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ON THE ACTIVITY OF ZrO_2 PREPARED BY DIFFERENT METHODS

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Abstract

Zirconia samples with different structures (monoclinic, tetragonal or a mixture of the two) was prepared by different methodologies, including a novel procedure involving the precipitation of an oxalate precursor and the formation of pure tetragonal ZrO_2.

The different precursors obtained by varying the preparative procedure (ex oxychloride, ex oxalate, and ex gel) were studied by means of differential thermal analysis and thermogravimetric analysis under air and under N_2, while the final oxides were characterized by BET, porosimetry and XRD analysis. The surface acid-base properties of the different oxides were assessed via the catalytic decomposition isopropanol. A prevalence of acid sites found for the ex-oxalate ZrO_2 seems to justify the different mechanism of chain growth observed in the carbonylation of methanol with CO/H_2 mixtures in the presence of Rh.

Keywords: activation, methanol carbonylation, preparation method, ZrO_2system

Introduction

Zirconia is a polymorphic material with three known structures: monoclinic, tetragonal and cubic. This material is often combined with cationic dopants (Y_2O_3, Cr_2O_3, MgO, CaO or La_2O_3), which contribute to stabilization of the tetragonal phase at low temperatures [1–4], or with anionic elements (SO_4^{2-}, CO_3^{2-} or Cl^-), which may strongly modify its surface properties [5–8].

In catalysis, ZrO_2 is widely applied both as a catalyst and as a catalytic support [9], thanks to its high mechanical and thermal stability and to the presence of both acidic and basic sites on its surface [10]. Zirconia is often used to support metal catalysts which are active under reducing atmospheres [11–17].

The usual preparative procedures based on precipitation with ammonia from a solution containing an oxychloride precursor lead to the formation of a mixture

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of tetragonal and monoclinic phases, with higher contents of the former phase [18]. In the present work, the importance of the zirconia preparation methodology and of the choice of starting reagents has been investigated. Several preparative procedures have been applied, including sol-gel processes. Each procedure has been characterized with regard to the effect of thermal activation of the precursor on the physico-chemical and catalytic properties under different atmospheres.

Experimental

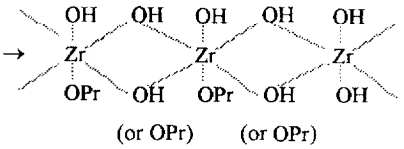
Support preparation

The different preparative methods used to obtain the zirconia precursors are illustrated by the following equations:

$$ZrOCl_2 + 2NH_4OH \rightarrow ZrO(OH)_2 + 2NH_4Cl \quad (1)$$

$$Zr(NO_3)_4 + 2H_2C_2O_4 \rightarrow Zr(C_2O_4)_2 + 4HNO_3 \quad (2)$$

$Zr(OC_3H_7)_4$, $C_3H_7OH + C_3H_6O_2$ $\rightarrow$



(3)

The first method (ex oxychloride) involved the precipitation of zirconium hydroxide starting from $ZrOCl_2$. Depending on the pH, different amounts of residual chloride ions remained dispersed in the ZrO_2 precursor. Two samples were prepared by dissolving $ZrOCl_2$ in distilled water under continuous stirring at 80°C and precipitating at pH 4 or 9. Ammonia (30% solution, Fluka) was added to establish the desired pH. The resulting precipitate was filtered off, washed several times with 1% NH_4OH solution and dried overnight at 120°C.

The second preparative procedure (ex oxalate) consisted in the dropwise addition of 2.2 M oxalic acid solution to 1 M aqueous $Zr(NO_3)_4$ solution under constant stirring at 80°C. When the resulting pH (1.1–1.4) was further lowered to 0.6, a white precipitate was formed. Careful attention was paid to the final pH. Under more acidic conditions, the excess of oxalic acid can dissolve the precipitate, which is normally filtered off and dried overnight at 120°C.

The third method (ex gel) involved a sol–gel process. Zirconium propylate (73% in propanol, Aldrich) was dissolved in propionic acid at 40°C under constant stirring, and hydrolysed with a few drops of distilled water. On evaporation of the solvent, the condensation led to a gel, formed by polymerization. The gel was quenched in liquid nitrogen, ground and transferred to a quartz crucible for thermal activation.

