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TEM characterization of sol-gel-processed alumina–silica and alumina–titania nano-hybrid oxide catalysts

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Abstract

Alumina–silica nano-particle mixtures and alumina–titania nano-mixtures with molar ratios 3:1, 3:4 and 1:0.5, 1:5 were synthesized by a sol-gel technique, during which the co-precipitates are formed. The resolved precursor powder calcined at 400 °C was characterized by thermo-gravimetric analysis, BET specific surface area measurement, adsorption isotherm characteristics and transmission electron microscopy. The results show, that the specific surface area of alumina–silica gel decreases with increase of silica content. On the other hand, specific surface area increases with increase in the amount of Ttitania content, in the case of alumina–titania powder. Considerable extent of meso-porosity is developed in 3:1 composition compared with pure alumina. TEM micrographs show a highly homogeneous distribution of the constituent phases in all specimens. In alumina–titania samples fine uniform needle like particles of ~10 nm size are observed, while for alumina–silica mixture having less silica content while for high silica containing sample, non-uniform needle like particles with particle sizes ranging from 20 to 75 nm are observed. The diffraction patterns also show more crystallinity for low silica content and high titania containing samples. Thus it is possible to synthesize materials with different porosity features and surface morphology, which may be having different applications by changing the ratio of individual components in a mixed oxide system.

Keywords: Al_2O_3–SiO_2; Al_2O_3–TiO_2; Catalysts; Electron microscopy

1. Introduction

Alumina–silica and alumina–titania composite materials have the potential for application as catalyst materials in various chemical reactions like Diels-Alder reactions, degradation of polyolefins, selective epoxidation of bulky cyclic olefins, isomerization of 2-butene, dehydration of 2-propanol, cracking of cumene, Friedel Craft's alkylation, etc.[1–3] The catalytic property is determined by the ratio of constituent oxides as a detailed study on Al_2O_3-SiO_2 aerogels and xerogels showed.[4] The important structural parameters are the amount of surface area [5] and the Al/Si ratio.[6]

Also in alumina–titania nano-composites the Ti/Al ratio:[7] is important: If it is less than 17.5%, no TiO_2 particles were detected, but Ti is dissolved substitutionally into alumina.[8] A series of x $TiO_2/(1-x)$ Al_2O_3 mixed oxides were prepared by the amount of TiO_2, from pure alumina and pure titania by both non-hydrolytic and hydrolytic sol-gel route.[9,10] Toba et al. synthesized alumina–titania by complexing agent-assisted sol-gel, coprecipitation and hydrogen kneading and found that the complexing agent assisted sol-gel method gave the most homogeneous mixture.[11] It was also observed that the acidities and specific surface areas of complexing agent assisted sol-gel mixtures depend on the Ti/Al ratios of the raw materials, while kneading alumina/titania mixtures were relatively heterogeneous and properties did not depend on the Ti/Al ratio.

The properties of coprecipitated alumina–titanias were intermediate between complexing agent assisted sol-gel and the kneading ones. Studies on series of Al_2O_3–TiO_2 mixed oxides with different TiO_2 concentration prepared by sol-gel methods showed,[12] that the structure as well as texture was affected by different alumina:titania ratios. The Ti^{4+} was highly dispersed and presumably incorporated into the alumina precursor, affecting the morphology, the aggregation state and atomic short-range order. At higher temperatures, at about 900 °C, both sintering and the crystallization process of TiO_2 and Al_2O_3 was accelerated by the Ti^{4+} segregation. Further, the surface area decreases and the

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average pore diameters increases during thermal treatment. Many papers are published about chemical processing techniques resulting in homogeneous mixture of oxides and they point out, that the properties of mixed oxides are influenced by the Al:Si or Al:Ti ratios. However, a systematic correlation based on the various reported literature is difficult.

This paper describes a novel approach, which has been adopted to synthesize alumina–silica and alumina–titania in different ratios by an innovative hybrid method involving colloidal route through hydrolysis-peptization of Boehmite derived from aluminum nitrate as well as the acid catalyzed and controlled hydrolysis of alkoxides. A systematic approach has been done in studying the effect of silica and titania with respect to thermal changes, specific surface area, adsorption patterns, pore size distribution and microstructural features, in silica and titania incorporated alumina mixed oxides.

