1 nm SiO_2 layer.

as well as one at 151 eV for the semi-conducting silica substrate. In this case the charge shift of both the ZrO_2 and the SiO_2 amounts to 1 eV only [7].

The rather large charge shifts observed in the spectra of the insulating samples are caused by the use of a monochromatic XPS. Here the X-ray source is at a large distance from the sample, and hence secondary electrons and Auger electrons from the source, which compensate to some extent for charging in standard XPS instruments, do not reach the sample.

XPS spectra were measured of the 8, 16 and 24 wt.-% $\text{ZrO}_2/\text{SiO}_2$ catalysts prepared from zirconium nitrate and the 16 wt.-% catalyst from ethoxide, as a function of calcination temperature. All spectra yielded a Zr $3d_{5/2}$ binding energy in the range 182.5 ± 0.5 eV, which indicates that zirconium is present in the 4+ oxidation state. O 1s spectra showed one broad peak at a corrected binding energy of 532.3 ± 0.3 eV. A weak N 1s signal with a binding energy of 407.3 eV, consistent with the presence of nitrate [8], was observed in the impregnated catalysts after drying at 110 and 200°C. The intensities are shown in Table 1. The spectra of the catalysts from ethoxide showed a broad C 1s signal at a binding energy of 284.5 eV. Contributions at higher binding energies which would be characteristic of ethoxide could not be detected due to a poor signal to noise ratio. The intensity of the C 1s signal is given in Table 2. The data indicate that catalysts calcined at 320°C and higher contain significantly less carbon than those calcined at lower temperatures.

Fig. 2 shows XPS spectra of the $\text{ZrO}_2/\text{SiO}_2$ catalysts after calcination in air

TABLE 1

Intensity ratio of the N 1s and Si 2s peaks in the XPS spectra of the $\text{ZrO}_2/\text{SiO}_2$ catalysts prepared from zirconium nitrate for two calcination temperatures

Loading (wt.-%)	N 1s/Si 2s	
	110°C	200°C
8	$3.9 \cdot 10^{-2}$	$1 \cdot 10^{-2}$
16	$7.2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$
24	$12.0 \cdot 10^{-2}$	$5 \cdot 10^{-2}$

TABLE 2

Intensity ratio of the C 1s and Si 2s peaks in the XPS spectra of the 16 wt.-% $\text{ZrO}_2/\text{SiO}_2$ catalysts prepared from zirconium ethoxide as a function of calcination temperature

Calcination temperature (°C)	C 1s/Si 2s
25	0.9 ± 0.15
200	0.4 ± 0.10
320	0.16 ± 0.07
410	0.11 ± 0.05
490	0.12 ± 0.06
615	0.22 ± 0.08
680	0.16 ± 0.07

at 700°C. All spectra were corrected for charging by positioning the Si 2s peak at a binding energy of 154 eV.

The intensity of the zirconium signal relative to that of silicon is determined by the ZrO_2 content of the catalyst and by its dispersion over the silica. For the three catalysts prepared from nitrate, Fig. 2 shows that, as expected, the zirconium intensity goes up as the ZrO_2 loading increases. Note however, that the Zr 3d intensity of the catalyst prepared from zirconium ethoxide is significantly larger than that of the nitrate-derived catalyst with the same ZrO_2 loading. This forms evidence that the dispersion of the catalyst from ethoxide is higher than that of the conventionally impregnated catalysts.

Zirconium-to-silicon XPS intensity ratios for the four catalysts treated at a number of calcination temperatures are given in Fig. 3. The zirconium-to-silicon ratio of the catalyst from ethoxide decreases from about 1.1 for the freshly dried catalyst to about 1.0 for the catalysts calcined at around 700°C. The weak dependence of the zirconium-to-silicon intensity ratio on the calcination temperature indicates that the catalysts are rather stable with respect to sintering.

