

Effect of preparative conditions on the surface characteristics of mixed zirconium and titanium oxides

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Abstract The surface characteristics of mixed zirconium and titanium oxides prepared from different starting materials are investigated. One mode of preparation entailed the use of zirconium sulfate and titanium oxysulfate as starting materials and ammonium hydroxide as precipitating agent. The produced oxides were washed to different extents to obtain samples with different sulfate content. A second preparative mode used zirconium oxychloride and titanous chloride as starting materials also with ammonium hydroxide as precipitating agent. The oxidation of the titanous to the titanic form for these oxides was carried out by means of oxygen gas. Resulting samples were heat treated at 400 °C and 600 °C, and textural characteristics determined from the adsorption of N₂ at 77 K, complemented by infrared and thermal studies.

The samples precipitated from the oxychloride and chloride salts of zirconium and titanium, as well as those precipitated from the sulfate and oxysulfate salts and washed free of the sulfate ions displayed quite similar textural characteristics. The unheated samples and those heat-treated at 400 °C were mesoporous, with some microporosity, and relatively large surface areas in the order of 200–300 m²/g. Heat treatment to 600 °C led to a relative decrease in surface area, in the order of 100 m²/g, and to the disappearance of microporosity.

The mixed zirconium and titanium oxides with a sulfate content of ≈17% displayed significantly lower surface areas, smaller than 10 m²/g, with a prevalence of micro and mesoporosity. Infrared and thermal studies indicated the

presence of differently bounded sulfato groups, which seem to have a blocking effect on the pores, resulting in the observed smaller surface areas.

Keywords Mixed oxides · Titanium oxide · Zirconium oxide · Surface area · Porosity

1 Introduction

Mixed zirconium and titanium oxides have been the subject of a number of studies (Das et al. 2002, 2003; Dongsen et al. 2003; Lai et al. 2000; Maity et al. 2001; Niwa et al. 1997) investigating their structural and textural properties, as well as their catalytic activity. The latter is closely related to the presence of acidic sites within the oxides matrices, and a commonly used method for promoting acidic properties of metal oxides is their enrichment with sulfate ions. Indeed, sulfate-promoted oxides of titanium and of zirconium are known for their catalytic activity for a large number of processes, such as isomerization of hydrocarbons, esterification and alkene polymerization (Arata 1996; Babou et al. 1995; Chuah et al. 1996; Hess and Kemnitz 1997; Stichert and Schuth 1998; Tran et al. 1998; Vera et al. 1998). Sulfated mixed zirconium and titanium oxides have been the subject of a number of investigations (Barthos et al. 2000; Lonyi et al. 1996; Miao et al. 1996), and the presence of sulfate ions has been found to have a bearing on the surface and textural properties of these mixed oxides (Ramadan et al. 2007).

In this respect, the present work aims at complementing the above mentioned investigation by probing the effect of the different modes of preparation of mixed zirconium and titanium oxides. This is carried out through a comparison

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between the oxides obtained through two methods of preparation. The first entails the use of zirconium sulfate and titanium oxysulfate as starting materials to obtain mixed zirconium and titanium oxides for which the sulfate content varies to comprise an oxide washed free of sulfate, and another with a high sulfate content. The second method entails the use of zirconyl chloride and titanous chloride as starting materials to obtain mixed zirconium and titanium oxides with no sulfate content.

2 Experimental

2.1 Sample preparation

Two different modes of preparation were employed to obtain different mixed zirconium-titanium hydrous oxides. These comprise three samples: TZ1 and TZ2, prepared from the sulfate and oxysulfate salts of zirconium and titanium, respectively, and with different sulfate contents; and TZ3, prepared from the chloride salts of zirconium and titanium, and free of chloride content.

