Organic polymers as pore-regulating agents in TiO_2–Al_2O_3 mixed oxide catalytic supports

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The synthesis of TiO_2–Al_2O_3 mixed oxide catalytic supports with a $TiO_2/(TiO_2 + Al_2O_3)$ molar ratio equal to 0.5, was made by the co-precipitation of the corresponding metallic isopropoxides using different organic polymers as pore-regulating agents. The influence of the preparation parameters (type of polymeric additive, its amount, molecular weight and method of additive incorporation into the hydroxide precipitate) on the surface area and pore structure of the final solid were studied. It was found that organic polymers added during the hydrolysis step, in general, resulted in a significant increase in surface area and total pore volume. In all cases the pore-size distribution becomes clearly bimodal with two maxima in the pore-size distribution curve around 3 and 30–50 nm. In order to investigate the action mechanism of the polymeric additives, characterizations by Fourier transform-infrared, thermogravimetric/differential thermogravimetry and differential thermal analysis, as well as a TEM study of the hydroxide precipitates before calcination, were carried out. The results from these characterizations indicate that the textural changes induced by the polymeric additives can be rationalized in terms of a ''filler'' effect in the case where the additive is incorporated during the filtration step, and that when the additive is added during the hydrolysis step it is the chemistry of the polymer functional groups which determines the final texture of the solid. © *1998 Chapman & Hall*

1. Introduction

The role of the oxide support in the performance of heterogeneous catalytic systems is very important, because in many cases the activity and stability of the catalyst is known to depend not only on the inherent catalytic properties of the active phase, but also on the textural and physicochemical characteristics of the support. Among the catalysts in which the support characteristics plays an important role, are the hydrotreatment catalysts which are normally supported on alumina. In the case of these catalysts, in view of the increased concern over environmental problems, some new catalytic systems have been studied in order to obtain more active and selective catalysts. In these attempts, the use of new supports, such as Ti–Al mixed oxides, has shown promising results. In this case, greater catalytic activity has been observed, due to the effect of the support [1].

In general, sol–gel methods have been preferred to produce such mixed oxide systems. However, the control of the surface area and porosity of the catalysts still remains a problem when titanium and aluminium alkoxides are used as support precursors. In this case, small pore diameters of the order of 2–3 nm are obtained [2]. This pore dimension is useful only when light petroleum fractions are to be processed. However, for the effective processing of heavier petroleum fractions, larger pore diameters are needed. Therefore, control of the textural properties of the support is an important issue.

Organic polymers have been used with some success in the past, as additives to control textural properties of catalysts supported on single oxides [3–5], as well as in some mixed oxides systems such as Al_2O_3– SiO_2 [6, 7]. However, the role and the action mechanism of these additives is not yet clear. Furthermore, it is known that the same polymer can cause different changes in the textural properties of the different oxides. For example, it was noted that with alumina and silica–alumina gels, the use of polyethylene glycols brings about only a small increase in the surface area. In contrast, the same additive used in a silica gel system causes a marked decrease in the surface area [3]. Therefore, each polymeric additive and gel system must be considered separately.

Here we study the effectiveness of the use of different organic polymers, added at different stages of the sol–gel preparation of the support with the aim to control the porosity and the surface area of a TiO_2–Al_2O_3 mixed oxide. The effect of the type of polymeric additive, its amount, molecular weight and sequence of addition of the reactants on the surface area and pore-size distribution in TiO_2–Al_2O_3 mixed oxides is reported. Additionally, in order to understand better the changes occurring in the mixed

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oxides, some experiments were also performed with pure TiO_2 and Al_2O_3 oxides.

2. Experimental procedure

2.1. Synthesis of TiO_2–Al_2O_3 mixed oxides

The Al–Ti mixed oxide samples with molar ratio $TiO_2/(TiO_2 + Al_2O_3) = 0.5$ were prepared by co-precipitation of the titanium and aluminium isopropoxides as precursors and *n*-propyl alcohol as solvent. In the hydrolysis step, water, in an excess of 30 times the stoichiometric amount required, was used to produce the formation of the metallic hydroxides. A number of polymers such as polyethylene glycol (PEG), polypropylene glycol (PPG), polyacrylamide (PAA) and polyvinyl alcohol (PVA) with different degrees of polymerization for each type of polymer were used in order to study the effect of the polymer molecular weight and its functional groups on the surface area and pore-size distribution of the final solid. Two series of samples were prepared. In Series 1 the polymer was added together with the water to the alkoxide precursors during the hydrolysis step, i.e. the polymer was present before the formation of the metal hydroxides. In the second series (Series 2), the polymer was added into the already formed precipitates, after the hydrolysis step.

2.2. Characterization

In order to investigate the action mechanism of the polymers, characterization of the hydroxide precipitates before calcination was carried out by means of infrared (IR) spectroscopy, thermogravimetric/differential thermogravimetry (TGA/DTG) and differential thermal analysis (DTA) and transmission electron microscopy (TEM). The infrared spectra were recorded in a Nicolet 510 FT–IR spectrometer operating in the transmission mode, using KBr pressed discs. The differential thermal analysis and thermogravimetric experiments were performed using a DuPont 2000 apparatus in an air atmosphere with a heating programme rate of $20\,^{\circ}C\ min^{-1}$. The TEM observations were made with a Jeol 100CX electron microscope, equipped with a side-entry stage. For this characterization, the gel samples dispersed in an *n*-propanol–water solution (6:1 vol/vol) were deposited on copper grids coated with a holey carbon film.

