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## Synthesis, characterization and catalytic properties of sol–gel derived mixed oxides

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### Abstract

Alumina and 1:1 mixed oxides of  $\text{Al}_2\text{O}_3\text{--ZrO}_2$ ,  $\text{Al}_2\text{O}_3\text{--TiO}_2$ ,  $\text{SiO}_2\text{--TiO}_2$  and  $\text{ZrO}_2\text{--TiO}_2$  were synthesized via a sol–gel process by the so-called neutral amine route, followed by calcination at 600 °C. The mixed oxides were characterized before calcination by X-ray diffraction, revealing ordered hexagonal ( $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\text{--ZrO}_2$ ,  $\text{ZrO}_2\text{--TiO}_2$ ) and lamellar ( $\text{SiO}_2\text{--TiO}_2$ ,  $\text{Al}_2\text{O}_3\text{--TiO}_2$ ) structures. After calcination, all samples exhibited amorphous structures. Surface areas and pore characteristics of all materials were determined by nitrogen adsorption isotherms. The calcined oxides are active catalysts in the epoxidation of cyclooctene with *tert*-butyl hydroperoxide as oxidant. Epoxide yields from 14 to 45% were found for reaction times of 24 h. The titanium oxide containing catalysts are the most active and selective ones. On the other hand, the poisoning of acidic centers yields a decreasing activity while increasing selectivity.

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### 1. Introduction

The sol–gel process [1] is an useful synthetic approach for the preparation of amorphous, as well as structurally ordered materials. Through sol–gel process, it is possible to control the properties of the synthesized samples, such as porosity and surface area, to obtain homogeneous matrices. It has been shown that metal-doped lamellar silica [2–4] and mixed oxides of  $\text{ZrO}_2\text{--TiO}_2$  [5] with hexagonal structure can be synthesized via the sol–gel method by the so-called neutral amine route.

The synthesis and industrial application of titanium silicalite 1 (TS-1) [6] have been focused on the development of new heterogeneous oxidation catalysts. In this context, transition metal containing micro- and mesoporous

materials, the so-called redox molecular sieves [7], were extensively investigated.

Besides a wide variety of crystalline silicalites, zeolites, aluminophosphates and silicoaluminophosphates, amorphous metallosilicates and mixed oxides, prepared by sol–gel techniques, were found to be useful heterogeneous oxidation catalysts [8–12]. The use of TS-1 and related catalysts is limited to substrates which can enter the well defined pores of the crystalline materials. Sol–gel techniques, on the other hand, allow a wide structural variation and adaptation of the catalysts to the requirements of the catalytic reaction.

The present investigation focus on sol–gel synthesis of alumina and 1:1 mixed oxides of  $\text{Al}_2\text{O}_3\text{--ZrO}_2$ ,  $\text{SiO}_2\text{--TiO}_2$ ,  $\text{ZrO}_2\text{--TiO}_2$  and  $\text{Al}_2\text{O}_3\text{--TiO}_2$ . Due to their species with acidic sites of different types (mainly Brönsted sites for  $\text{SiO}_2$  and Lewis sites for the other oxides) and strengths, the mixed oxides are interesting matrices from a catalytic point of view. These oxides were synthesized through the neutral amine route and were characterized by X-ray diffraction, nitrogen physisorption and thermogravimetry. The catalytic

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activity of these materials towards cyclooctene epoxidation with *tert*-butyl hydroperoxide was tested.

## 2. Experimental

### 2.1. Synthesis and characterization of the oxides

Tetraethoxysilane, titanium(IV) butoxide, zirconium(IV) butoxide and aluminum *sec*-butoxide were used as alkoxide precursors (all of them from Aldrich). The compounds 1,10-diaminododecane, 1,12-diaminododecane, and dodecyltrimethylammonium bromide were used as organic templates, and *n*-propanol was employed as solvent for all reactions. All reagents were of analytical grade and were used without further purification.