The $\text{ZrO}_2/\text{SiO}_2$ catalyst with the same loading but prepared by incipient wetness impregnation exhibits not only a lower dispersion but also a lower

Fig. 2. XPS spectra in the range from 150 to 200 eV, showing the Zr 3d and Si 2s peaks of the $\text{ZrO}_2/\text{SiO}_2$ catalysts after calcination at 700°C . All XPS spectra have been corrected for electrical charging by positioning the Si 2s peak at 154 eV. The spectra labelled 'nitrate' correspond to the catalysts prepared by incipient wetness impregnation with an aqueous solution of zirconium nitrate, the spectrum labelled 'ethoxide' to that prepared by contacting the support with a solution of zirconium ethoxide and acetic acid in ethanol. The latter preparation leads to a better ZrO_2 dispersion over the SiO_2 than the standard incipient wetness preparation does, as is evidenced by the high Zr 3d intensity of the bottom spectrum.

thermal stability, as Fig. 3 shows. The catalyst with the highest loading, 24 wt.-%, shows the largest decrease in zirconium-to-silicon ratio, whereas the ratio of the catalyst with 8 wt.-% ZrO_2 loading is almost constant. We further note that the most significant loss of dispersion occurs at calcination temperatures between 25 and 400°C .

In order to interpret the zirconium-to-silicon ratios quantitatively, we have used the model published by Kuipers et al. [9]. These authors showed that for randomly oriented samples a unique relationship exists between the XPS intensity ratio of the supported phase and the support on one hand and the dispersion of the supported phase on the other. Hence, the zirconium-to-silicon ratios of Fig. 3 can be converted to dispersions, and to characteristic dimensions of some likely particle geometries: layers with a uniform thickness d , spheres with a diameter $2R$ ($=3d$) or half spheres with radius r ($=2.25d$). Table 3 summarizes these values for the catalysts which were calcined at 700°C . Fig. 4 presents a highly schematic but instructive visualisation of what the calculated dispersions and support coverages mean if the ZrO_2 particles were present in the form of half spheres.

To summarize, the XPS spectra clearly show that the ethoxide-derived $\text{ZrO}_2/\text{SiO}_2$ catalyst is highly dispersed and exhibits a satisfactory thermal stability.

Fig. 3. Zr 3d/Si 2s intensity ratios calculated from the XPS spectra for the $\text{ZrO}_2/\text{SiO}_2$ catalysts prepared from ethoxide (■) and from nitrate: (◇) 24 wt.-%; (□) 16 wt.-%; (○) 8 wt.-%: as a function of calcination temperature.

TABLE 3

Dispersion and support coverage in $\text{ZrO}_2/\text{SiO}_2$ catalysts calcined at 700°C as derived from the Zr 3d/Si 2s XPS intensity ratios by means of Kuiper's model [9]

Loading (wt.-%)	Zr/Si (XPS)	Dispersion: D (%)	Θ^α (m^2/g)	Effective layer thickness: d (nm)	r^β (nm)
<i>Catalysts from zirconium nitrate</i>					
8	0.22 ± 0.01	12 ± 1	5	2.7	6.0
16	0.37 ± 0.04	8 ± 1	7	4.2	9.5
24	0.55 ± 0.02	7 ± 0.5	9	4.8	10.8
<i>Catalyst from zirconium ethoxide</i>					
16	1.0 ± 0.05	75 ± 15	67	0.42	0.95

$^\alpha$ Area of silica covered by ZrO_2 ; total support area is $250 \text{ m}^2/\text{g}$.

$^\beta$ Effective radius of a half spherical particle.

The $\text{ZrO}_2/\text{SiO}_2$ catalysts prepared from nitrate solution have a considerably lower dispersion. In both type of catalysts, zirconium is present in the 4+ oxidation state irrespective of the calcination temperature. Nitrate residues

Fig. 4. Schematic representation of the dispersion of ZrO_2 particles and the extent to which the silica support is covered in three $\text{ZrO}_2/\text{SiO}_2$ catalysts prepared by impregnation with an aqueous zirconium nitrate solution, and one prepared via an exchange reaction of the support with zirconium ethoxide. The rectangles represent 100 nm^2 of silica support area, the circles represent a half-spherical particle of ZrO_2 seen from above. See Table 3 for corresponding numbers.

can be observed in XPS spectra of samples calcined at temperatures up to 200°C .