The mixed oxides formed after drying at 373 K for 24 h and subsequent calcination at 773 K for 24 h were characterized by surface area, S_{BET}, and porosity using a Micromeritics ASAP 2000 apparatus. Immediately after a pre-treatment (3 h at 523 K under vacuum), surface area measurements were performed by nitrogen adsorption at 78 K using a five-point BET method. The Barret-Joiner-Halenda (BJH) method [8] was applied to determine pore-size distribution. The average pore-diameter was calculated as $4V/S_{BJH}$.

A potentiometric method was used to determine, by titrating with *n*-butylamine, the total number of surface acid centres and the relative acid strength of the surface sites of the prepared solids [9]. In this method, a small quantity (0.2 ml) of 0.1 N *n*-butylamine in acetonitrile was added to 0.15 g solid and kept under agitation for 3 h. Later, the suspension was titrated adding $0.1\ ml\ min^{-1}$ of the same base. The electrode potential variation was registered on a Metrohm 691 digital pH meter with a combined glass and Ag/AgCl electrode. The reproducibility of the electrode potential curve was ± 5 mV.

3. Results

3.1. Surface area and porosity

3.1.1. Effect of polymer functional group

The results from the textural characterizations show that, in general, for the first series of samples, when the polymer is added during the hydrolysis step, the use of organic polymers results in a large increase of surface area and total pore volume accompanied by significant changes in the pore-size distribution (Table I). A strong influence of the polymer functional group is also noted. Thus, for the same type of polymeric additives – poly-glycols; the change from PEG to PPG of similar molecular weight does not alter significantly the specific surface area. On the other hand, it can be noted that a larger increase in surface area and total pore volume was observed in the case of PAA and PVA, using additive amounts of 20 times less than those used in the case of poly-glycols.

The $dV/d\log D$ versus D curves show a bimodal pore-size distribution for all the samples prepared with polymers, with a first maximum at about 3 nm and a second one at around 30–50 nm (Fig. 1). In contrast, the TiO_2–Al_2O_3 mixed support prepared without additive presents a monomodal pore-size distribution (curve 1 in Fig. 1).

A detailed analysis of Fig. 1 shows differences in the behaviour of the different polymers which may be related to the differences in the type of functional

TABLE I S_{BET} and porosity of the Series 1 samples of TiO_2–Al_2O_3 mixed oxides

Sample	Organic polymer	Molecular weight ($g\ mol^{-1}$)	Amount of polymer (ml/1.2 g support)	S_{BET} ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Average pore diameter (nm)
1	–	–	–	247	0.210	3
2	PEG	3400	5.0	301	0.448	5
3	PPG	3000	5.0	303	0.396	3.8
4	PVA	89000–98000	0.25	361	0.471	4.7
5	PAA	200000	0.25	380	0.733	6.1

group present in the polymer but also to differences in the solubility of the polymer. Similar bi-modal pore-size distributions were obtained for the TiO_2–Al_2O_3 mixed oxides synthesized with PEG, PPG and PVA. In the case of PAA, one can observe that the use of this polymer leads to an increase in the pore volume due to pores with diameters between 3 and 80 nm. Moreover, the two maxima in this pore-size distribution curve are wider and less defined than in the samples prepared with the other polymers.

For comparison, the results from similar experiments, carried out with pure Al_2O_3 and TiO_2, adding the polymer during the hydrolysis process, are shown in Table II. Here it is possible to observe that the behaviour of the alumina is quite different from that of titania. In the case of alumina, the addition of polymers leads to increased surface area, pore volume and pore diameter. On the contrary, in the case of titania the addition of polymers results in lower surface area and pore volume, but larger diameter pores.

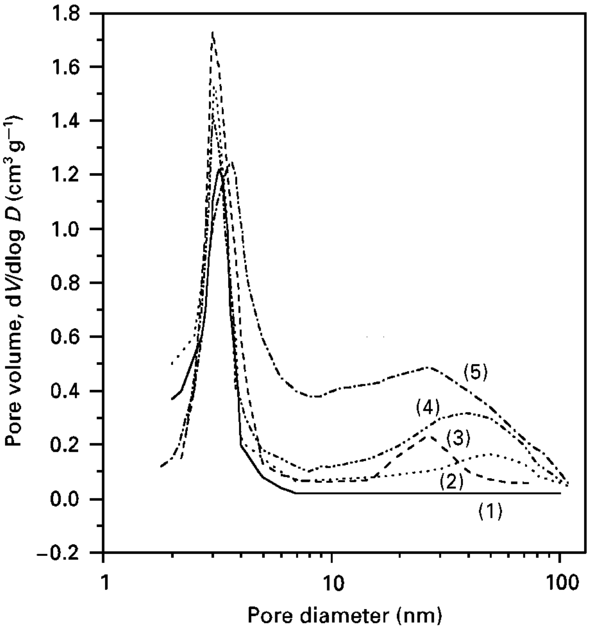

Figure 1 Pore-size distributions of TiO_2–Al_2O_3 mixed oxides (Series 1) prepared (1) without polymer, and with organic polymers added during hydrolysis: (2) PVA (89 000–98 000 g mol^{-1}), (3) PPG (3000 g mol^{-1}), (4) PEG (3400 g mol^{-1}), (5) PAA (200 000 g mol^{-1}).

3.1.2. Effect of polymer molecular weight

The textural characteristics of the samples prepared with PEG, PPG and PVA with different molecular weights, which are presented in Table III, show that increasing the polymer molecular weight leads only to minor changes in the surface area and pore volume, and that these variations do not follow a definite pattern of behaviour.

