High-Temperature Catalyst Supports and Ceramic Membranes: Metastability and Particle Packing

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Parameters and/or processes responsible for the stability of catalyst supports and ceramic membranes are discussed. Two major parameters/processes were identified which are responsible for the stability of sol-gel derived nanostructured oxides at elevated temperatures. They are metastable-to-stable phase transformation and structure and packing of primary particles within the aggregate. Based on these observations, strategies to develop thermostable nanostructured oxides for high-temperature membrane and catalyst applications are discussed by taking titania and titania-alumina nanocomposites as examples.

Introduction

Catalysts and ceramic membranes which can be used at relatively higher temperatures are finding increasing importance, because it is more practical to carry out many chemical reactions and separation at elevated temperatures (Xu and Anderson, 1993; Lin et al., 1994; Church et al., 1994; Mizukami et al., 1992; Leduc et al., 1996). Porous nanostructured materials are ideal candidates for this purpose because of their high surface area and large porosity. The simple fact that the initial surface area of these materials are very high, usually above 100 m^2/g, will make them texturally unstable during high-temperature treatments. In this article a generalized picture on the thermal stability of sol-gel derived nanostructured oxides is presented based on our findings on the stability of titania and titania-alumina nanocomposites. A major part of the research reported in this was mainly carried out with an objective to develop thermostable ceramic membranes and later it was extended to catalyst supports. The major difference is only in the macroscopic geometry, and the influence of this on the pore-structure stability is minimal when the membrane is in the unsupported form. Note that membranes supported on rigid supports showed higher thermal stability compared to their unsupported counterpart (Kumar et al., 1993).

It is a general observation that when nanosized (5 to 10 nm) particles are prepared through the Solution-Sol-Gel route, the least stable phase is precipitated first. In the case of titania anatase, the metastable phase is formed first and upon heat treatment it will convert to the stable rutile form. This type of metastable-to-stable transformation has important consequences on the thermal stability of these *metastable* precursors. During any metastable-to-stable phase transformation, there is a drastic reduction in surface area (faster densification) due to the enhanced mass transport (Kumar et al., 1992).

The level of packing (and particle coordination number) has direct influence on the thermal stability of the pore-structure of catalyst supports and ceramic membranes. It has been shown by Liniger and Raj (1988) that the densification rate of particulate compacts increases with increasing particle coordination. Coordination here means the number of the nearest neighbors having actual physical contact. The level of packing (coordination number) has a direct influence on the actual number of necks formed, which influences sintering and crystallite growth. This can also influence nucleation growth type of transformations (Kumar et al., 1994). A high level of packing will assist embryo growth to achieve the critical nuclei size (Kumar et al., 1994).

Strategies to manipulate the above mentioned parameters

Table 1. Approaches to Stabilize the Texture

	Retarding Phase Transformation	Avoiding Phase Transformation
Chemical	*By Doping:* Changing the surface/bulk chemistry, defect chemistry	*By in-situ Nucleation and Epitaxy* Changing the nucleation-growth behavior
Phy./Mech.	*By Making Nanocomposites or Supported Membranes:* Changing the nanostructural environment/configuration (Stress field, rigid inclusions, level of packing)	*By Introducing External Nuclei*

and/or processes in order to retard sintering to improve the thermal stability of catalyst supports and membranes will be discussed. For example, the drastic reduction in surface area and porosity due to the enhanced mass transport during metastable-to-stable phase transformation can be controlled either by retarding the phase transformation or by avoiding the transformation. Table 1 summarizes the different approaches followed in the present study. This article covers examples from different stabilization techniques. One of the most effective techniques is the method of porous nanocomposite formation to stabilize the matrix phase. Nanostructural evolution of titania-alumina nanocomposites is also detailed.

Porous Nanocomposites

Making nanocomposites is an effective way to stabilize the pore structure of the matrix phase (Kumar, 1994). It is expected that one of the major effects of the second phase will be in the decreasing of the particle coordination in the matrix phase. This will retard sintering and porosity reduction (Liniger and Raj, 1988; Kumar et al., 1994, 1995). Other effects are chemical modification of the matrix phase by the second phase, back-stress effect and the effect due to the possible rigid network formation of the second phase (Kumar, 1994). Network formation will be important only for volume fractions of the second phase above the percolation threshold. When selecting the second phase there are two important considerations to be taken into account:

(1) The second phase should have minimum solubility in the matrix phase and vice versa.

(2) The radius ratio $r = r_M/r_S$ (r_M and r_S are the radii of the primary particles in the matrix phase and in the second phase respectively) should be more than 1. A radius ratio of 6 is the limit above which the second phase particles may not decrease the coordination of the primary particle in the matrix phase, but they simply go into the interstitial voids in the matrix phase.

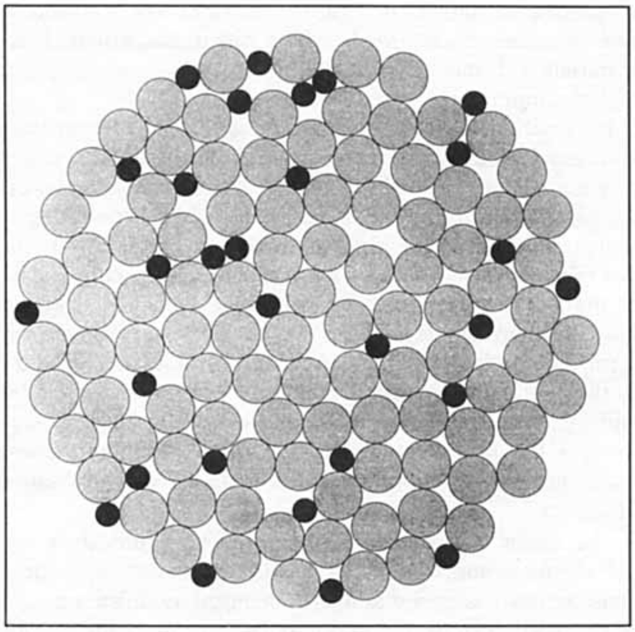

Figure 1. Porous nanocomposite containing 3.5 vol. % of the second phase (small dark circles) for a radius ratio of 2 and assuming same density (Kumar, J., 1995).