2. Experimental procedure

Boehmite sol and tetraethoxysilane [TEOS–$Si(OC_2H_5)_4$] were used as the precursors for alumina and silica and titanium isopropoxide (Aldrich Chemicals, USA) was used as the titania source. Boehmite is synthesised from aluminum nitrate, $Al(NO_3)_3 9H_2O$ by controlled precipitation followed by peptization by dilute nitric acid at pH 3–3.5.[13] In the present experiment, the concentration of alumina in the Boehmite sol was found to be 0.166 g/ml. In a typical experiment, 10 g of aluminosilicate having alumina:silica molar ratio 3:1 was prepared by mixing 503.5 ml Boehmite sol and 5.7 ml TEOS, stirring for 5 h followed by flocculating at pH 3 using dilute nitric acid. The flocculated gel was then dried at 60 °C in an air oven. Following a similar procedure, aluminosilicate samples of Al_2O_3:SiO_2 ratio 3:4 were synthesized.

For the preparation of alumina–titania mixture with a molar ratio of 1:0.5, 9.99 g of titanium isopropoxide was stabilized in 35 ml acetic acid in an ice bath with a temperature less than 10 °C. While stirring the solution, 432.8 ml of Boehmite sol was added. The clear solution was allowed to gel at room temperature for 24 h and the resultant gel concentrated over a water bath and dried at 70 °C. In a similar way, mixtures with Al_2O_3:TiO_2 ratios 1:5 were prepared. TGA of the gel samples were conducted in a TGA Shimadzu 50 H (Japan) thermal analyzer in nitrogen atmosphere at a heating rate of 10 °C/min up to 1000 °C. For this study four specimens were produced, 3 Al_2O_3 – 1 SiO_2, 3 Al_2O_3 – 4 SiO_2, Al_2O_3 – 0.5 TiO_2, and Al_2O_3 – 5 TiO_2 in the following referred as 3:1, 3:4, 1:0.5, and 1:5.

The BET specific surface area of the calcined samples were determined by nitrogen gas adsorption at 77 K (Micromeritics, Gemini model no: 2360, USA) after degassing the samples in a flowing nitrogen atmosphere at 300 °C for 5 h. in a separate degassing unit attached to the instrument before the measurements. Pore size distribution was calculated using the Orr and Dall Valle method.[14] TEM-observations of the samples are performed in a Jeol 3000EX with acceleration voltage 300 kV, a resolution of less than 0.2 nm and an EDS detector for quantitative analysis. Diffraction pattern were taken with a camera length of 80 cm in order to distinguish amorphous from crystalline particles. The powder was dispersed in Ethanol, and homogenized in ultrasonic bath for 5 min. Then the 3 mm carbon-coated Cu-grid for TEM observation was dipped into this dispersion, so that the powder particles were attached to the grid. Since the particles sizes are much smaller than the upper thickness limit of about 250 nm, they are translucent for the electron beam.

3. Results and discussion

The thermo-gravimetric (TG) analysis of the alumina–silica and alumina–titania composite powders are shown in Fig. 1. The complexity of the precursor species formed during the hydrolysis reactions makes it difficult to assign the correct reaction path during the dehydroxylation. The alumina–silica samples show a residue value of 41.5 and 46% for 3:1 and 3:4, respectively. In the TG-plot in Fig. 1a and more clearly in its derivative (DTG-) plot in Fig. 1b. the major peak at 265 °C corresponds to the chemically bound water. A continuous weight loss from 150 to 300 °C indicates the overlapping of different decomposition processes viz. dehydroxylation of $Si(OH)_4$, hydrated aluminium oxide and chemically bound alcohol molecules. The high weight loss for 3:1 is due to the presence of more associated water to hydrated alumina. In general total weight loss is found to be higher in all precursors than reported in the literature.[9] This indicates polymerization of primary product of hydrolysis to a lower extent in our case.