The observed changes in the pore-volume distribution curves, when the polymer molecular weight is increased, consist mainly in an increase in the volume of the pores which lie between 20 and 100 nm, and a displacement of the curve maximum from 35 to 50 nm.

3.1.3. Effect of the amount of the organic polymer

In the case of PEG with molecular weight of 600 g mol^{-1}, an increase in the amount of polymer leads to an increase in the values of the surface area and pore volume, and to slight variations in the pore diameter towards larger diameter pores (Table IV). These changes are in line with the small variations observed in the pore-size distribution plot which shows that the maximum corresponding to pores of diameters between 40 and 60 nm shifts from 45 nm to 55 nm and that the area under the curve is slightly increased when the amount of polymer is also increased.

3.1.4. Effect of addition method

The addition of the polymers to the already formed precipitates, before drying and calcination of the latter (Series 2), results in an increase in the average pore diameter of all samples which is larger than the increase observed when the same polymers are added during the hydrolysis step (Series 1). The surface area and pore volume of the Series 2 sample prepared with PPG (Table V) are larger than those of the corresponding Series 1 sample. In the case of PEG, PAA and PVA, the effect on the surface area and porosity was substantially less than that reported in Table I.

Fig. 2a and b show a comparison of the changes which occur in the pore-size distribution plots when

TABLE II S_{BET} and porosity of the Series 1 samples of pure TiO_2 and Al_2O_3

Sample	Oxide	Organic polymer	Molecular weight (g mol^{-1})	S_{BET} (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)
1	Al_2O_3	–	–	180	0.293	4.7
2		PEG	3 400	351	0.879	6.9
3		PPG	3 000	333	0.951	7.4
4		PVA	13 000–23 000	365	1.058	7.7
5		PAA	200 000	312	0.650	6.2
6	TiO_2	–	–	28	0.067	7.7
7		PEG	3 400	14	0.034	8.1
8		PPG	3 000	13	0.033	8.5
9		PVA	13 000–23 000	16	0.057	13.0
10		PAA	200 000	29	0.105	10.4

TABLE III Effect of the polymer molecular weight on S_{BET} and porosity of the Series 1 samples of TiO_2–Al_2O_3 mixed oxides

Sample	Organic polymer	Molecular weight ($g\ mol^{-1}$)	S_{BET} ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Average pore diameter (nm)
1	PEG[a]	400	361	0.445	4.9
2		1 000	321	0.467	5.0
3		2 000	340	0.410	4.0
4		3 400	301	0.448	5.0
5		4 000	332	0.458	5.2
6	PPG[a]	425	362	0.549	6.1
7		1 000	335	0.429	4.9
8		2 000	355	0.531	6.2
9		3 000	303	0.396	3.8
10		4 000	302	0.409	4.6
11	PVA[b]	13 000–23 000	320	0.380	3.9
12		89 000–98 000	361	0.471	4.7
13		124 000–186 000	305	0.455	4.7

Amount of polymer: [a] 5 ml/1.2 g support, [b] 0.25 ml/1.2 g support.

TABLE IV Effect of the amount of the organic polymer (PEG, 600 $g\ mol^{-1}$) on S_{BET} and porosity of the Series 1 samples of TiO_2–Al_2O_3 mixed oxides

Sample	Amount of polymer (ml/1.2 g support)	S_{BET} ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Average pore diameter (nm)
1	2.5	328	0.421	4.4
2	5.0	353	0.463	4.7
3	7.5	371	0.464	5.0

PEG or PAA are added during hydrolysis or during the filtration step. In the case of PEG (Fig. 2a), the addition of the polymer during filtration leads to an increase in the population of pores of 20–100 nm and a decrease of the small pores in the range 2–4 nm. In contrast, the standard preparation without polymer additive only shows the existence of small pores. The behaviour of the PAA (Fig. 2b), when added to the precipitate, is similar to that of PEG because the hydroxide particles have already been formed. However, when PEG or PAA are added to the hydrolysis solution, a comparison of the corresponding pore-size distribution plots (Fig. 2) indicates that the mechanism of action of PAA is completely different from that of PEG. In the case of PAA it is possible that the interaction of the functional groups with the hydroxide structures promotes the formation of pores of different sizes. In agreement with this, as will be shown later, the FT–IR results show a shift in the frequency of the PAA C = O and C–N vibrations.

3.2. FT–IR study

The results from FT–IR show that all the Series 1 precipitates, obtained when the organic polymer is added during the hydrolysis step, contain the corresponding polymer. In the case of PAA a displacement of the characteristic vibrational bands of the polymer functional groups was observed. Thus, the position of the C=O stretching vibration which appears at 1692 cm^{-1} for the pure polymer, shifts to 1661 cm^{-1} in the presence of the mixed oxide. Also, the C–N vibrational band of the pure PAA polymer shifts from 1605 cm^{-1} to 1628 cm^{-1} when the polymer is added to the mixed oxide. These changes in IR vibrational frequencies could be related to an interaction of the polymer with the support structure.

For the Series 2 samples, in which the polymer is added during the filtration step into the already formed precipitate, the intensity of the characteristic IR polymer bands suggests that the quantity of the polymer incorporated into the precipitate was much more that in the Series 1 samples. However, in the case of Series 2 samples, a displacement of the polymer IR vibrational bands was not detected, indicating a lower interaction of the polymer with the gel than in the case of Series 1 experiments.