Physico–chemical characterization

– The decompositions of the precursors were studied under N_2 and under air with a Mettler TA 2000C thermogravimetric analyser (TG, DTA and DTG). Samples of approximately 30 mg were placed in Pt and Al_2O_3 crucibles and heated to 600°C at 10°C min^{-1}. The gas feed (air or N_2) was 6 l h^{-1}.

– FTIR analyses were carried out on a BIORAD FTS-40 instrument, and porosimetry and BET surface measurements on a Quantasorb (Quantachrome Co) instrument.

– X-ray diffraction patterns of the samples were recorded with a Siemens D 5000 diffractometer, with filtered CuK_α radiation (count time 1 s in the 2θ range 10–70°).

– Surface acid-base properties were assessed via the catalytic decomposition of isopropanol under stationary conditions in the absence of O_2. The reaction was carried out in a differential flow microreactor (0.1–0.3 g of catalyst) attached to an on-line gas chromatograph (FID and TCD). Isopropanol was introduced at pressures ranging from 0 to 4 kPa, with He as carrier gas (total flow rate 15–60 $cm^3 min^{-1}$).

Results and discussion

Zirconia ex oxychloride

The quantity of residual chloride ions in the zirconia depended sensitively on the pH during the precipitation and during the washing of the precipitate [18, 19].

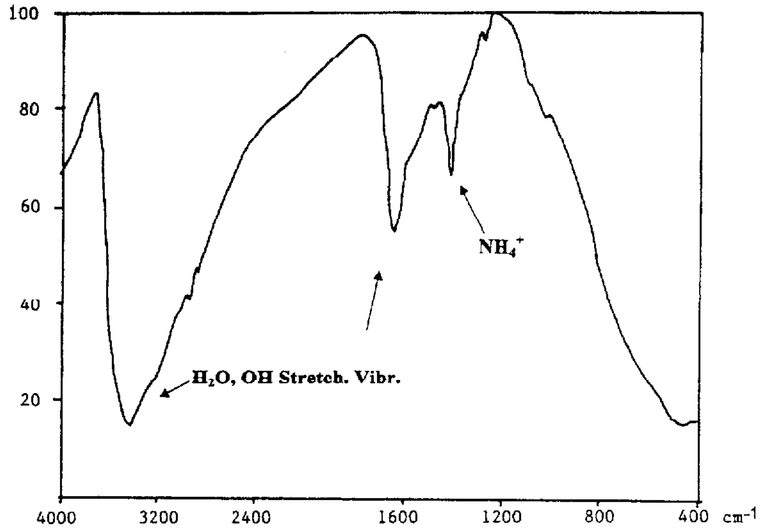


Fig. 1 The IR spectra of ex oxychloride ZrO_2 precursors obtained at pH 4 and at pH 9 are the same

Figures 1 and 2 depict IR spectra and DTA–TG curves recorded in air of the precursors obtained at pH 4 and pH 9. The precursor prepared at pH 9 (with lower chloride content) exhibits (Fig. 2b) an exothermic effect at 280°C, together with an abrupt increase in mass loss, probably due to the oxidation of ammonia in the Pt crucibles [20]. This effect is not observed for the precursor obtained at pH 4 (Fig 2a). The crystallization peak (Table 1) appears at 452°C (pH 9) or at 472°C (pH 4), the XRD data revealing that both samples lead to a mixture of tetragonal and monoclinic phases (Table 2). The sample obtained at pH 4 has a higher chloride content, which results in an increased stabilization of the tetragonal phase [18].