13.0 mmol of each metal precursors were mixed and magnetically stirred under a nitrogen atmosphere for 72 h. The resulting mixture was added to a solution of 10.0 mmol of one of the organic template in 500 mmol of propanol. Here 1,12-diaminododecane was used for titanium–zirconium oxides, dodecyltrimethylammonium bromide was employed for silicon–titanium oxide, and 1,10-diaminododecane was used as template for all other oxides. During this step is critical to prevent water from reaction in order to control the reaction rate and avoid undesirable hydrolysis and polycondensation reactions. Different template molecules were employed to provoke variations in the pores diameters of the prepared catalysts. Then, in this stage, 1.0 mol of water was added at once to the resultant solution. The formed powder was aged for 48 h and then was washed with distilled water and was aged again at room temperature for 48 h. The materials were dried under vacuum at 80 °C for 8 h and finally calcined at 600 °C (with a heating rate of 50 °C min<sup>-1</sup>) for 6 h.

X-ray diffraction patterns of the materials were recorded on a Shimadzu XD-3A apparatus using Cu K $\alpha$  radiation (35 kV, 25 mA). Specific surface areas of the calcined samples were determined by the BET method using nitrogen adsorption isotherms recorded on a Micromeritics Flowsorb II 2300 equipment. Pore diameters as well as micro and mesopore volumes were determined from the corresponding Horvath–Kawazoe pore size distribution curves. Thermogravimetric data were obtained on a Shimadzu TGA-50 instrument under argon atmosphere with a heating rate of 5 °C min<sup>-1</sup>.

### 2.2. Catalytic epoxidations

The reactions were carried out at ambient atmosphere using a glass tube placed in a temperature equilibrated oil bath and fit with a reflux condenser.

A mixture of 10.0 mmol of cyclooctene (Aldrich, 95%), 15.0 mmol of *tert*-butyl hydroperoxide (TBHP, 88% in cyclohexane; Nitrocarbonyl SA), 50.0 mg of catalyst and

2.5 mmol of *n*-decane (Aldrich, 99%) as internal standard for gas chromatography (GC) was magnetically stirred at 80 °C for 24 h. Aliquots were taken from the reaction mixtures after 3 and 24 h. The samples were analyzed, using an Hewlett Packard HP 5890 Series II gas chromatograph equipped with an HP Ultra 2 capillary column (50.0 m  $\times$  0.2 mm  $\times$  0.33  $\mu$ m film thickness; crosslinked by 5% phenylmethylsilicone) and a flame ionization detector (FID). Products were quantified using calibration curves obtained with standard solutions.

In order to increase the selectivity of the catalytic reaction, 100 mg of Al<sub>2</sub>O<sub>3</sub> and the mixed oxides Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> and SiO<sub>2</sub>–TiO<sub>2</sub> were treated with 10 cm<sup>3</sup> of a 0.5 mol dm<sup>-3</sup> lithium acetate solution for 4 h under magnetic stirring. Then the powders were filtered under vacuum, washed with 40 cm<sup>3</sup> of distilled water and then dried at 120 °C for 12 h. Such an experimental procedure was also used to neutralize the Brønsted acidic sites on the matrices [13].

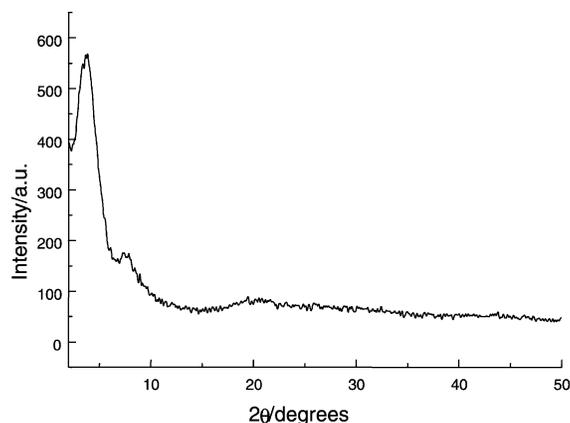
## 3. Results and discussion

### 3.1. Characterization of the mixed oxides

All oxides are fine white powders. Powder X-ray diffraction patterns of the uncalcined materials reveal hexagonal structures for Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> and ZrO<sub>2</sub>–TiO<sub>2</sub> and lamellar structures for Al<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> and SiO<sub>2</sub>–TiO<sub>2</sub>. X-ray data for the uncalcined materials are summarized in Table 1 and the diffraction pattern of Al<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub>, which exhibits a lamellar structure [14], is given as example in Fig. 1. Upon calcination the template molecules are removed, as shown by thermogravimetric analysis, causing the collapse of the hexagonal or lamellar structures, which were sustained by the presence of the template molecules, then producing amorphous samples. It is worth noting that at 600 °C TiO<sub>2</sub> sol–gel derived materials will be crystallized after calcinations. However, as in this case, the crystallization of a mixed SiO<sub>2</sub>–TiO<sub>2</sub> matrix will occur at much higher temperatures than the single titanium oxide, as verified by Kumar and co-workers [15].