In case of alumina–titania precursors, a profile with three well-defined weight loss steps are obtained as shown in Fig. 1c. The total weight loss is less in alumina–titania precursor with 1:5 ratio compared to that containing lower percentages of titania, as seen in Fig. 1c. A sharp weight loss is seen in 1:0.5 at ~270 °C which is due to the decomposition of titanium isopropoxide. The second peak at 342 °C, also remarkable in the DTG Fig. 1d, may be assigned to nitrate decomposition.

Alumina–silica precursor heated at 400 °C shows that the specific surface area decreases with increase in silica content, though the difference is marginal. A specific surface area of 287 m^2/g is obtained for 3:1 sample while a value of 262 m^2/g is observed for the 3:4 sample. The

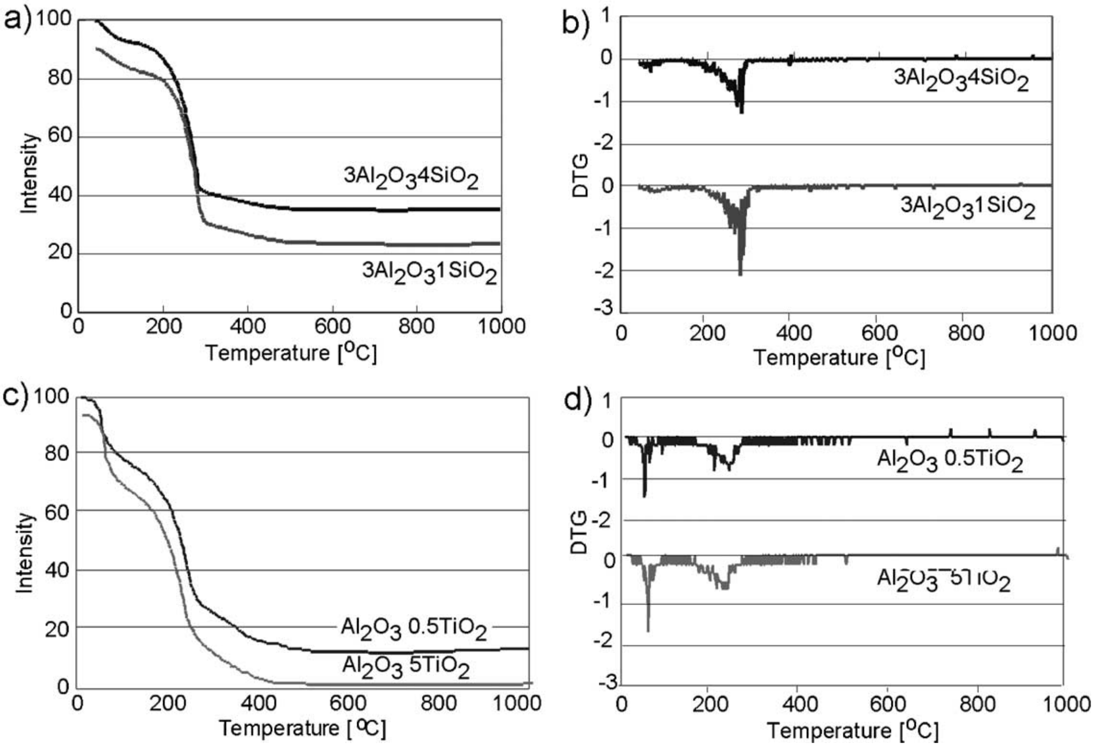

Fig. 1. (a) Thermo-gravimetric (TG) and (b) differential TG-measurements.