The first mode of preparation entailed mixing equal volumes of 0.35 M zirconium sulfate (Aldrich, 99.99% purity) and 0.35 M titanium oxysulfate (Aldrich) each prepared in 1 M sulfuric acid (Aldrich A.R. grade), and heating the mixture to about 350 K in a water bath. Ammonium hydroxide (Fischer A.R. grade) was then added to the mixture with constant stirring until strongly basic pH (≈ 9). A white precipitate was formed. This was kept in contact with the mother liquor for two hours at 350 K, followed by 48 hours at room temperature (Mahal et al. 1981). The precipitate was then filtered, air dried at room temperature, and divided into portions, which were washed with different volumes of distilled water with the purpose of varying their sulfate content. One portion was washed free of sulfate content, denoted as TZ1, while another, TZ2, was washed with 100 ml distilled water. These were then air dried at 325 K to constant weight. Their sulfur contents were found to be $<0.10\%$ and $\approx 17\%$ by weight, respectively, and the Ti/Zr mole ratio was found to be 8:1 Ti to Zr for the two samples.

The second mode of preparation entailed mixing equal volumes of 0.50 M zirconium oxychloride (Aldrich, 99.99% purity) and 0.50 M titanous chloride (Fisher, 20% stabilized solution, 99.99% purity) in distilled water. Ammonium hydroxide (Fischer A.R. grade) was then added to the mixture at room temperature, with constant stirring, until strongly basic pH (≈ 9). A gray precipitate was formed, in which oxygen gas was bubbled till the precipitate became white, with the titanium (III) oxidizing to titanium (IV). This was kept in contact with the mother liquor for 24 hours at room temperature. The precipitate was then filtered, washed free of chloride content, then dispersed in distilled water and

left for 48 hours with regular stirring. This was followed by re-filtering, then washing with 0.05 M hydrochloric acid (Fisher, AR grade), followed by washing with distilled water (Ragai 1987; Ragai et al. 1991). The precipitate, TZ3, was then air dried at 325 K to constant weight. The chloride content was found to be $<0.10\%$, and the Ti/Zr mole ratio was found to be 2:1 Ti to Zr.

The dried samples, TZ1, TZ2 and TZ3, were subjected to heat treatment in air, at different temperatures, chosen according to their thermal behaviour, namely: 400 °C (loss of coordinated water, and for the sulfated sample, some ionic sulfate), and 600 °C (for the sulfated sample, loss of differently bound sulfato ligands). This heat treatment gave the samples TZ1(400), TZ2(400), TZ3(400), TZ1(600), TZ2(600) and TZ3(600).

2.2 Techniques

Adsorption measurements were carried out at 77 K using a conventional volumetric technique. Typically, the sample was out gassed overnight at room temperature to residual pressures of $\sim 3.3 \times 10^{-1}$ Pa. The gas pressures were measured on a mercury manometer. The time required for each point of the adsorption or desorption isotherm to attain equilibrium was between 15–20 minutes.

The infrared studies were carried out using a FTIR Paragon 1000 Perkin Elmer spectrophotometer. Solid samples were prepared in the form of KBr pellets, for which two milligrams of the compound were mixed with approximately 200 mg of KBr (spectroscopic grade), and the mixture then subjected to a pressure of about 200 lb/inch² in a hydraulic press.

Differential thermal analyses were carried out using a Shimadzu DTA-50, and the thermogravimetric analyses were carried out using a Shimadzu TGA-50H, under nitrogen gas with flow rate of 20 ml/min and a heating rate of 10 °C/min.

Sample images were obtained using a Leo Supra 55 field emission scanning electron microscope, and the mole ratio of titanium to zirconium in the samples was determined using an Oxford Instruments INCA-insight energy dispersive X-ray spectroscopy.

The sulfur content of the samples was determined by an EA1108 elemental analyzer, and the chloride content by the oxygen flask combustion method.

3 Results and discussion

3.1 Thermal studies

All three samples, TZ1, TZ2 and TZ3, gave thermograms with an initial broad endothermic peak, the maximum of