Secondary ion mass spectrometry

Fig. 5A shows a typical positive SIMS spectrum of a catalyst prepared from zirconium ethoxide. It contains peaks of H^+ , C^+ , O^+ , Na^+ , Si^+ , K^+ , Ca^+ , SiO^+ , SiOH^+ , Zr^+ , ZrO^+ , In^+ , and ZrO_2^+ . The relatively high intensities of sodium, potassium and calcium are a well-known artefact of SIMS; traces of these elements already give high yields in SIMS⁺. The In^+ peak arises from the indium foil in which the catalyst powder was pressed.

We found that the most useful SIMS information is in the relative intensities of the Zr^+ , ZrO^+ , ZrOH^+ and ZrO_2^+ ions. This is illustrated in Figs. 5B and 5C which show the isotopic pattern of these ions of a freshly dried (Fig. 5B) and a calcined (Fig. 5C) catalyst. Note that the SIMS spectrum of the freshly dried catalyst contains small but significant contributions of ZrOH^+ ions. See for example the peaks at 107 amu ($^{90}\text{ZrOH}^+$ and $^{91}\text{ZrO}^+$) and 111 amu ($^{94}\text{ZrOH}^+$). ZrOH^+ is probably a fragment ion from zirconium ethoxide or acetate. In the sample which was calcined at 400°C the isotopic pattern of

Fig. 5. Positive SIMS spectrum of the 9 wt.-% $\text{ZrO}_2/\text{SiO}_2$ catalyst prepared from ethoxide, dried at 40°C (A), and two spectra of the Zr - ZrO - ZrO_2 region for a dried catalyst (B) and a calcined one (C).

ZrO resembles the pattern of Zr , indicating that no more ZrOH species are present.

Fig. 6 contains the ZrO^+/Zr^+ and $\text{ZrO}_2^+/\text{Zr}^+$ ratios from the SIMS spectra for the ethoxide-derived catalysts as a function of calcination temperature. We also included these ratios for zirconium ethoxide and zirconium oxide reference samples. The figure clearly shows that catalysts prepared from zirconium ethoxide which were calcined below 200°C have ZrO^+ to Zr^+ and ZrO_2^+ to Zr^+ ratios about equal to those of the zirconium ethoxide reference compound. However, samples calcined above 300°C have ZrO^+ to Zr^+ and ZrO_2^+ to Zr^+ ratios which decrease towards those measured for ZrO_2 .

Hence, the SIMS spectra clearly indicate that the formation of ZrO_2 in catalysts prepared by ion exchange from zirconium ethoxide occurs during calcination in air at temperatures between 300°C and 400°C .

The SIMS spectra of the zirconium catalysts which were prepared by incipient wetness impregnation from a nitrate solution are of comparable quality to the spectra in Fig. 5. The spectrum of the freshly prepared sample dried at 40°C gives clear evidence that the zirconium species present on the silica surface is not $\text{Zr}(\text{NO}_3)_4$. Pure $\text{Zr}(\text{NO}_3)_4$ has a high ZrO^+ to Zr^+ ratio of about 2 (see Fig. 7). The ratio for the spectra of the fresh catalyst, however, is about 0.35, which is more characteristic of zirconium oxide or, perhaps, hydroxide or

Fig. 6. SIMS⁺ ZrO⁺ to Zr⁺ and ZrO₂⁺ to Zr⁺ ratios as a function of calcination temperature for a 9 wt.-% ZrO₂/SiO₂ catalyst prepared from zirconium ethoxide, along with the ZrO⁺ to Zr⁺ and ZrO₂⁺ to Zr⁺ ratios measured from zirconium ethoxide and zirconium oxide reference samples.

oxyhydroxide. The ZrO⁺ to Zr⁺ ratio increases at calcination temperatures above 400°C and finally drops back to the value characteristic of ZrO₂. The ZrO⁺ to Zr⁺ of the zirconium nitrate reference sample decreases continuously with time spent in the vacuum system, which is probably caused by decomposition of the nitrate [10].