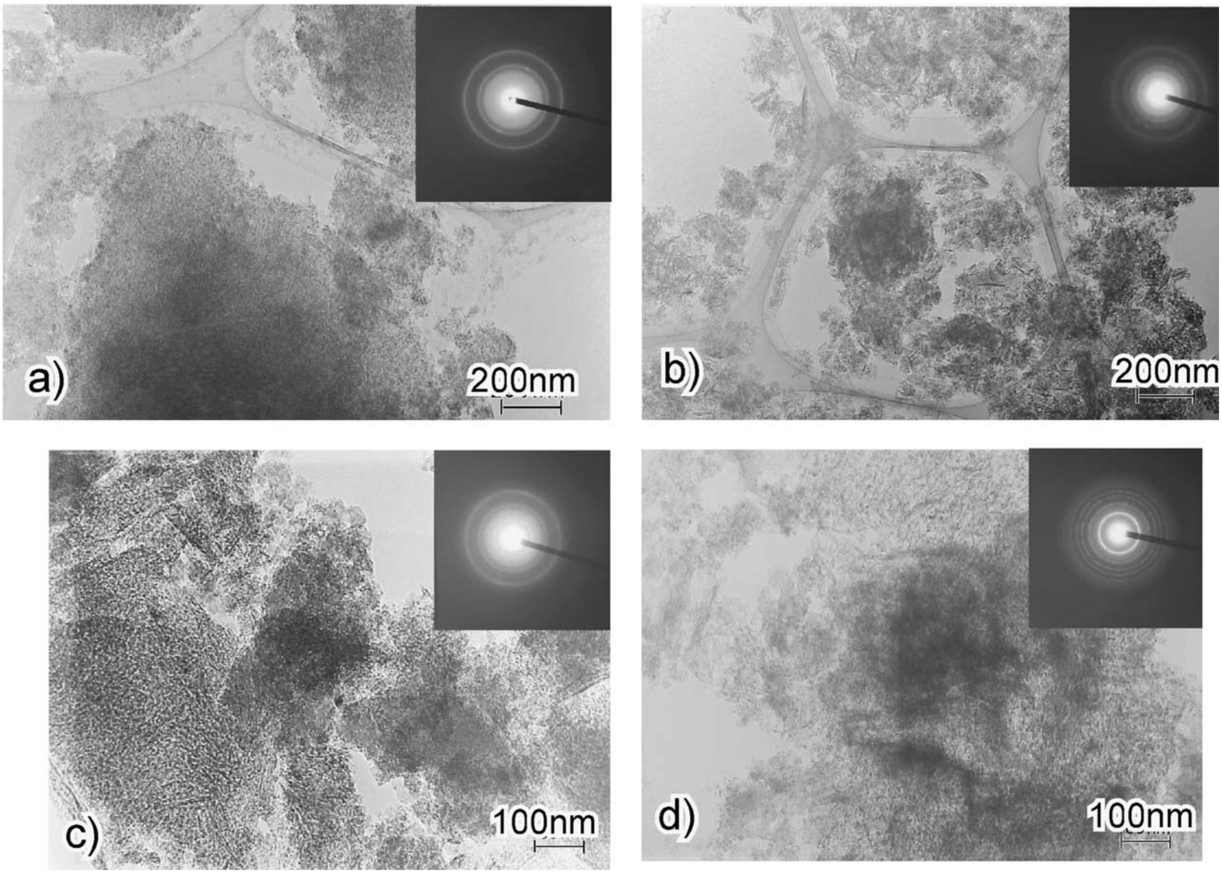

Fig. 2. TEM micrographs and corresponding diffraction pattern of the agglomerates in (a) 3 Al_2O_3–1 SiO_2, (b) 3 Al_2O_3–4 SiO_2, (c) Al_2O_3–0.5 TiO_2, and (d) Al_2O_3–5 TiO_2 composites.

specific surface area in sol-gel derived alumina is generally contributed by the micropores. When a small percent of silica, which is microporous at 400 °C, is added to the alumina matrix, silica diffuses into the matrix and this interaction possibly favors coarsening of micropores resulting in pores of large size. This further depends on the amount of silica and therefore there is an increase of surface area for the sample with low silica content. When excess amount of silica is added to the alumina matrix, number of silica molecules is large enough to fill even the micropores of alumina, with some silica excess, which is microporous. Thus, a high silica content causes a decrease in the surface area as well as porosity for alumina–silica mixtures. In the case of titania the specific surface area of the composite increases with increase in the amount of titania content. A maximum surface area of 291 m^2/g is obtained for 1:5 while a specific surface area of 256 m^2/g is observed for 1:0.5 composition. Dehydroxylation is not fully complete at this temperature and the high surface area for the titania-rich sample is due to the increase in the amount of Anatase phase.