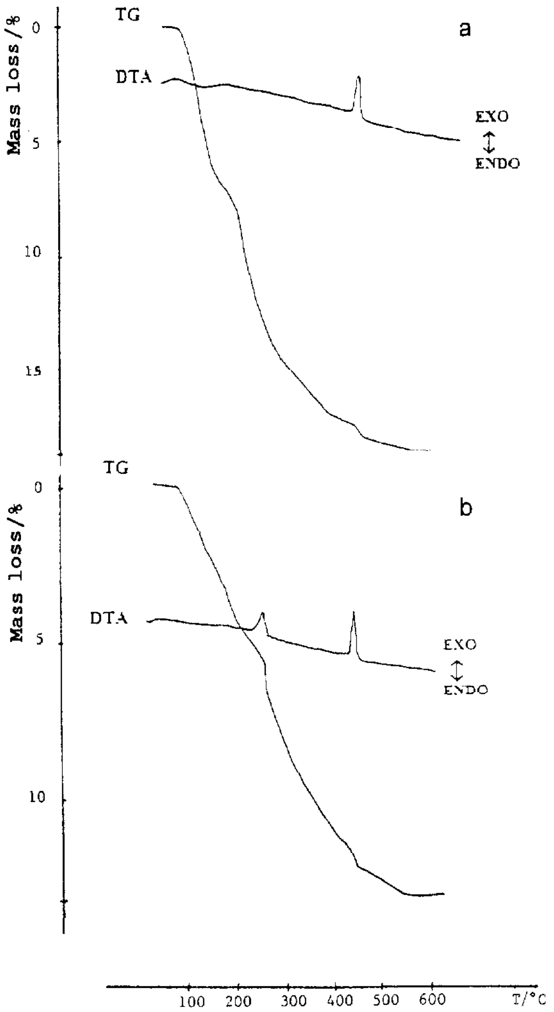


Fig. 2 DTA-TG curves of ex oxychloride ZrO_2 precursors obtained at pH 4 and at pH 9

Table 1 Thermal data recorded under air for the different ZrO_2 precursors

ZrO_2 precursor	$T_{crystallization}$/ °C	$\Delta H_{crystallization}$/ J (g precursor)$^{-1}$	Total mass loss/ %
Ex oxychloride (pH=9)	452	–146	13
Ex oxychloride (pH=4)	470	–150	19
Ex oxalate	420	–252	47
Ex gel	370	–1173	56

Table 2 Typical data of the ZrO_2 based catalysts obtained from different precursors

ZrO_2 precursor	Calcination temperature/°C	Phase composition	S_{BET}/m^2 g^{-1}	$R^{1)}$
ex oxychloride (pH=9)	500°C/air/0.5 h	T+M	90	0.10
	500°C/air/2 h	T+M	70	0.22
	500°C/N_2/2 h	T+M	94	0.90
ex oxychloride (pH=4)	500°C/air/2 h	T+M	90	2.60
ex oxalate	420°C/N_2/2 h	T	125	
	420°C/air/2 h	T	97	
	420°C/air/12 h	T	94	
ex propionate	450°C/N_2/2 h	T	04	
	450°C/air/2 h	T	14	
	450°C/air/12 h	T	13.7	

$^{1)}R$ = 100% XRD band of the tetragonal ZrO_2 (T)/100% band of the monoclinic form (M)

As concerns the porosity and BET surface areas, the surface area of the oxide obtained from the precursor with the lower chloride content (prepared at pH 9), activated for 2 h at 500°C, is lower (Table 2) if the activation is carried out in air rather than in N_2. In this case, the oxide crystallizes with a prevalence of the monoclinic phase (Table 2) and different pore distributions are observed for the air and the N_2-treated samples (Fig. 3).

Zirconia ex oxalate

The oxalate precursor (see the IR spectrum in Fig. 4a) is a pure compound presenting several well-defined XRD peaks, which are different from those reported for $Zr(C_2O_4)_2 \cdot 4H_2O$ obtained by adding oxalic acid to a methanolic $ZrCl_4$ solution [21]. The differences probably arise from chloride ion interferences.