Table 1  
X-ray diffraction data for hybrid matrices consisting of aluminum, silicon, titanium or zirconium oxides

Sample	2 $\theta$ (°)	<i>d</i> (nm)	Diffraction planes	Structure
Al <sub>2</sub> O <sub>3</sub>	3.2	2.80	100	Hexagonal
ZrO <sub>2</sub> –TiO <sub>2</sub>	4.5	1.96	100	Hexagonal
Al <sub>2</sub> O <sub>3</sub> –ZrO <sub>2</sub>	3.3	2.88	100	Hexagonal
Al <sub>2</sub> O <sub>3</sub> –TiO <sub>2</sub>	3.8; 7.6	2.32; 1.16	001; 002	Lamellar
SiO <sub>2</sub> –TiO <sub>2</sub>	4.1; 8.2	2.20; 1.10	001; 002	Lamellar

Fig. 1. X-ray diffraction pattern of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> oxide.

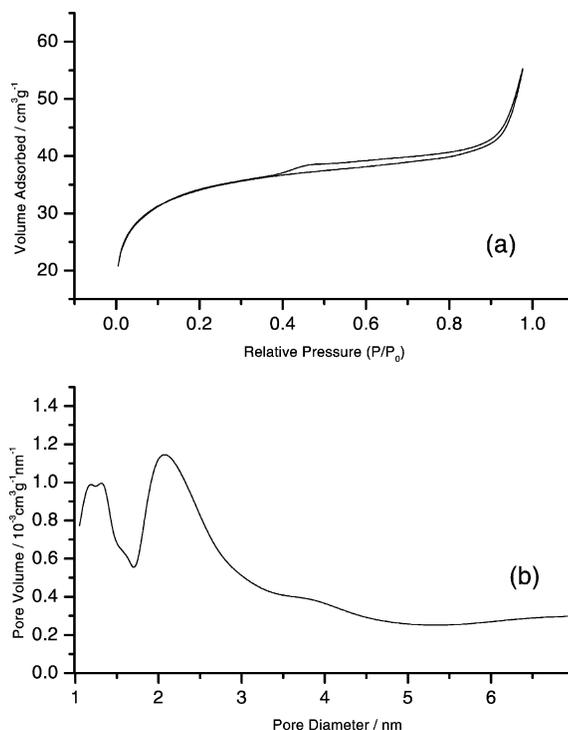
Surface areas, pore volumes and pore diameters were determined by nitrogen physisorption and are summarized in Table 2. Surface areas between 100 and 160 m<sup>2</sup> g<sup>-1</sup> were determined for the mixed oxides and a remarkably higher surface area of 343 m<sup>2</sup> g<sup>-1</sup> was found for Al<sub>2</sub>O<sub>3</sub>. The mixed oxides exhibits mesopores with pore diameters between 1.64 and 3.54 nm, whereas a pore diameter of 6.61 nm was determined for Al<sub>2</sub>O<sub>3</sub>.

Two adsorption isotherm types for the calcined materials were found. The oxides Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> and ZrO<sub>2</sub>-TiO<sub>2</sub> presented MCM-41 like isotherms [16]. On the other hand, the isotherm of SiO<sub>2</sub>-TiO<sub>2</sub>, Fig. 2(a), is a type IV isotherm, which is typical of capillary condensation taking place in mesoporous. It exhibits a type H4 hysteresis loop, often associated with narrow slit-like pores [17]. For SiO<sub>2</sub>-TiO<sub>2</sub> the medium pore diameter is 1.64 nm. The Horvath-Kawazoe differential pore volume plot, Fig. 2(b), indicates that the pore volume attributable to micropores is low, showing that the material is mainly non-porous. Adsorption on amorphous surface is thermodynamically more favorable than capillary condensation, thus giving a type I isotherm. It is worth noting that, as shown in Fig. 2(b), the SiO<sub>2</sub>-TiO<sub>2</sub> matrix exhibits two kinds of pores: some in the range 1.0–1.5 nm (with maximum values at ~1.15 nm) and others with diameters in the range 1.9–3.0 nm (with