In negative SIMS the following species were observed: C⁻, O⁻, OH⁻, H₂O⁻, F⁻, C₂⁻, C₂H⁻, C₂H₂⁻, Si⁻, SiO⁻, SiOH⁻, SiO₂⁻, ZrO⁻ and ZrO₂⁻. Neither higher ethoxide fragments nor any nitrate fragments were found. A major problem is that a number of potentially interesting ions have the same masses, e.g. SiO⁻ and CO₂⁻ (mass 44) and SiOH⁻ and C₂H₅O⁻ (mass 45).

In summary, the SIMS measurements clearly reflect the transition from the precursor to ZrO₂ in the catalysts prepared from ethoxide. Furthermore the spectra indicate that the zirconium species in the freshly prepared catalysts from nitrate solution is not a zirconium nitrate but a compound which already resembles an oxide, hydroxide or oxyhydroxide.

Infrared spectroscopy

In order to obtain more insight in the transformation of the precursor to zirconium oxide, the catalysts were studied with IR. A spectrum of each sample

Fig. 7. SIMS⁺ ZrO⁺ to Zr⁺ ratio for a 20 wt.-% ZrO₂/SiO₂ catalyst prepared by incipient wetness impregnation from an aqueous solution of zirconium nitrate. For comparison the ZrO⁺ to Zr⁺ ratios of zirconium nitrate and zirconium oxide reference samples have been included.

was recorded in the range from 4000 to 400 cm⁻¹. In addition, zirconium oxide, ethoxide and nitrate and silica spectra were recorded as references.

Catalyst prepared from ethoxide

Fig. 8 shows the infrared spectra of the catalyst prepared from zirconium ethoxide as well as those of Zr(OEt)₄ and ZrO₂ references, in the range of 1800 to 1200 cm⁻¹. In the zirconium ethoxide reference spectrum peaks are visible at 1635 cm⁻¹ (O-H bend), 1590 cm⁻¹ (COO), 1475 and 1430 cm⁻¹ (C-H bend), and 1390 cm⁻¹ (O-H bend).

The IR spectrum of the freshly prepared catalyst, which was dried at 40°C, differs from that of zirconium ethoxide in at least three points. First, the IR spectrum of the catalyst exhibits a broad band due to Si-O between 1000 and 1300 cm⁻¹. Second, the O-H bending vibration at 1390 cm⁻¹ is much weaker than in the zirconium ethoxide reference sample. Third, the spectrum of the catalyst contains an extra band at 1710 cm⁻¹, characteristic of a C=O vibration. This band arises from the acetic acid we used to make the zirconium ethoxide more soluble. The assignment is confirmed by blank experiments in which we added acetic acid to a suspension of silica in ethanol and then filtrated and dried the silica. The same peak as above, at 1710 cm⁻¹, was found, which we assign to acetate groups adsorbed on the silica surface.

Fig. 8. Infra-red spectra in the range from 1200 to 1800 cm^{-1} as a function of calcination temperature for the 9 wt.-% $\text{ZrO}_2/\text{SiO}_2$ catalyst prepared from ethoxide. Spectra for zirconium ethoxide and zirconium oxide references are also included.

With calcination temperature increasing to 200°C the spectrum basically does not change. However, after calcination at 300°C the C=O band has disappeared and the C-H bands have very much decreased in intensity. After calcination at 400°C, no more organic species could be detected in the IR spectrum, and the spectrum resembled that of the ZrO_2 reference sample.