The TEM micrographs show the highly homogeneous microstructure in both the alumina–silica mixed oxides (Fig. 2a and b). A homogeneous distribution of the individual phases is observed in all heterogeneous systems. The agglomerates are 0.5–1 μm large with a grain size of about 10–50 nm. Particles with a needle-like shape and an aspect ratio of larger than 50 are rich in alumina, as confirmed by EDS measurements. Comparing the two Al–Si oxide samples, the Al-rich (3:1) one has still amorphous particles, while the Si-rich (3:4) one contains more crystalline particle with a size around 10 nm. On the other hand, in the Si-rich sample, the particles possess needle like morphology with non-uniform sizes in a range from 20 to 75 nm. These needles are less in number but large in size.

The TEM investigations of the alumina–titania composite samples show homogeneous distribution with alumina rich needle like structure of about 20 nm size (Fig. 2c and d).The diffraction pattern shows a higher grade of crystallinity for the high titania containing sample.

The HRTEM micrographs in Fig. 3 shows typical particles with round shape in the 3:1 sample (Fig. 3a) compared with the needle shape in the 3:4 sample (Fig. 3b). For the sample with higher titania content (1:5) the particles are much finer in size of less than 10 nm (Fig. 3d) compared with about 20 nm for 1:0.5 alumina–titania (Fig. 3c).