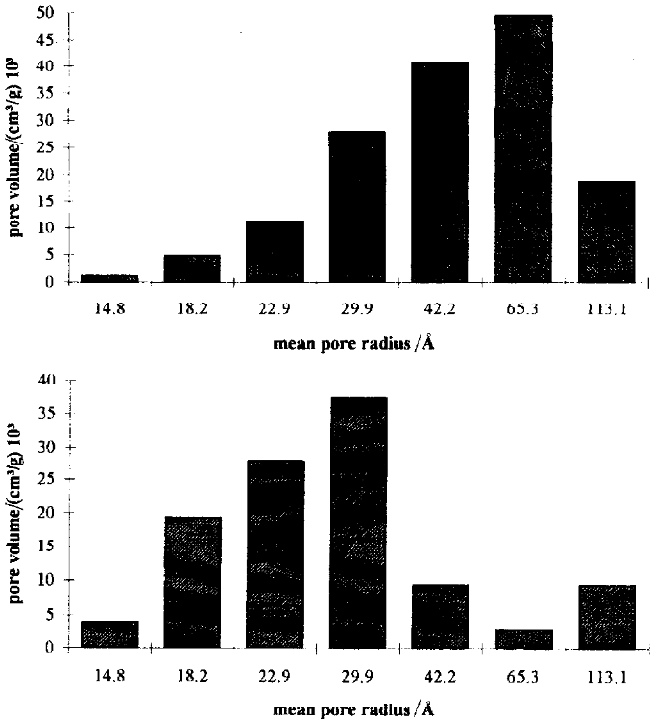


Fig. 3 Pore volume distribution of ZrO_2 obtained the ex oxychloride precursor on heating for 2 h at 500°C: a) under air, and b) under N_2

The decompositions of this precursor under air and under N_2 are very similar. The DTA–TG curves (Fig. 6, Al_2O_3 crucibles) reveal a small exothermal peak at approximately 220°C, together with a limited mass loss, probably due to the elimination of free oxalic acid. The main endothermal decomposition starts at above 300°C, and is completed at 400°C. This decomposition to CO and CO_2 is similar under air and under N_2, since the alumina crucibles used prevent the exothermal effect due to CO oxidation. The total mass loss under either air or N_2 is 47%. On further increase of the temperature, an exothermal peak at approximately 420°C demonstrates crystallization of the oxide in the pseudotetragonal form under either atmosphere (Fig. 7a) [22]. The pore volume distribution too seems to be relatively unaffected by the nature of the gaseous atmosphere under which crystallization occurs (Fig. 8).

This oxide is a suitable catalytic support since it does not contain impurities; with the oxychloride precursor, extensive treatment is needed to eliminate chlorine. The BET results show that, relative to the ex oxychloride samples, similar or even larger surface areas may be obtained, particularly when the precursor is heated under N_2 (Table 2).

Zirconia ex gel

The IR spectrum is reported in Fig. 4b. The DTA–TG curves obtained under air or under N_2 (Figs 9a and 9b) indicate that the endothermal elimination of free propionic acid begins at nearly 160°C. Only in the presence of O_2 does a second sharp exothermal peak appear, starting at 330°C, due to carbon oxide formation resulting from the elimination of the organic component of the gel. The exothermal crystallization can be better identified under N_2 (the small peak at 460°C). The total mass loss at 500°C is 56% in both cases.