Catalyst prepared from nitrate

Fig. 9 shows the IR spectra of the nitrate-derived catalyst calcined at different temperatures. Also included are the spectra of zirconium nitrate and zirconium oxide references. The IR spectrum of zirconium nitrate has peaks at 1610 cm^{-1} (O-H bending vibration), 1550 cm^{-1} (asymmetrical NO_2 stretch-

Fig. 9. Infra-red spectra in the range from 1200 to 1800 cm^{-1} as a function of calcination temperature for the 20 wt.-% $\text{ZrO}_2/\text{SiO}_2$ catalyst prepared from zirconium nitrate. Spectra for zirconium nitrate and zirconium oxide references are also included.

ing vibration), 1310 cm^{-1} (NO_2 stretching vibration) and (1400 cm^{-1} , symmetrical N–O stretching vibration) [11–14]. Such a combination of IR bands is characteristic for complexes in which the metal nitrate bonds have covalent character [11,12]. The last three have about equal intensity. These peaks are also present in the IR spectrum of the catalyst dried at 110°C but note that here the symmetric N–O stretch at 1400 cm^{-1} is very intense. According to Gatehouse et al. [11,12], this band is characteristic of a purely ionically bound nitrate ion. In this case, the bands at 1550 and 1310 cm^{-1} are absent.

Thus, the IR spectra suggest that there are two nitrate species on freshly impregnated catalysts: one with a spectrum similar to that of the zirconium nitrate reference, which disappears after calcination between 100 and 200°C,

and the other with the IR spectrum of purely ionic nitrate, which disappears after calcination between 300 and 400°C. We propose that the latter nitrate species form the counter ions of the silica support which is positively charged in solutions of low pH.

In summary, the IR spectra of the ethoxide-derived catalyst clearly show the presence of acetate and ethoxide groups on samples calcined below 300°C. These species disappear from the catalyst upon calcination at 300–400°C. IR spectra of the nitrate-derived catalyst show that there are two nitrate species present after impregnation. Nitrate groups coordinated to zirconium decompose mainly below 200°C whereas nitrate groups on the silica support disappear after calcination at 300–400°C.

Temperature-programmed oxidation

Temperature-programmed oxidation was carried out to monitor the evolution of products formed during calcination of the freshly prepared and dried catalysts. The spectra are shown in Fig. 10 for the ethoxide and Fig. 11 for the nitrate-derived catalyst. The TPO is not entirely conclusive because several masses cannot be assigned unambiguously. For example, mass 28 can be due to carbon monoxide, formed by incomplete oxidation of the zirconium ethoxide

Fig. 10. TPO signals of the 9 wt.-% $\text{ZrO}_2/\text{SiO}_2$ catalyst prepared from zirconium ethoxide showing the signals of mass 18 ($\times 1$), mass 27 ($\times 40$), mass 28 ($\times 7$), mass 32 ($\times 3$), mass 42 ($\times 40$) and mass 44 ($\times 3$).

Fig. 11. TPO signals of the 20 wt.-% $\text{ZrO}_2/\text{SiO}_2$ catalyst prepared from zirconium nitrate showing the signals of H_2O ($\times 1$), NO ($\times 9$), O_2 ($\times 45$) and NO_2 ($\times 175$).

precursor, but it can also be a fragmentation of the ethanol solvent. Similar considerations apply to other masses. Nevertheless, the spectra allow for a number of conclusions.

Catalyst prepared from ethoxide

The TPO curves consist of two regions, one with peaks in the range from 50 to 225°C when hardly any oxygen is consumed and an other from 275 to 500°C. In order to attribute these signals we carried out some additional experiments. A solution of silica in ethanol was heated until all the ethanol had evaporated. The silica was dried at 40°C for three hours and a TPO experiment was carried out in the same way as described above. Small peaks were visible in the mass 18, 28, 42 and 44 signals at 150°C. These signals can all be assigned to adsorbed ethanol. The experiment was then repeated with acetic acid added to the solution. The same peaks were observed, only at a slightly higher temperature of 160°C. Mass 31 (typical of ethanol) and mass 60 (typical of acetic acid) could not be detected in any of the TPO experiments. Hence, we assign the peaks in the region from 50 to 225°C to the desorption of ethanol and acetic acid from the solvent and water present on the silica.