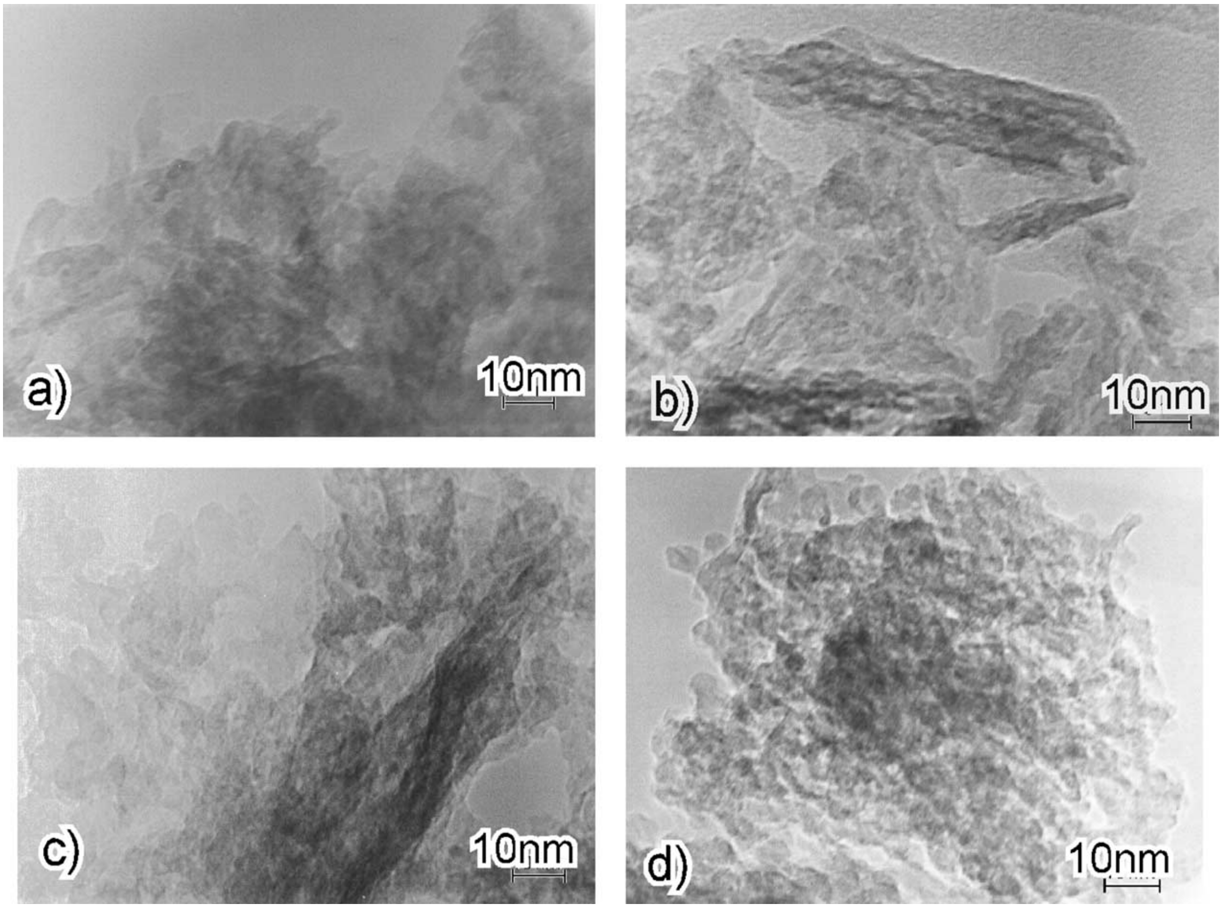

Fig. 3. HRTEM micrographs of nano-grains in (a) 3 Al_2O_3–1 SiO_2, (b) 3 Al_2O_3–4 SiO_2, (c) Al_2O_3–0.5 TiO_2, and (d) Al_2O_3–5 TiO_2 composites.

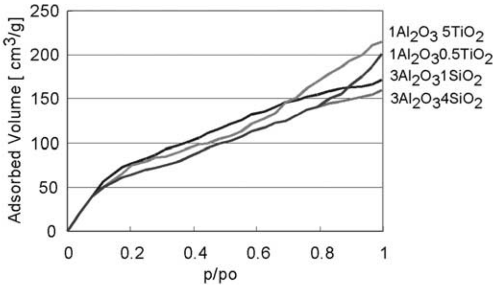

Fig. 4. Adsorption isotherms of the four observed specimens.

The adsorption isotherm patterns of the alumina–silica and alumina–titania composites are represented in Fig. 4. All the samples show almost the same type of pattern (Type IV), but the volume adsorbed for alumina is less compared with the mixed oxides in all the P/P_o range indicating less porosity for alumina. Among the alumina–silica sol-gel mixtures, the total porosity is much higher for the sample containing low silica content. The remarkable increase in the adsorption in the high relative pressure region (above $\sim 0.7\ P/P_o$) compared with other samples shows large extent of mesoporosity in the sample compared to microporosity.[11] Measurements of the pore size distribution showed a broad pore size distribution almost reaching the mesoporous region, for the 3:1 alumina–silica specimen. The 3:4 specimen has a significant peak at a pore size around 2 nm, while the 1:0.5 specimen has the lowest density of pores. Among the titania-doped alumina samples, the sample with the titania rich composition has a larger amount of pores in the micropore region than in the mesopore region, but in the sample with low titania composition it is opposite. Hence, the pore size can be adjusted by the composition according to needs of the applications.

4. Conclusion

Specific surface area, porosity characteristics and surface morphology of sol-gel derived alumina–silica and alumina–titania mixtures with different individual component compositions have been studied by analyzing the BET specific surface area, adsorption isotherm patterns, pore size distribution and TEM. At 400 °C, specific surface area of 287 and 262 m^2/g for 3:1 and 3:4, respectively, while a value of 291 and 256 m^2/g is observed for 1:5 and 1:0.5 compositions, respectively. The adsorption isotherm shows nearly a Type IV pattern irrespective of composition. The pore size distribution curves show a considerable amount of mesoporosity for sample with low silica compared with all samples where extent of mesoporosity is less. TEM observations confirmed the homogeneity of the mircostructure, with grain size of 10–50 nm, and agglomerate size of 0.5–1 μm. The morphology of the composites consists of Al-rich needles, with high aspect ratio, especially in Si-rich and Ti-poor samples. The diffraction patterns also show a higher grade of crystallinity for low silica content and high titania containing samples. Thus, it is possible to synthesize materials with different porosity features and surface morphology, which results in different applications by changing the ratio of individual components in a mixed oxide system.

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