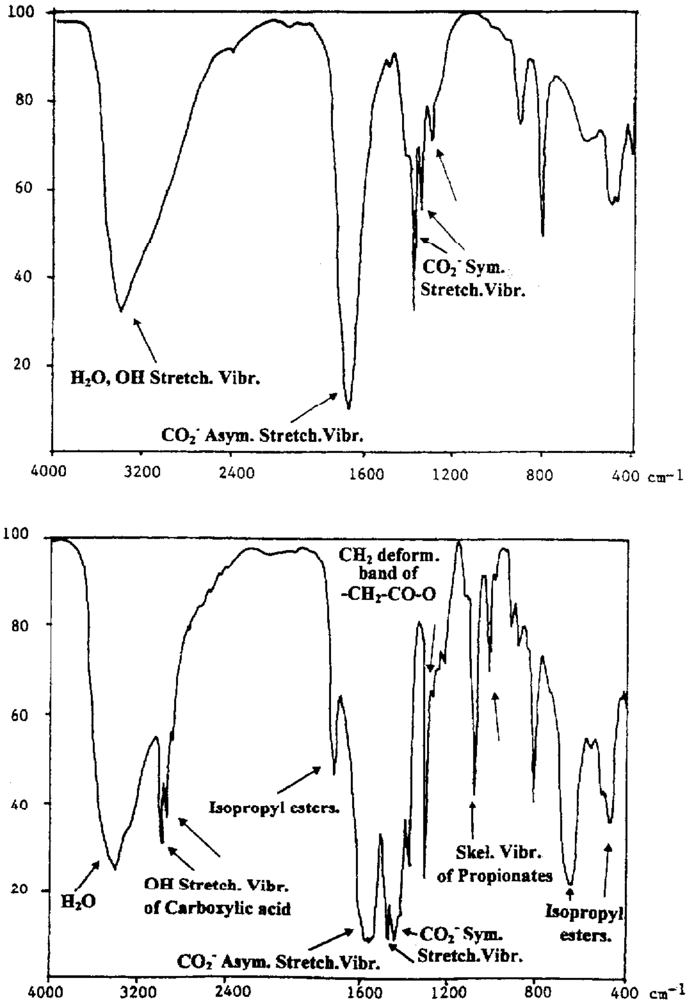


Fig. 4 IR spectra of ZrO_2 precursors: a) ex oxalate, and b) ex gel

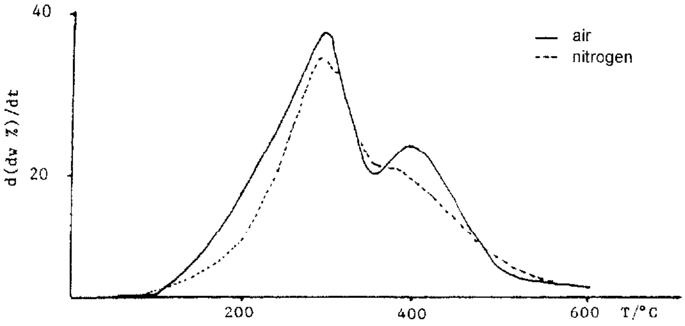


Fig. 5 Decomposition rates of ex gel precursors: a) under air and b) under N_2

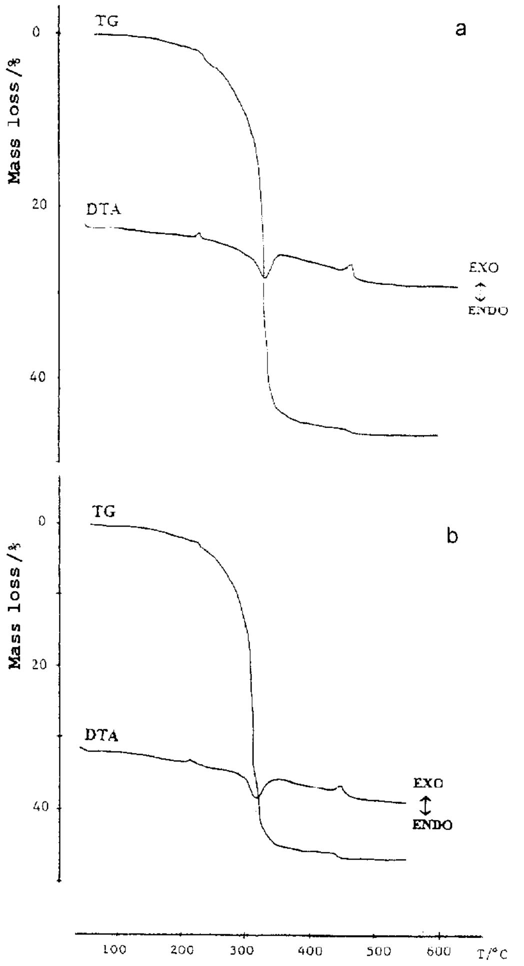


Fig. 6 DTA-TG curves of ex oxalate ZrO_2 precursor

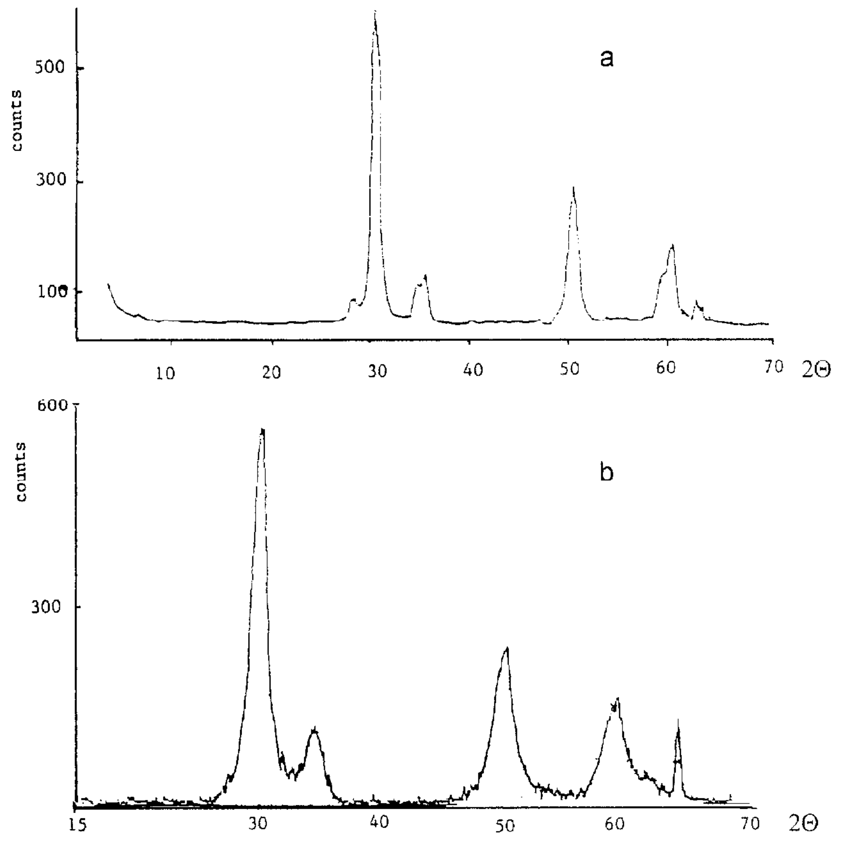


Fig. 7 XRD spectra of ZrO_2 obtained starting from a) an oxalate precursor, and b) a gel precursor

All gel samples treated at 450°C and characterized by the presence of the low-temperature tetragonal form (Fig. 7b) have very low surface areas (Table 2), analogously as observed by other authors who prepared zirconia via a sol–gel method, but using the acetate instead of the propionate [23].