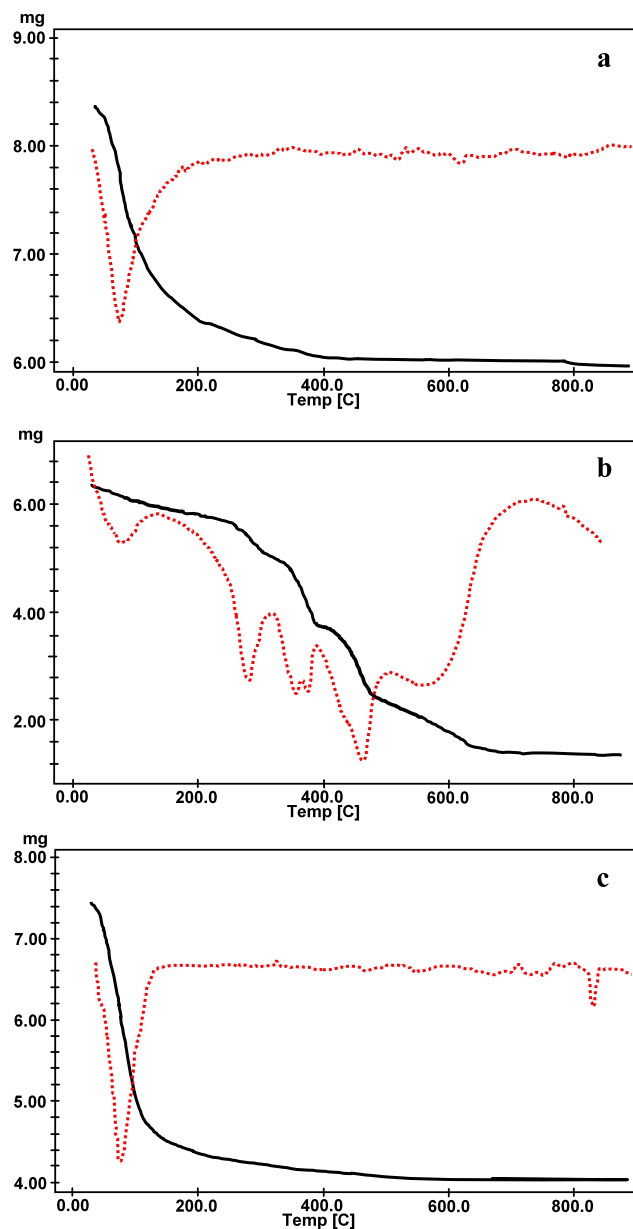


Fig. 1 Thermogravimetric (—) and differential thermal (···) behaviors of samples: (a) TZ1; (b) TZ2; (c) TZ3

which came around 90 °C with a weak shoulder at around 110 °C. These peaks may be associated with the loss of free or interstitial water followed by the desorption of water or possibly ammonia molecules “coordinatively bound” to the zirconium and titanium ions (Ragai 1989; Ragai et al. 1993). The desorption of NH_4^+ ions as ammonia may also have been a contributing factor to these endotherms.

Corresponding weight losses of $\approx 23\%$ for TZ1, $\approx 11\%$ for TZ2, and $\approx 35\%$ for TZ3, as shown in Fig. 1, are observed. The significant variation of these values is noteworthy. In the case of sample TZ3 the initial titanous chloride used in the preparation of this mixed oxide, with the tita-

nium ions present as hexa-aquo complexes, is probably a contributing factor to an increased amount of bulk water and hence may possibly account for the high initial percentage weight loss for this sample. The observed relatively high percentage loss observed for sample TZ1 (23%) as compared to sample TZ2 (11%) is in agreement with the larger volume of water used for washing the TZ1. For sample TZ2, additional endotherms and weight losses are observed at 280 °C, 370 °C, 390 °C, 480 °C, and 580 °C. The high sulfur content (17%) of this sample and the results obtained by the infrared studies, as explained below, suggest that these endotherms are related to the elimination of sulfate ions and of differently bound sulfato ligands. No such endotherms and weight losses are observed for samples TZ1 and TZ3, devoid of sulfate ions.

3.2 Adsorption studies

Nitrogen adsorption isotherms for these three series of mixed oxides are shown in Fig. 2, with the corresponding “ α_s ” plots in Fig. 3. In the construction of each “ α_s ” plot the volume of nitrogen adsorbed is plotted as a function of the reduced adsorption “ α_s ” as measured on a nonporous reference oxide ZrO_2 (Selim 1991). As explained previously (Gregg and Sing 1982), α_s is defined as the amount adsorbed at a particular value of relative pressure/amount adsorbed at relative pressure $p/p_0 = 0.4$.