3.3. Sample thermal behaviour

In line with the IR characterization, the results from the thermal behaviour of the intermediate species (the precipitates before calcination) confirm the existence of a polymer–precipitate interaction.

3.3.1. *Series 1 samples*

Before analysing the effect of adding the polymers on the thermal behaviour of the samples, the results from the thermal behaviour of the samples without polymer is described. The thermogravimetric results obtained for the titanium–aluminium precipitate prepared without polymer (Fig. 3a) show two weight-loss peaks in the temperature range 300–600 K. The low temperature peak (T_{max} at 342 K) can be related to the elimination of solvent and physisorbed water and the high-temperature peak, centred at 476 K, is most probably related to the dehydration process leading to the formation of the TiO_2–Al_2O_3 mixed oxide [10]. In line with these results, two endothermic peaks in this temperature range are observed in the corresponding DTA curves for the same sample.

The thermogravimetric results for the sample containing PEG polymer are presented in Fig. 3b. Three peaks are clearly observed. The low-temperature

TABLE V S_{BET} and porosity of the Series 2 samples of TiO_2–Al_2O_3 mixed oxides

Sample	Organic polymer	Molecular weight (g mol^{-1})	Amount of polymer (ml/1.2 g support)	S_{BET} (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)
1	PEG	3400	5.0	266	0.438	7.1
2	PPG	3000	5.0	380	0.565	5.9
3	PVA	89000–98000	0.25	280	0.363	6.1
4	PAA	200000	0.25	240	0.346	6.6

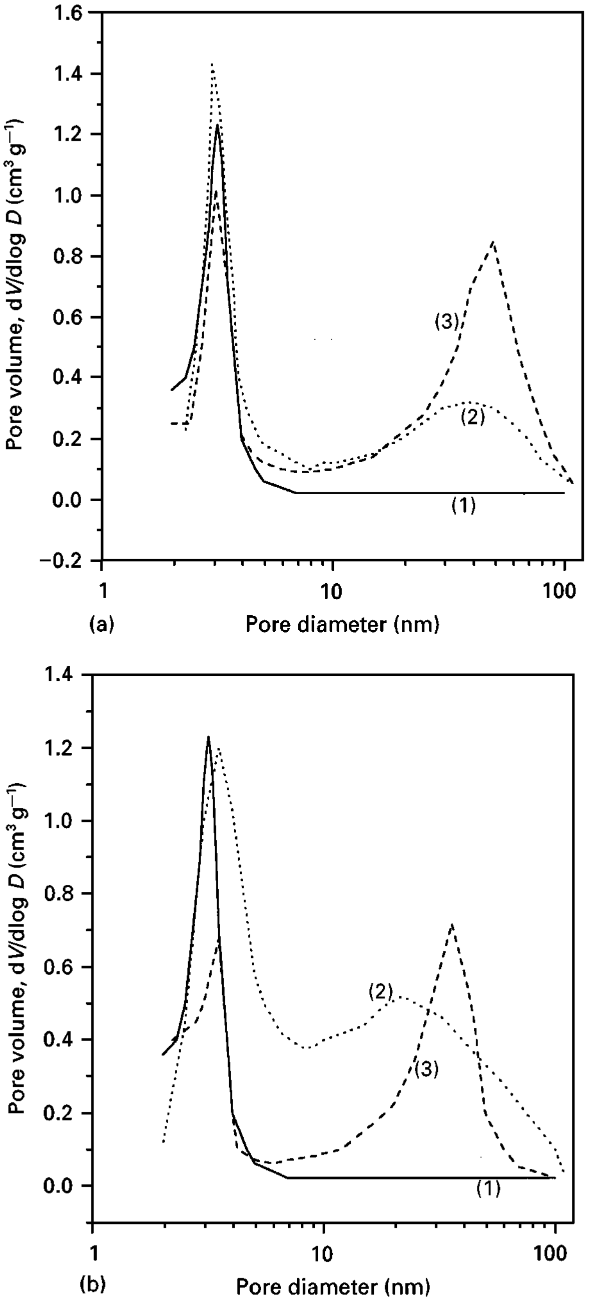

Figure 2 Pore-size distributions of TiO_2–Al_2O_3 mixed oxides for preparations (1) without polymer, (2) polymer added during hydrolysis, (3) polymer added during filtration; (a) PEG (3400 g mol^{-1}), (b) PAA (200000 g mol^{-1}).