The porosity of samples calcined under N_2 is mainly due to mesopores, while for those treated under air micropores also have to be considered (Figs 10a and 10b). This could originate (Fig. 5) from the different decomposition patterns observed in the two cases at the end of the crystallization peak, at nearly 450°C.

Finally, if the decomposition rates of the ex gel and ex oxalate samples under air are compared (Fig. 11), it can be seen that the elimination of propionate groups from the ex gel sample is faster than that of oxalate groups from the corresponding precursor, and that the associated exothermal contribution (Figs 9a and 6a) is also much more pronounced. This leads to sintering of the surface of the ex gel zirconia, characterized by poor BET surface areas and pore volumes.

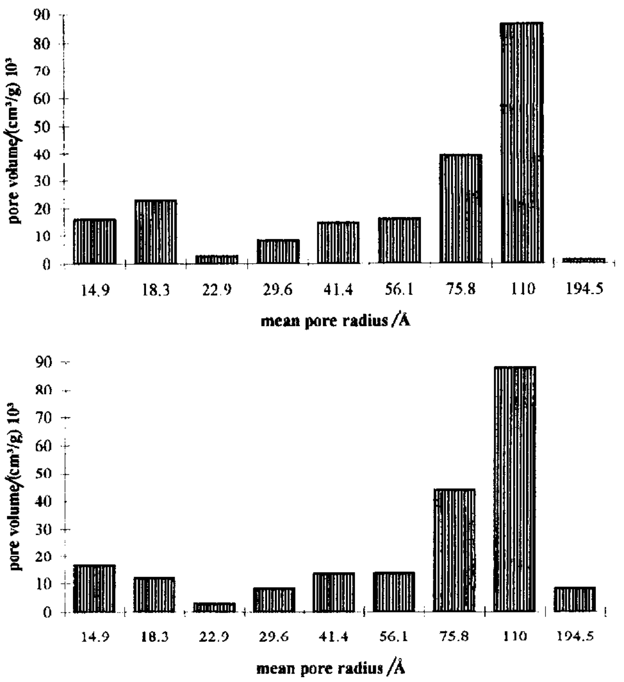


Fig. 8 Pore volume distribution of ex oxalate ZrO_2 heated a) under air and b) under N_2