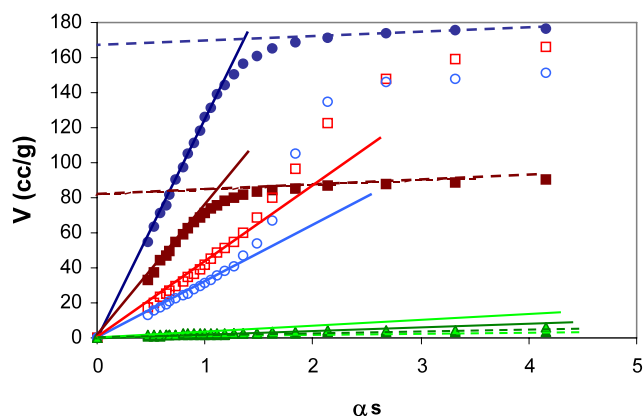
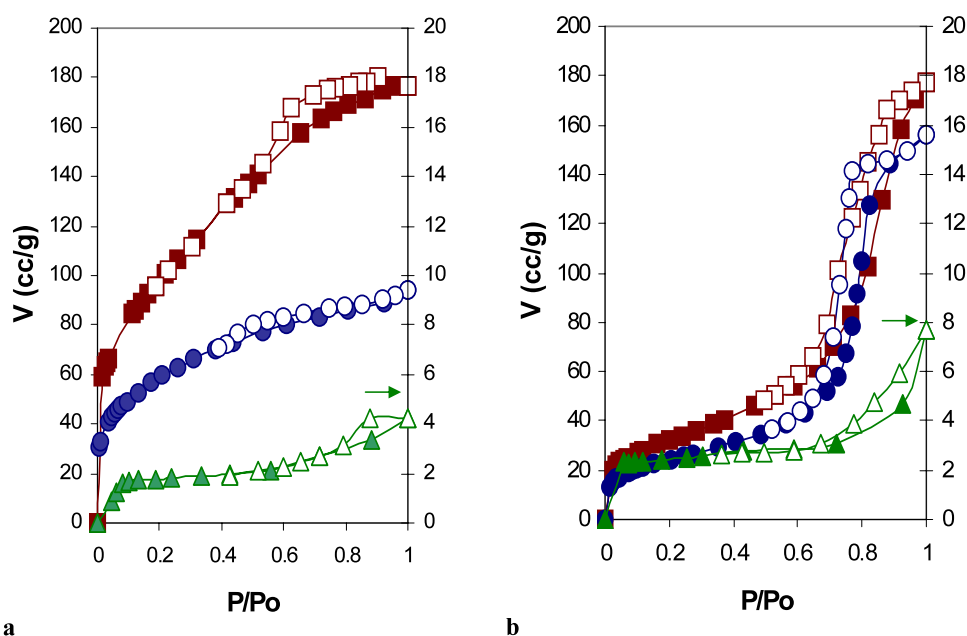
The isotherms belonging to the original samples TZ1, TZ2, and TZ3, exhibit features of both Type I and IV isotherms. These isotherms when analyzed in conjunction with their α_s plots allow the conclusion that these mixed oxides contain both micropores as well as mesopores. A marked upward deviation from linearity of these plots is generally obtained by capillary condensation taking place in well defined mesopores whereas a flattening of the α_s plot in the multilayer range as in could be attributed to the compensation between micropore filling at low p/p_0 followed by restricted capillary condensation at high p/p_0 .

Table 1 summarizes the results. The values of the BET surface areas are based on the fact that each nitrogen molecule occupies 0.162 nm^2 in the completed monolayer. The values of S_s are obtained from the slope of the initial part of the α_s plots with the BET surface area of the nonporous reference having been adopted as the standard area. It is noteworthy that sample TZ2, containing sulfate ions displays a strikingly lower surface area than samples TZ1 and TZ3 which are devoid of any sulfate. A concomitant drastic decrease in total and micropore volumes is observed in the case of this sample.