Table 2

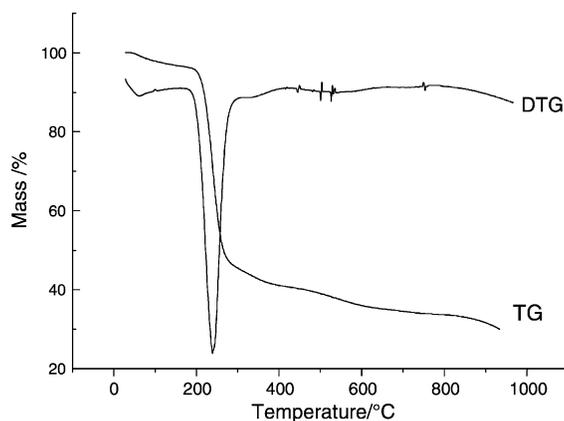
BET surface area (*S*), micro (*V*<sub>micro</sub>) and mesopores (*V*<sub>meso</sub>), and mean pore diameter (*d*<sub>p</sub>) of sol-gel derived mixed oxides determined by the corresponding Horvath-Kawazoe pore size distribution curve

Oxide	<i>S</i> <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	<i>V</i> <sub>micro</sub> (cm <sup>3</sup> g <sup>-1</sup> )	<i>V</i> <sub>meso</sub> (cm <sup>3</sup> g <sup>-1</sup> )	<i>d</i> <sub>p</sub> (nm)
Al <sub>2</sub> O <sub>3</sub>	343	0.1359	0.4784	6.61
Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	154	0.0550	0.1062	3.54
ZrO <sub>2</sub> -TiO <sub>2</sub>	107	0.0408	0.0278	1.74
Al <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub>	115	0.0417	0.0482	2.31
SiO <sub>2</sub> -TiO <sub>2</sub>	124	0.0508	0.0427	1.64

Fig. 2. Adsorption isotherm (a) and differential pore volume plot (b) for SiO<sub>2</sub>-TiO<sub>2</sub>.

maximum value at ~2.25 nm). So, the 'mean' value shown in Table 2 has the following physical meaning: if all pores of the considered sample have the same value, (which is not true, of course) this value will be around 1.64 nm. The same argument is valid for the other samples. So, the values shown in Fig. 2 could be used to compare the different samples porosity.

The thermogravimetric curve for non-calcined SiO<sub>2</sub>-TiO<sub>2</sub> is shown in Fig. 3. Two clearly distinguishable weight losses due to the release of water and the template molecules

Fig. 3. Thermogravimetric and derivative curves for SiO<sub>2</sub>-TiO<sub>2</sub>.

are observed. These mass losses are evidenced in the derivative forms of the curve, with the presence of two distinct peaks, respectively. The curves for other materials show a similar profile. Since the template molecules are completely removed only at temperatures around 600 °C, this temperature was chosen for calcination, to obtain template-free oxide samples. On the other hand, this temperature is already critical for the mixed oxides, since pure ZrO<sub>2</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are known to lose surface area and pore volume at temperatures above 350 °C [18].

### 3.2. Catalytic epoxidation tests

The results of catalytic cyclooctene epoxidation with *tert*-butyl hydroperoxide are given in Table 3. Epoxide selectivities of 100% were observed after 3 h, except for the reaction catalyzed by SiO<sub>2</sub>–TiO<sub>2</sub>, for which a selectivity of 93% was observed (*ter*-butylic alcohol is the byproduct). However, selectivities decreased significantly with prolonged reaction times. On the other hand, epoxide yields are remarkably higher after reaction times of 24 h compared to only 3 h reactions. Epoxide yields around 22% were obtained after 24 h, using Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> as catalysts. The observed catalytic activity of Al<sub>2</sub>O<sub>3</sub> is in agreement with previously reported results [19]. Epoxide yields of up to 45% after 24 h were obtained using titanium containing mixed oxides. Cyclooctene conversions and epoxide selectivities increase in the order ZrO<sub>2</sub>–TiO<sub>2</sub> < Al<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> < SiO<sub>2</sub>–TiO<sub>2</sub>. The relatively low catalytic activity of ZrO<sub>2</sub>–TiO<sub>2</sub> could be interpreted by the lower mesopore volume of the oxide (Table 2), and these results suggest that at least part of the cyclooctene molecules react inside the mesopores. However, some differences in surface activity could not be disregarded.