The peaks above 275°C are then related to the zirconium ethoxide-acetate complexes on the support. At temperatures around 390°C oxygen consumption reaches a maximum and the products formed are characterized by masses

18, 28 and 44. We attribute these peaks to the oxidation of carbonaceous species towards carbon dioxide and water and perhaps carbon monoxide. The maxima in these signals around 350°C are accompanied by maxima in those of mass 27 and 42 and can therefore be assigned to the decomposition of ethoxide-acetate.

Catalyst prepared from nitrate

Fig. 11 shows the signals of H₂O (mass 18), NO (30), O₂ (32) and NO₂ (46) in the TPO of the catalyst prepared from zirconium nitrate. Again at a low temperature we see desorption of water. Then starting at a temperature of $\pm 150^\circ\text{C}$ until the end of the temperature scale NO and NO₂ are evolving. Oxygen evolution starts at about 300°C. These data are in agreement with data obtained by Gimblett et al. [15] on bulk Zr(NO₃)₄.

DISCUSSION

The most important difference between a ZrO₂/SiO₂ catalyst prepared via the ethoxide-hydroxyl reaction and one prepared by incipient wetness impregnation is the much higher dispersion of the former. This is clearly reflected by the zirconium-to-silicon XPS intensity ratios in Fig. 3 and the quantitative interpretation based on Kuiper's model [9] in Table 3. Although the dispersions in particular of the ethoxide-derived samples are sensitive to input parameters such as ZrO₂ loading and support area, the values in Table 3 show that the characteristic linear dimensions of the ZrO₂ particles originating from zirconium ethoxide are at least an order of magnitude smaller than in the catalysts derived from zirconium nitrate. Fig. 4 illustrates what this means in terms of particle size and coverage of the silica support. Hence we conclude that the ZrO₂/SiO₂ catalysts prepared via the ethoxide-hydroxyl reaction route are by far superior to the catalysts prepared via the standard incipient wetness impregnation technique.

Owing to the results from TPO, SIMS and IR we have a fairly detailed understanding of the way zirconium oxide forms on silica from the precursors. We propose that the following steps take place in the formation of ZrO₂ from zirconium ethoxide on silica.

(1) In the solution of zirconium ethoxide and acetic acid in ethanol, ethoxide and acetate groups interchange following this mechanism:

This is a well-known reaction of metal alkoxides with organic acids and it increases the solubility of zirconium ethoxide. x is small, typically 1 [16].

(2) When silica is added the following reaction takes place:

The IR band at 1710 cm^{-1} gives evidence of the presence of the CH_3COO^- ligand. Also, small amounts of ethanol and acetic acid adsorb on the silica surface.

(3) The TPO experiments indicate that water desorbs from the surface at about 50°C and that acetate and ethanol desorb around 175°C .

(4) During calcination between 200°C and 300°C , zirconium ethoxide ligands of the zirconium desorb as ethanol or decompose to leave carbonaceous residue on the surface and ZrO_2 begins to form. This is concluded from the decreasing ZrO^+ to Zr^+ and ZrO_2^+ to Zr^+ ratios in SIMS, the decreasing intensity of the C–O and C–H vibrations in IR, and the decrease in carbon content as observed in XPS (Table 2). The TPO experiments suggest that the decomposition of ethoxide occurs at temperatures above 300°C . We do not believe that this is in contradiction with the IR and SIMS results, because catalysts used in TPO experiments are necessarily treated differently than those used for IR and SIMS analysis: the latter were calcined for several hours, whereas in TPO a fresh sample was heated in situ at a rate of $3^\circ\text{C}/\text{min}$. Kinetic limitations are expected to shift features to higher temperatures.

(5) After calcination at 400°C the formation of ZrO_2 is complete (SIMS) and almost all organic species have disappeared (IR). Carbonaceous residues are burned off with oxygen at temperatures between 350 and 500°C as follows from the TPO experiments.