Heat-treatment of TZ3 at 400 °C led to an increased surface area as well as to an increase in the total pore and total micropore volumes. This is in agreement with thermal studies results indicating that even at temperature values lower

Table 1 Analysis of the nitrogen adsorption data for the different Zr-Ti oxide samples

Sample	V_m ml	BET C-const	S_{BET} $m^2 g^{-1}$	S_s $m^2 g^{-1}$	Total pore volume $ml g^{-1}$	Micro-pore volume $ml g^{-1}$	Porosity
TZ1	80.7	124	351.0	344.6	0.273	0.257	Micro + Meso
TZ2	1.4	215	6.1	6.0	0.006	0.002	Micro + Meso
TZ3	47.1	190	204.8	205.4	0.140	0.127	Micro + Meso
TZ1(400)	48.1	208	209.3	213.2	0.270	0.221	Meso
TZ2(400)	1.0	88	4.4	4.1	0.008	–	Meso
TZ3(400)	49.7	86	216.3	209.5	0.264	0.243	Micro + Meso
TZ1(600)	20.2	124	87.8	86.9	0.233	–	Meso
TZ2(600)	1.8	55	7.6	8.1	0.009	0.004	Micro + Meso
TZ3(600)	26.0	130	113.1	115.0	0.257	–	Meso

Fig. 2 Representative nitrogen adsorption isotherms: (a) the original unheated samples, TZ1 (●), TZ2 (▲), and TZ3 (■); (b) samples heat-treated at 600 °C, TZ1 (○), TZ2 (△), and TZ3 (□)**Fig. 3** Representative α_s plots: TZ1 (●), TZ1(600) (○); TZ2 (▲), TZ2(600) (grey triangle); TZ3 (■), TZ3(600) (□)

than 400 °C a large amount of interstitial as well as coordinated water is eliminated from TZ3. The upward deviation from linearity of the α_s plots confirms the mesoporous texture whereas the flattening of these plots in the multilayer region is likely to be the result of micropore filling at low p/p_0 followed by multilayer adsorption on a small external surface. Heat-treatment of TZ1 at 400 °C led to a somewhat similar behaviour, however with a decrease in surface area and micropore volume. Further heat-treatment of both TZ1 and TZ3 samples at 600 °C led to a further decrease in surface areas, possibly due to sintering, and the prevalence of very limited microporosity. Finally the very low surface areas and pore volumes displayed by samples TZ2(400) and TZ2(600) are noteworthy. They point at the crucial role played by the sulfate ions (free as well as ligated) in reducing the surface area, possibly as a result of pore blocking.

Fig. 4 SEM images of samples: (a) TZ1; (b) TZ2; (c) TZ3; (d) TZ1(600); (e) TZ2(600); (f) TZ3(600)