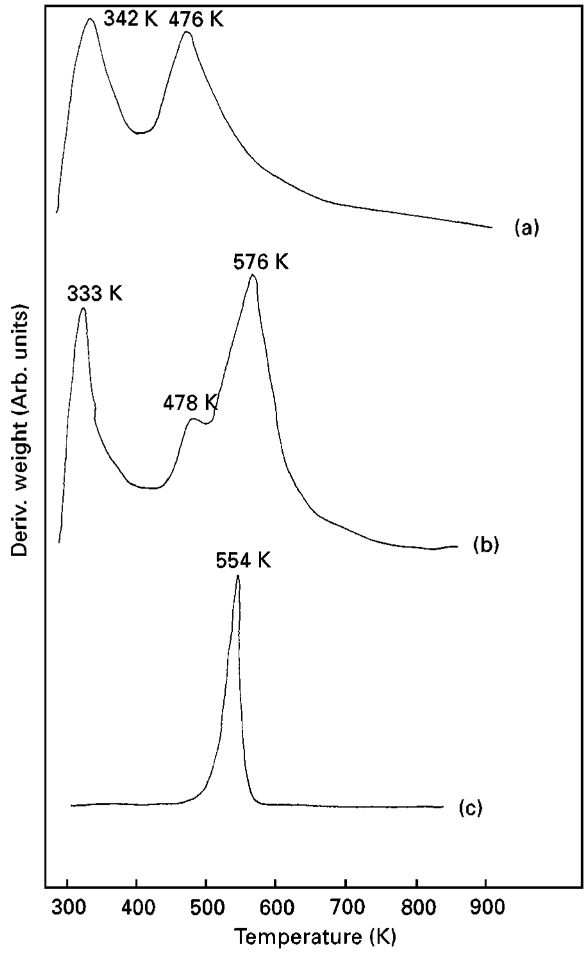

Figure 3 Differential TGA curves of TiO_2–Al_2O_3 mixed oxides prepared (a) without polymer and (b) with PEG 3400 g mol^{-1} added during hydrolysis and (c) of pure PEG 3400 g mol^{-1}.

peaks (333 and 478 K) have identical positions with the peaks observed for the sample without polymer and are obviously related to the dehydration process. The third peak is observed at 576 K and can be assigned to the thermal decomposition of the polymer. However, this peak is shifted to higher temperature in comparison to the peak of the pure polymer which decomposes at 554 K (Fig. 3c). This shift could be due to some structural changes and interactions between the polymer chain and the functional groups of the Ti–Al hydroxide precipitate. Similar shifts to higher temperatures are observed for all polymers used in this investigation (Table VI).

3.3.2. Series 2 samples

In this case, in which the polymer was added into the already formed precipitate after the stage of hydrolysis, the weight loss corresponding to the polymer decomposition process is larger, and the corresponding T_{max} shift is less pronounced. For example, for PAA

TABLE VI T_{max} of the decomposition process of polymers

Sample	Polymer	Molecular weight (g mol^{-1})	T_{max}, pure polymer (K)	T_{max}, Series 1 samples (K)
1	PEG	3400	554	576
2	PPG	3000	525	597
3	PVA	89000–98000	559	587
4	PAA	200000	569, 682, 874	645, 813, 933

incorporated into the Ti–Al precipitate during the filtration step, three peaks are observed at 563, 685 and 863 K. The positions of these peaks are similar to those observed for the pure PAA polymer (Table VI).

3.4. Sample morphology

The typical morphology of the unmodified titanium–aluminium precipitate prepared by the sol–gel method is shown in Fig. 4a. It can be observed that the sample is composed of irregular aggregates with size from 20–200 nm. In view of the regular pore-size distribution with a maximum about 3 nm of this sample (Fig. 1, curve 1), it is concluded that these aggregates are formed of very fine primary particles of regular size, which create mesopore voids between them.

The morphology of the different samples obtained with organic polymers seems to be sensitive to the type of the polymeric additive (Fig. 4b–e). It should be noted that their size and form are quite different, depending on the polymer used in the synthesis.

3.5. Acidity measurements

The results from the characterization of acid properties of TiO_2–Al_2O_3 mixed oxide samples after calcination are reported in the Table VII. It can be observed that all the polymers used in this study produced only minor changes in the total number of acid sites. However, the measured maximum acid strength changed in the case of the samples prepared using PVA and PAA.

4. Discussion

The use of water-soluble organic polymers as additives during the synthesis of inorganic ceramic materials by soft chemistry methods, as was reported earlier [3, 6], are able to modify the drying process or radically change both the hydrogel structure and therefore the subsequent dehydration process, and thus alter the porosity and specific surface area of the final calcined solid. However, the mechanism of action of these additives may be completely different depending on the nature of the polymer. It has been mentioned that the action of the polymers will depend on whether or not they possess reactive functional side groups [3]. According to this, polymers which do not have reactive functional side groups will mainly alter the drying process. In this case, the function of the polymer will be to prevent the collapse of the gel structure, either by reducing the surface tension or acting as "separator" in the gel network. Some of these polymers will also preserve the pore structure through the "filling-removal" mechanism. In contrast, polymers with a reactive functional group will form chemical bonds with the metal cations and will therefore change the hydrous gel structure and, consequently, the dehydration process. In general, these types of polymer will produce radical changes in the pore structure of the final solid. However, the results from the above study [3], show that polyglycols, which have side functional groups, behave more as non-reactive polymer additives. In contrast, other work shows that the addition of glycols before precipitation is more effective in the modification of the alumina structure, in part due to the adsorption of the polymer on the particle surface as it is formed [5]. Clearly, the behaviour of some polymer additives with low reactivity groups will show the characteristics of the two main groups, i.e. reactive and non-reactive polymers.

As has been shown previously [4], other effects can also play a role in determining the pore structure of solids when polymers are used as additives to regulate the pore structure. Steric stabilization would be a result of the affinity by the solvent and by the particle of the lyophilic and lyophobic part of the polymer molecule, respectively. If the medium is a good solvent for the lyophilic polymer tail, the particle–solvent affinity will increase and the particle would be stabilized. If the medium is not a good solvent for the polymer tails, flocculation will occur. According to this, the final pore structure, which depends on the size of the primary particles and aggregates, will be the result of the many possible interactions between solvent, polymer and gel. At the same time, the organic tail of the polymer may act as a "filler", leading to an increase in mesoporosity the importance of which will depend on the size and concentration of the polymer chains.