Acid-base properties of ex oxychloride, ex oxalate and ex gel ZrO_2

Table 3 reports surface acidity data obtained via isopropanol decomposition. All the examined samples exhibit a definite prevalence of acid sites, which is particularly evident for the ex oxalate ZrO_2. The limited amount of acetone observed appears to indicate that basic sites are not completely absent.

The different acid-base properties found for the ZrO_2 samples obtained from the various precursors seem to affect the catalytic activity observed when the same oxides are used as supports in the carbonylation of methanol with CO/H_2 mixtures in the presence of Rh. Indeed, within the frame of a Brite-Euram research project (contract N° CT91-0458), it has been found [24] that the marked

Table 3 Isopropanol decomposition on ex oxychloride, ex oxalate and ex gel zirconia

Sample	Surface area/m^2 g^{-1}	$V_{propene}$/μmol h^{-1} m^{-2}	$V_{acetone}/V_{propene}$ 10^{+4}
ZrO_2 (ex oxychloride)	94	1.45	0.03
ZrO_2 (ex oxalate)	125	2.8	0.01
ZrO_2 (ex gel)	4	1.7	0.02

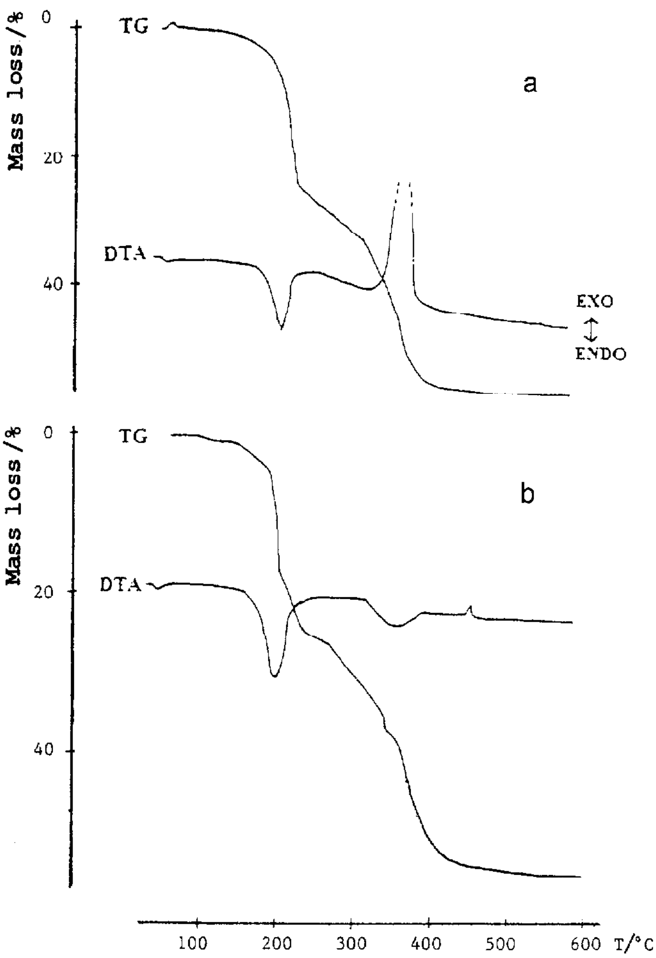


Fig. 9 DTA-TG curves of ex gel ZrO_2 precursor heated a) under air and b) under N_2

Table 4 Methanol carbonylation with Rh catalysts[1] supported on ex oxychloride, ex oxalate and ex gel ZrO_2