In summary we can state that a zirconium ethoxide–acetate species reacts with the silica surface upon impregnation. At the same time acetate and ethanol adsorb on the surface. Upon calcination, these species desorb first. After calcination at 200 – 300°C ethoxide groups decompose and ZrO_2 is formed. Finally the remaining carbon species are burned off between 350 and 500°C .

The catalyst prepared from zirconium nitrate behaves quite differently. The SIMS spectra and in particular the ZrO^+ to Zr^+ ratios indicate that at least the majority of the phase deposited on the silica during impregnation is not zirconium nitrate but probably zirconium hydroxide or oxyhydroxide. Nitrate groups are nevertheless present after impregnation (XPS, IR and TPO). The IR spectra suggest that there are two nitrate species: one bonded to zirconium, the other present as negative counter-ion for the silica surface, which is positively charged in solutions of low pH. Upon heating, the nitrate groups coordinated to zirconium start to decompose and desorb as NO_x at about 150°C (TPO, IR). In XPS, the intensity of the nitrate signals decreases by a factor of 2–3 after heating the samples to 200°C and goes to zero after heating to 300°C . The N–O vibrations of the nitrate counter-ions of the silica disappear from the IR spectrum after calcination of the catalysts at 300 – 400°C .

The zirconium-to-silicon XPS intensity ratio indicates that the initially deposited zirconium phase has characteristic dimensions of the order of a few nm. Upon calcination some loss of dispersion occurs in the catalysts with 16 and 24 wt.-% ZrO_2 loading. For temperatures above 300°C all samples are more

or less stable with respect to sintering. The final dispersion of the catalysts is below 10%.

The combination of XPS, SIMS, IR and TPO appears valuable for investigating the genesis of these oxide on oxide systems. The most useful information from XPS in this work is that on the dispersion of the ZrO_2 over the support. The XPS binding energies did not give detailed information about the chemical changes in the zirconium compounds on the silica during the calcination procedures. Due to inhomogeneous charging, subtleties in peak positions which can be observed in conducting model systems [7] are lost in the spectra of insulating samples. In future work we intend to exploit the opportunities that these conducting model systems offer for the investigation of catalyst preparation by means of surface spectroscopies.

Chemical state information is provided by the other spectroscopies used in this work: SIMS, IR and TPO. These techniques readily reveal the conversion of the zirconium precursors to the final oxide. TPO monitors the evolution of fragments from decomposed precursors or their oxidation products when they desorb from the surface, as well as the oxygen consumption of the catalyst. IR detects the presence of nitrate, ethoxy or acetate ligands of zirconium on the surface of the catalyst. It is interesting to note that where the data from TPO and IR concern the ligands of zirconium, SIMS gives sensitive information on the zirconium itself. Through comparison with spectra of reference compounds, the SIMS patterns of the Zr^+ , ZrO^+ , and ZrO_2^+ ions reveal the chemical state of the zirconium phases in catalyst.

CONCLUSIONS

(1) Preparation of $\text{ZrO}_2/\text{SiO}_2$ catalysts via the reaction between surface hydroxyl groups of the silica and the ligands of the zirconium ethoxide–acetate complexes dissolved in ethanol leads to a catalyst with a dispersion of the order of 75%. Formation of the zirconium oxide from the ethoxide precursor takes place upon calcination at 300–400°C. The catalysts are rather stable with respect to sintering for temperatures up to at least 700°C.

(2) Preparation of $\text{ZrO}_2/\text{SiO}_2$ catalysts by means of incipient wetness impregnation from an aqueous zirconium nitrate solution results in catalysts with dispersions of the order of 10% or less.

(3) XPS, SIMS, IR and TPO form a useful combination for characterizing these $\text{ZrO}_2/\text{SiO}_2$ catalysts in different stages of the preparation. XPS gives important information on the dispersion of the ZrO_2 phase over the support but provides little chemical information, partly because of charge broadening of the XPS peaks. SIMS, IR and TPO, on the other hand provide detailed information on the transformation of the catalyst precursors to the final ZrO_2 phase.

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