Clearly, if the analysis of the interaction of polymers with a single type of gel is not easy due to the complexity of the different and possible concurrent phenomena taking place at the same time, the study of mixed oxide systems becomes even more difficult. Nevertheless, here we will try to discuss the results obtained for the Al_2O_3–TiO_2 mixed oxide synthesis when PEG and PPG, non-reactive polymers according to Basmadjian *et al.* [3], and PVA and PAA (reactive polymers) were used to modify the textural properties of the solids.

In order to discern if the different polymers were affecting the structure of the gel, TEM observations of the modified gels were compared to those of the unmodified gel. Apparently, from the conclusions of previous reports [3], one would expect a great similarity

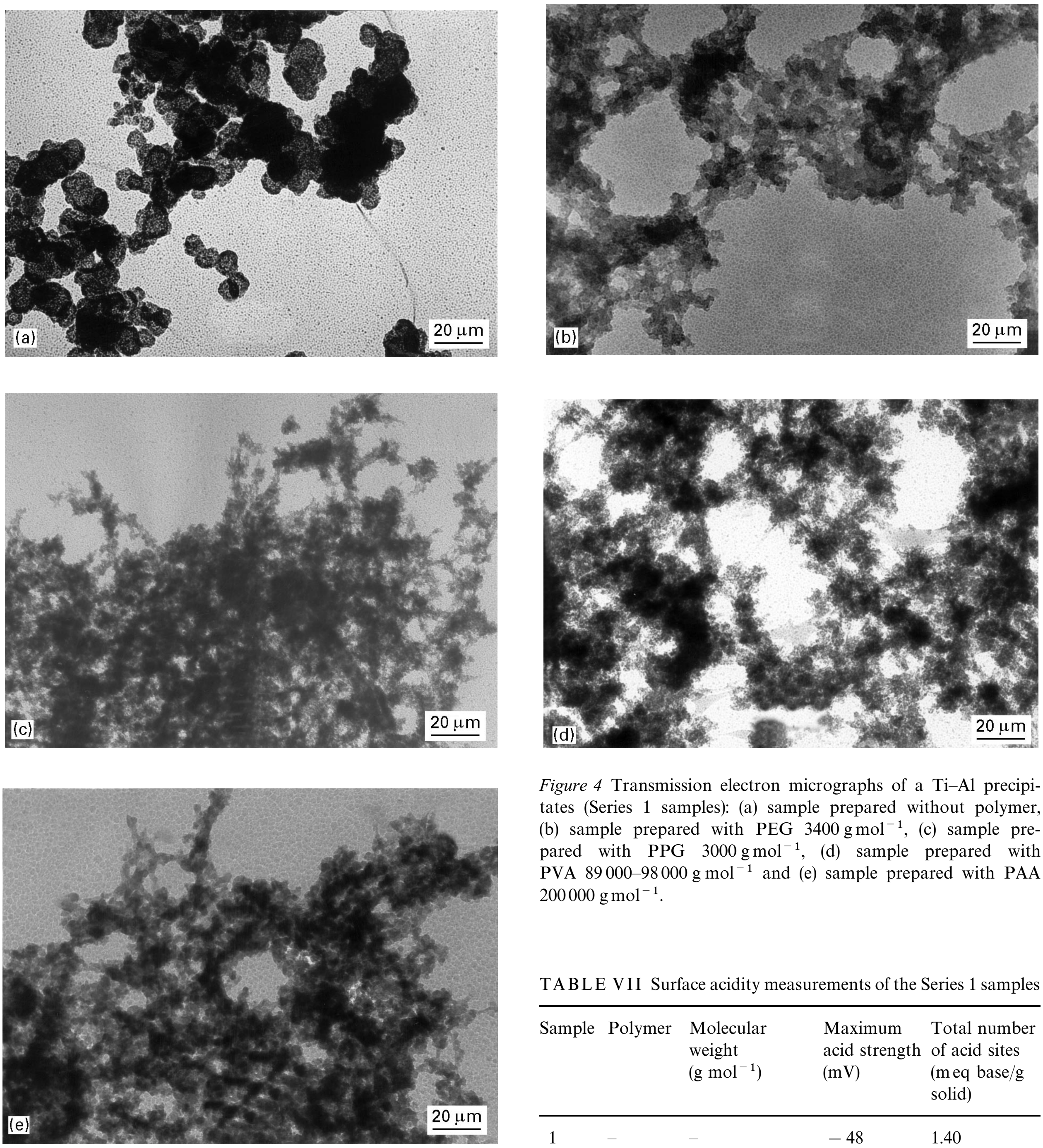

Figure 4 Transmission electron micrographs of a Ti–Al precipitates (Series 1 samples): (a) sample prepared without polymer, (b) sample prepared with PEG 3400 g mol^{-1}, (c) sample prepared with PPG 3000 g mol^{-1}, (d) sample prepared with PVA 89 000–98 000 g mol^{-1} and (e) sample prepared with PAA 200 000 g mol^{-1}.