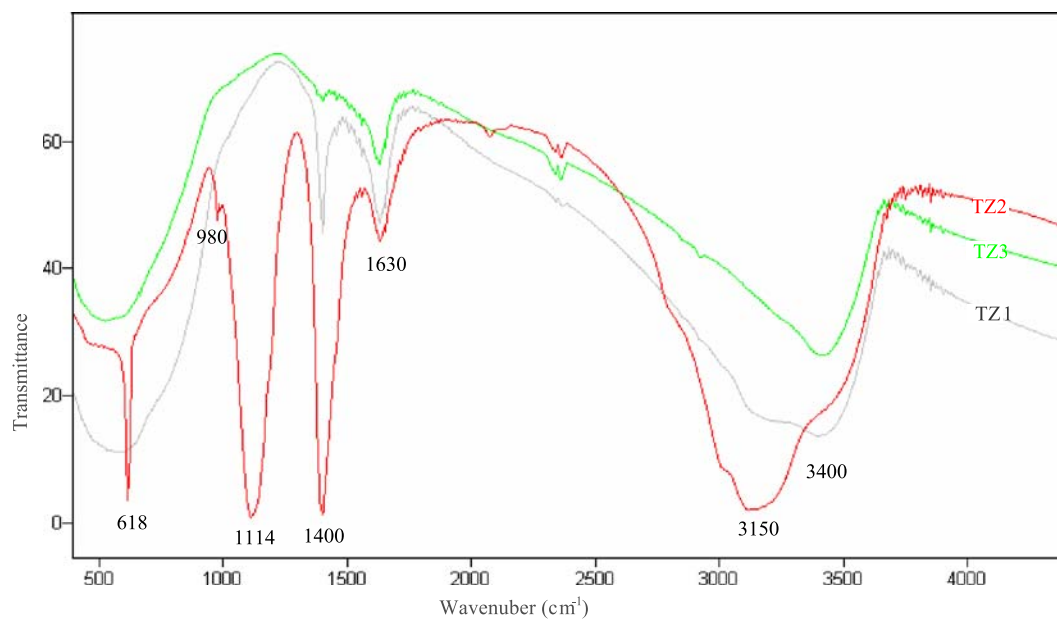
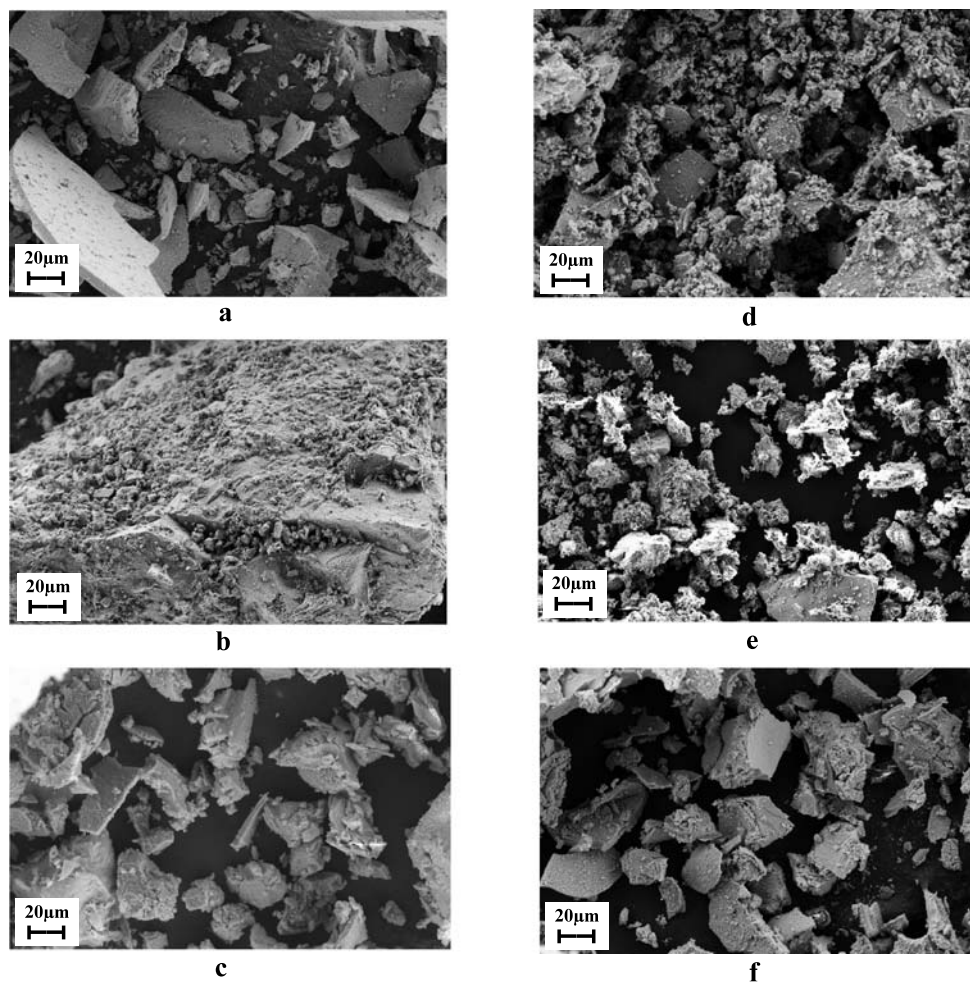