The catalytic results for the samples treated with lithium acetate solution are shown in Table 4. Comparing Tables 3

Table 3

Epoxidation of cyclooctene with TBHP catalyzed by mixed oxides by using the reaction conditions: 10.0 mmol cyclooctene, 15.0 mmol TBHP (88% in cyclohexane), 2.5 mmol *n*-decane, 50.0 mg of catalyst at 80 °C

Catalyst	Cyclooctene conversion (%)		Selectivity (%)		Epoxide yield (%)	
	3 h	24 h	3 h	24 h	3 h	24 h
Without catalyst	3	36	100	39	3	14
Al <sub>2</sub> O <sub>3</sub>	7	43	100	53	7	23
Al <sub>2</sub> O <sub>3</sub> –ZrO <sub>2</sub>	8	37	100	56	8	21
ZrO <sub>2</sub> –TiO <sub>2</sub>	11	41	100	63	11	26
Al <sub>2</sub> O <sub>3</sub> –TiO <sub>2</sub>	25	54	100	69	25	37
SiO <sub>2</sub> –TiO <sub>2</sub>	28	62	93	73	26	45

Table 4

Epoxidation of cyclooctene with TBHP catalyzed by mixed oxides by using the reaction conditions: 10.0 mmol cyclooctene, 15.0 mmol TBHP (88% in cyclohexane), 2.5 mmol *n*-decane, 50.0 mg of catalyst at 80 °C

Catalyst	Cyclooctene conversion (%)		Selectivity (%)		Epoxide yield (%)	
	3 h	24 h	3 h	24 h	3 h	24 h
Without catalyst	3	36	100	39	3	14
Al <sub>2</sub> O <sub>3</sub>	5	35	100	65	5	18
Al <sub>2</sub> O <sub>3</sub> –ZrO <sub>2</sub>	10	30	100	47	10	20
SiO <sub>2</sub> –TiO <sub>2</sub>	22	48	100	70	25	45

All oxide samples were previously treated with a lithium acetate solution.

and 4 data, it can be observed that, as a general behavior, the treatment with lithium acetate (neutralization of the Brønsted acidic sites) leads to an increase in the selectivity of the oxide matrices. On the other hand, the cyclooctene conversion and the epoxide yield are reduced, which is an evidence of the prominent role of the Brønsted acidic sites on the considered epoxidation reaction.

The better results obtained for titanium containing catalysts in the present work, that is, higher cyclooctene conversion (consumption of the main reagent) and epoxide yield (formation of the main product), could be explained taking into account the well known catalytic activity of TiO<sub>2</sub> due to its strong oxidant power, as observed also for SrTiO<sub>3</sub> samples [20]. Furthermore, for WO<sub>3</sub>/TiO<sub>2</sub> systems [21] it was observed a photocatalytic activity 2.8–3 times higher than those observed for pure TiO<sub>2</sub> (gas phase decomposition of 2-propanol). The higher acidity of the double oxide system, in comparison with pure TiO<sub>2</sub> could be used to explain such facts [21].

The low catalytic activity of Al<sub>2</sub>O<sub>3</sub> despite its higher mesoporosity, could be explained taking into account that alumina exhibits almost only Lewis acidic sites, and, as verified by comparison of Tables 3 and 4 data, the presence of Brønsted acidic sites is of prominent importance to catalyze the considered reaction. This fact is also confirmed by the higher activity of the silica–titania catalyst, since silica have a large number of OH groups (an average value of 5.0 OH groups per nm<sup>-2</sup>) [1] whereas alumina and zirconia are, in essence, Lewis acidic oxides, exhibiting a minor amount of surface OH groups.

## 4. Conclusions

A wide variety of mixed oxides can be prepared via the sol–gel method by the neutral amine route.

The characteristics of the materials can be tuned by the choice of the monomeric precursors as well as the preparation parameters. It is possible to vary the composition of the materials within a wide range, provided that appropriate organometallic precursors are available. Without optimizing the preparation parameters it was possible to synthesize epoxidation active catalysts via a simple and fast preparation route. Modifying the materials, it should be possible to obtain useful heterogeneous oxidation catalysts even for industrial purposes. It is worth noting that the titanium containing catalysts are the most active and selective ones. On the other hand, the poisoning of acidic centers yields a decreasing activity while increasing selectivity.

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