TABLE VII Surface acidity measurements of the Series 1 samples

Sample	Polymer	Molecular weight (g mol^{-1})	Maximum acid strength (mV)	Total number of acid sites (m eq base/g solid)
1	–	–	– 48	1.40
2	PEG	200	– 52	1.43
3		600	– 49	1.20
4		1 000	– 57	1.37
5		4 000	– 43	1.47
6	PPG	1 000	– 49	1.35
7		3 000	– 43	1.47
8		4 000	– 45	1.35
9	PVA	89 000–98 000	– 66	1.39
10		124 000–186 000	– 78	1.33
11	PAA	200 000	– 26	1.34

between the structure of the unmodified gel and those obtained with PEG and PPG. However, the micrographs shown in Fig. 4a–e, which were taken at the same magnification, indicate that the gel morphology of the polymer-modified gels is quite different from that of the unmodified sample. This change of morphology is most probably related to changes in the gel structure. According to this, all the polymers used here interact with the gel, leading to similar pore-size distributions (see Fig. 1), although the amount of polymer used in the case of PVA and PAA was 20 times less than in the case of PEG and PPG. This may be due either to the reactivity of the functional groups or to the amount of groups present in each polymer chain. In the case of PEG and PPG there are only two terminal OH groups which can be considered as capable of bridging two particles and therefore contribute to the formation of larger aggregates [5]. In the case of PVA and PAA, the greater number of functional groups present all along the polymer molecule will lead to a greater probability of interaction between two particles. The formation of aggregates will then need a smaller amount of polymer than in the case of PEG or PPG. This is in line with our experimental results. The case of PAA modification presents different features which we will discuss later.

A close analysis of Fig. 1 reveals that the polymer-induced bimodal pore-size distribution curves of the supports prepared using these three polymers (PEG, PPG and PVA) are very similar (curves 2–4 in Fig. 1) and that the first maximum at about 3 nm observed in the $dV/d\log D$ versus D curves could be attributed to inter-particle pores. The population of the interparticle pores of this diameter, promoted by the use of polymers, may be related to several effects, for example, to changes in the surface tension of the liquid within the pores [11, 12]. However, earlier it was demonstrated that organic polymers have only a small effect on the surface tension in comparison to surfactants; moreover, surfactants used as additives have little effect on the pore structure [3]. It is concluded, therefore, that the surface tension is not the principal cause of the textural changes in the present circumstances. The other mechanism that could be proposed to explain the increase in the first maximum in Fig. 1 is that in the early stages of the drying and calcination processes the adsorbed polymer molecules probably can also act as wall "separators" in the gel network, up to the temperature required to set the gel. Above the flash point of the polymer, the gel-structure supporting agent will oxidize out leaving the pure calcined gel [6]. This action mechanism is similar to what has been called the "filling-removal" mechanism [5].

In line with the above, the TGA/DTA characterization results of the precipitates obtained when the polymeric additive was added during the hydrolysis step (Table VI and Fig. 3), show that the polymer elimination occurs at temperatures higher than those required for the dehydration process. Therefore, the incorporated polymer can prevent the collapse of the porous structure during the drying and the first stages of the calcination processes. As a result of this, the structure of the calcined solid is not so different from that of the hydrous gel and this allows solid materials to be obtained with higher surface area and porosity. At the same time, the organic polymer chain might act as a "filler" to increase mesoporosity in the higher range of pore diameters (at about 30–50 nm) [5]. In agreement with this, mesopores in this range of pore diameters were consistently observed in all the Al_2O_3–TiO_2 mixed oxide samples prepared with polymeric additives. Moreover, pores in this range of diameters were not observed in the standard sample prepared without polymer (see Fig. 1, curve 1), hence its appearance is due to the incorporation of polymer into the hydrous gel. In line with this, it is also observed that the pore volume of pores between 30 and 50 nm diameter and the position of the second maxima in the pore-distribution curves shown in Fig. 1, depend on the amount and type of polymer used as additive (see Fig. 1, curves 2–5). These results show clearly that the "filler effect", which is evident in the case of PEG and PPG and absent in the case of PVA, results from the different amounts of polymer used in each case. The case of PAA modification presents different features, which will be discussed later.

For the same polymer, a regular increase in mesoporosity should be expected as the molecular weight of the polymer or its amount increase. Such increase in mesoporosity would not be expected to be linear, because coiling of the organic chain can occur [13]. In general, these predicted trends are consistent with our experimental results.

For the glycol-type polymers, a change in the molecular weight results only in a slight decrease in the surface area of the supports (Table III). This effect can be easily understood because in these experiments the same volumetric amount of polymer was used and therefore the small change in surface area must be due to the decrease in the concentration of terminal functional groups present. Also, if the same volumetric amount of polymer was used, no significant variations in the total pore volume of the final sample would be expected.

When the amount of the polymer added is varied (Table IV), a small increase in the surface area and total pore of the sample is observed. However, a close analysis of the pore-size distribution curve shows that increasing the amount of polymer additive leads to a slight decrease in the population of the small-diameter pores in the range of 3 nm, while the population of pores in the range 10–100 nm tends to increase also slightly. These two effects result in a small increase of the average pore diameter.

In the case of the samples modified by the use of PVA, the results show that an increase in the molecular weight of the polymer leads to a clearer "filler" type effect. In particular, an increase of ten times in the polymer molecular weight results in a change in the average pore diameter from 3.9 nm to 4.7 nm (Table III). In agreement with these results, the pore-size distribution curves show a slight shift of the second maximum, corresponding to the wider pores, from 45 nm to 50 nm, and an increase of about double in the contribution of these pores to the total pore volume.

An analysis of the results from Table I and of the pore-size distribution curves obtained with PVA and PAA (Fig. 1), indicate that the action mechanisms of these two polymers are quite different because the use of PVA generates a pore-size distribution curve similar to that obtained with polymers of the glycol type, whereas the use of PAA increases the proportion of pores of larger diameter leading also to a bimodal pore-size distribution curve but much less defined than those obtained with the other polymers. This result could be related to the factors that distinguish the PAA from the other organic polymers used in this study, i.e.