Fig. 5 Infrared spectra of the original samples TZ1, TZ2, TZ3

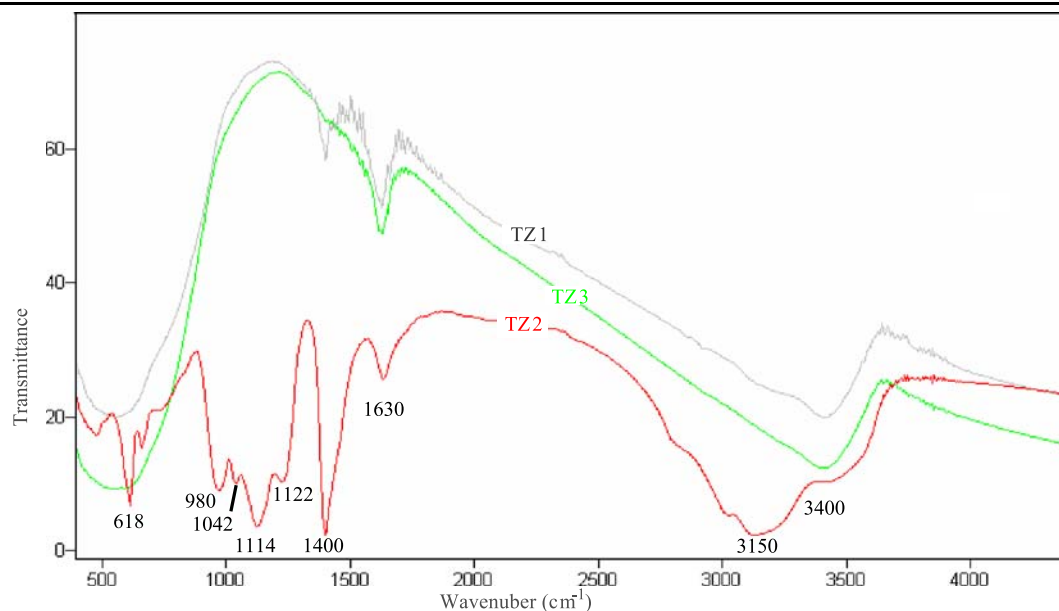


Fig. 6 Infrared spectra of samples TZ1, TZ2, TZ3 heat treated at 400 °C

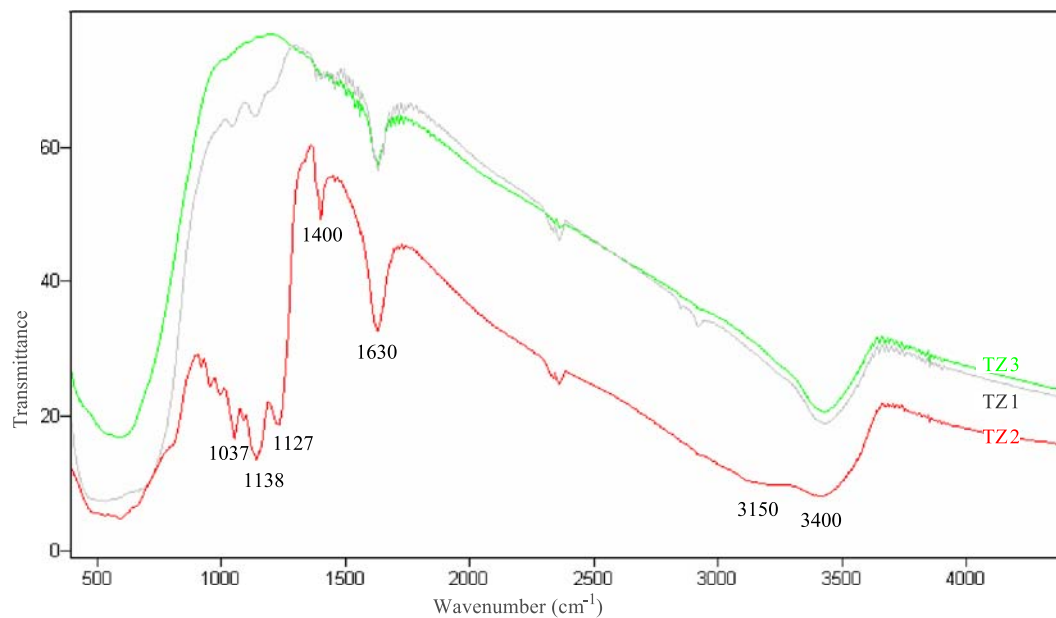


Fig. 7 Infrared spectra of samples TZ1, TZ2, TZ3 heat treated at 600 °C

Figure 4 comprises SEM images of the three samples TZ1, TZ2, and TZ3. Images clearly demonstrate the variation of surface morphology with sulfate content, as well as heat treatment.