Catalyst	C_2–C_6(g of product/g cat)			H_2O/%
	esters	alcohols	acids	
5%Rh/ZrO_2 (ex oxychloride)	1.0	0.6	0.60	32.6
5%Rh/ZrO_2 (ex oxalate)	3.0	0.9	0.80	78.6
5%Rh/ZrO_2 (ex gel)	0.6	4.0	0.06	16.6

[1] $Rh_4(CO)_{12}$ is used for impregnation [26]

P=21 MPa, T=230°C, CO/H_2=60/40, gas flow=3 l/h g cat, $MeOH/CH_3I$=7.7/1 mol flow CH_3OH+CH_3I=0.2 ml/h g cat prevalence of acid sites which characterizes the ex oxalate ZrO_2 probably justifies the preferred formation (Table 4) of C_2–C_6 mixtures of carboxylic esters rather than acids [25].

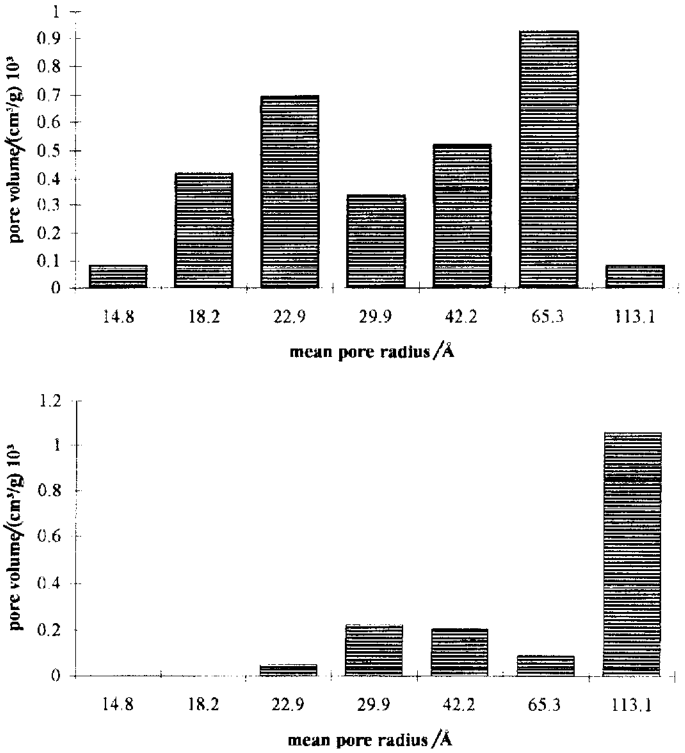


Fig. 10 Pore volume distribution of ex gel ZrO_2 heated a) under air and b) under N_2

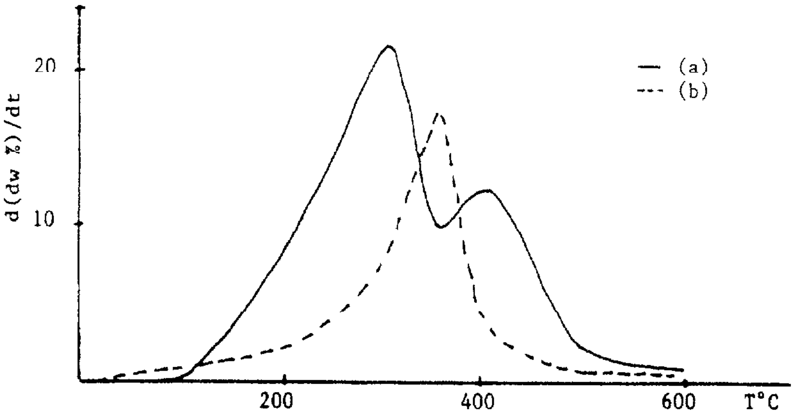


Fig. 11 Decomposition rates of a) ex gel precursor under air, and b) ex oxalate precursor under air

Conclusions

For catalytic purposes, pure tetragonal ZrO_2 was prepared by using a novel preparative procedure (ex oxalate) involving the precipitation of an oxalate precursor. Relative to more or less conventional procedures (ex oxychloride and ex gel), the new approach leads to different structural and morphological characteristics, which seems to imply a different catalytic activity.

* * *

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