(i) the more pronounced polarity of the functional groups of the PAA with respect to the other polymers leads to a stronger interaction of the polymeric additive with the surface of the Al–Ti gel. The formation of hydrogen bonds between di-alkyl substituted PAA and the surface of gels of alumina and silica–alumina has been reported previously [6]. Our infrared results from the intermediate species also support this proposal since a shift in the bands corresponding to the characteristic vibrations of the C=O and C–N bonds in PAA was observed when the polymer was in the presence of the Al–Ti gel, indicating the existence of an interaction of these groups with the Al–Ti gel;

(ii) the low solubility of PAA in the water–alcohol mixture which exists during the hydrolysis step, might give rise to the formation of polymer aggregates of different sizes on the surface of which small particles of the solid gel might adhere, thus creating a secondary porosity in all the pore-diameter size intervals [4]. To corroborate this point, an additional series of experiments using PAA, which is the polymer with the lowest solubility, were made by increasing the amount of water to make the polymer more soluble in the reacting medium. The results from these experiments show that as the amount of water is increased, the resulting pore-size distribution curve becomes better defined with two maxima at 3.3 and 60 nm and bears a greater resemblance to those of the more soluble polymers (see Fig. 5). Increasing the amount of water from 150 ml to 300 ml does not produce further significant changes in the texture of the final solid, because under these conditions, we are well below the solubility limit of the PAA in the water–alcohol mixture.

A comparison of Series 1 and Series 2 samples demonstrates that, in all cases, the formation of pores of larger diameter (30–50 nm) is promoted by the addition of polymer. It appears that the increase in the population of these pores in Series 2 samples is a result of the increased local polymer concentration, which results from the incorporation of the polymeric additive during the filtration process. This result can be rationalized by assuming that it is the agglomeration of the polymer in concentrated solutions which produces a "filler" effect responsible for the creation of the larger diameter pores. In contrast, when the polymer is added during the hydrolysis step, the system is highly diluted and under these conditions, the small particles of precipitate will be surrounded by a thin layer of adsorbed polymer which will change the morphology of the hydrogel. This leads to solids constituted by aggregates of small particles and with high surface areas and small-diameter pores.

Clearly, the process of interaction between the polymers and the gels is complex and there must be other effects besides those analysed here. For example, the change in the acid properties of the final solids with the nature of the polymeric additives, indicates a change in the composition or structure of the surface, possibly originated by differences in the titanium and aluminium alkoxides hydrolysis rates due to the presence of the polymer functional groups which alter the properties of the reactive medium.

The results of this study show that the action mechanisms of the different polymeric additives are quite similar when added to the precipitate during the filtration process, and may be explained by a "filler" effect, whereas in the diluted condition, when the polymer is added during the hydrolysis step, it is the chemistry of the polymer functional groups which is determinant for the final texture of the solid. In this latter case, the "filler" effect will be only of minor importance unless the solubility of the polymer in the solution is quite low.

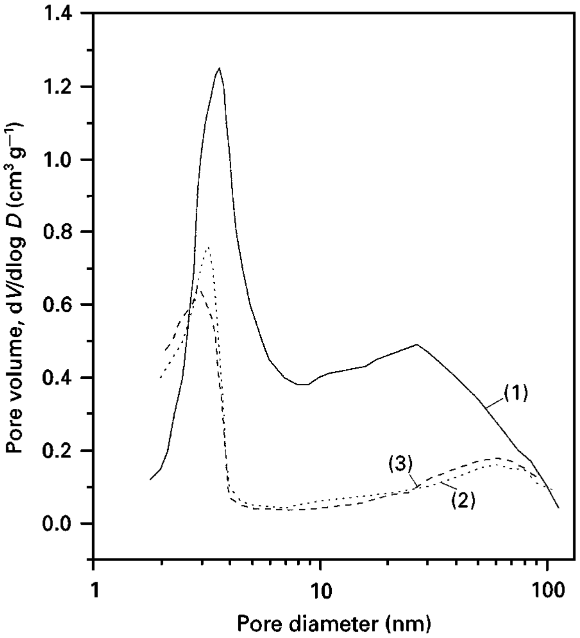

Figure 5 Pore-size distributions of TiO_2–Al_2O_3 mixed oxides (Series 1) prepared with PAA (200 000 g mol^{-1}) using different amounts of water: (1) 50 ml, (2) 150 ml and (3) 300 ml.

5. Conclusions

1. The surface area and pore volume of TiO_2–Al_2O_3 mixed oxides prepared by the methods used here are increased by the addition of polymers such as PEG, PPG, PVA and PAA.

2. The incorporation of the polymers allows the formation of bimodal pore-size distributions in contrast to the monomodal distribution obtained in the absence of polymers.

3. The addition of the polymers during the hydrolysis step leads to greater surface areas but the pore-size distribution shifts towards the smaller pores compared with adding the additive during filtration.

4. The effect of the type of polymer functional groups is observed clearly only when the polymer is in a diluted state, as in the case of addition during the hydrolysis step. On the contrary, the filler effect is dominant when the polymer is added to the precipitate during filtration and is therefore highly concentrated.

Acknowledgements

Financial support for this work by DGAPA-UNAM, CONACyT and the IMP FIES programme (Mexico) is gratefully acknowledged. One of us (E. C.) thanks PEMEX-Refinación for the grant received. We are grateful to Mr R. Hernández and Mr I. Puente for obtaining the transmission electron micrographs.

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Received 7 April
and accepted 5 December 1997