3.3 Infrared studies

Infrared spectroscopic studies carried out on the original TZ1, TZ2, and TZ3 samples exhibit two main peaks at $\sim 3150\text{ cm}^{-1}$ and $\sim 3400\text{ cm}^{-1}$ in the fundamen-

tional group region. The 3400 cm^{-1} band is attributed to the combined symmetric and asymmetric stretching modes of chemisorbed water, whereas the 3150 cm^{-1} band results from the stretching modes (symmetric and asymmetric) of adsorbed ammonia on the mixed oxide (Hair 1970). All three original samples also exhibit two characteristic peaks at $\sim 1400\text{ cm}^{-1}$ and $\sim 1630\text{ cm}^{-1}$. The 1400 cm^{-1} peak is characteristic of NH_4^+ ions (Hair 1970) and corresponds to the bending vibration of the H-N-H angle. The 1630 cm^{-1} band is associated with the bending mode of molecular wa-

ter (Parkyns 1970). Sample TZ2 exhibits additional bands at 618 cm^{-1} , 980 cm^{-1} and 1114 cm^{-1} . These are attributed to the ν_3 , ν_1 and ν_4 vibrational frequencies of the free sulfate ion SO_4^{2-} in T_d symmetry (Nakamoto 1986, 4th edition).

Heat treatment of samples TZ1 and TZ3 to 400°C and 600°C leads to the gradual decrease of the band at 1630 cm^{-1} and to the disappearance of the 1400 cm^{-1} band indicating, in the latter case, the completion of the desorption of NH_4^+ ions, probably as NH_3 gas. In the case of TZ1 the band at 3150 cm^{-1} also disappeared confirming the elimination of ammonia.

Heat treatment of TZ2 leads to interesting observations with regard to the sulfate ion. At 400°C new bands appear at $\sim 1042\text{ cm}^{-1}$ and 1122 cm^{-1} attributable to the unidentate sulfate ion. This is followed, at 600°C , by the appearance of bands at 1037 cm^{-1} , 1138 cm^{-1} , and 1227 cm^{-1} which are attributed to the sulfate ion in a bidentate state of ligation. The latter corresponds to the gradual lowering through heat treatment of the T_d symmetry of the sulfate ion to C_{2v} by complex formation (Nakamoto 1986, 4th edition).

Figures 5, 6, 7 represent the IR spectra of the original as well as the heat treated samples.

4 Conclusions

Mixed zirconium and titanium oxides display textural characteristics that are closely related to the presence of sulfate groups in the oxides matrices. Preparations using zirconium sulfate and titanium oxysulfate as starting materials and where the resulting mixed oxides are washed *free* of the *sulfate ions* display textural characteristics that are similar to the oxides precipitated from zirconium oxychloride and titanous chloride solutions and subsequently washed *free* from the *chloride ions*. Mesoporosity in conjunction with some microporosity as well as relatively large surface areas are observed in these preparations. On the other hand, oxides precipitated from zirconium sulfate and titanium oxysulfate, and with *sulfate ions* remaining within the oxides matrix (as a result of incomplete washing), display very different textural characteristics, namely significantly lower surface areas, and limited pore volumes.

Adsorption studies in conjunction with infrared and thermal studies indicate that weakly bound ligands such as water and ammonia when present in the inner coordination spheres of the titanium and zirconium ions influence the texture of the resulting oxides. Heat treatment at low temperatures results in the removal of these ligands and the formation of vacancies, leading to the generation of an overall microporosity. In other words, microporosity in these oxides can be considered to be largely dependent on the microstructure generated through the displacement of the coordinatively bound water and ammonia (Rouquerol et al. 1999).

Heat treatment of the sulfate containing oxides leads to the incorporation of differently bound sulfato ligands in the inner coordination sphere of the zirconium and titanium ions with a resulting prevalence of very low surface areas, very small total porosity and virtually no microporosity. In this respect, the sulfate ions as well as the differently bound sulfato ligands seem to have a blocking effect on the pores and to be responsible for this drastic decrease in surface area and pore volumes.

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