Figure 1 shows a nanocomposite containing 3.5 vol. % of a second phase with a radius ratio of 2. For any given volume fraction of the second phase, the interparticle contact between the particles of the matrix phase will decrease with an increase in the radius ratio (Gupta and Farooq, 1992).

Experimental Studies

Alumina (boehmite) sol was prepared from aluminum secondary butoxide, and titania sol was prepared from titanium isopropoxide. In both cases the sols were electrostatically stabilized with HNO_3. Detailed experimental procedures were reported elsewhere (Kumar et al., 1993a, 1995; Kumar, 1994). Titania-alumina nanocomposites were synthesized from a two-component sol made by mixing 1 molar boehmite sol with 0.3 molar titania sol in the proper ratio to obtain nanocomposites with approximately 1, 3, 6, 9 and 50 vol. % of alumina. Lanthana doped titania was produced by mixing appropriate amounts of lanthanum nitrate solution with the titania sol (Kumar et al., 1993b).

Results and Discussion

Phase transformation of titania was studied to see the importance of metastable-to-stable transformation. The volume free energy of rutile phase is always lower than that of anatase. Therefore, on heat treatment the anatase phase transforms to the stable rutile form. It was experimentally found in the present study that when the porous anatase (titania) precursor is completely transformed to rutile its porosity becomes zero (Kumar et al., 1993b). Moreover, it was never possible to make porous rutile titania from an anatase precursor sol (Kumar et al., 1993b). It has also been shown that sol-gel derived anatase can be densified to near theoretical densities at 600°C with a rutile content of more than 95% (Kumar et al., 1992). Based on these results, it is reasonable to think that if the anatase to rutile transformation can either be retarded or be avoided, one would obtain materials with much higher stability of the porous texture at higher temperatures.

Retardation of the transformation was effected by making lanthana doped titania. It is known from the literature that rare earth cations retard the anatase to rutile transformation. Avoiding the transformation was achieved by hydrolyzing titanium alkoxide in the presence of *in-situ* formed SnO_2 nuclei (Kumar et al., 1993c). This was achieved by cohydrolysis of titanium isopropoxide and anhydrous $SnCl_4$. It is known that SnO_2 always crystallizes in the rutile crystallographic form, and the lattice parameters a and c values are very close to those of rutile titania. For SnO_2, $a = 4.737$ and $c = 3.186$ and for TiO_2 (rutile) $a = 4.593$ and $c = 2.958$. Table 2 summarizes the results of above stabilizing techniques. These techniques come under chemical methods of stabilization (Table 1).

The major disadvantage with the above approach is that the chemical and catalytic behavior of the starting oxide is considerably changed due to the chemical modification. One of the most recent techniques in physical or mechanical stabilization to control the level of packing (coordination) is the porous nanocomposite approach. Level of packing can also be controlled by appropriate post precipitation treatments (Kumar, 1995). Particle coordination is defined as the number of nearest neighbors having actual physical contact with a given particle. Decreasing particle coordination has been achieved by introducing an inert second phase which would decrease the subcoordination of the particles in the matrix phase of the nanocomposite. The subcoordination number is defined as the number of neighboring particles, belonging to the same phase, having actual contact with the particle under consideration. Nanocomposites were made with different volume fractions of Al_2O_3. It is expected that the chemical nature and surface properties of the matrix phase may remain unaltered if we select a second phase which does not dissolve in the matrix phase within the temperature range studied. Previous studies on TiO_2-Al_2O_3 systems at high temperatures were aimed at producing a homogeneous phase, moreover, the purpose was not to stabilize the matrix phase (Toba et al., 1994). The decrease of particle coordination in titania (subcoordination in the case of nanocomposites) will retard both sintering and the anatase-to-rutile transformation. Retardation of the anatase-to-rutile transformation will also indirectly stabilize the pore structure of the titania phase (Kumar et al., 1994, 1995. However, it should be noted that in the case of nanocomposites there is a possibility of retardation of sintering of the matrix phase because of back stress effects and the influence of rigid second phase network formation. These effects will be especially predominant at larger volume fractions of the second phase.

Table 2. Surface Area and Average Pore Dia. of Pure, Lanthana Doped Titania and Sn Containing Rutile Titania Heated at 700°C

	Surface Area (m^2/g)	Pore Dia. (nm)
Pure Titania	0	0
La Doped (7.5 mol % $LaO_{1.5}$) Titania	33	7.2
Rutile Titania (18.5 mol % SnO_2)	37	17

Table 3. Surface Area (m^2/g) of Titania Nanocomposites Containing Different Amounts of Alumina*

Vol. % of Al_2O_3 in Titania	Anatase to Rutile Trans. Temp. (°C) from DSC (10°C/min)	Calc. Temp.		
		600°C (8 h)	700°C (8 h)	800°C (8 h)
0	560	0		
3	905	63 (58)	39 (35)	7 (2.4)
6	929	81 (73)	52 (44)	17 (8)
9	939	104 (93)	64 (54)	28 (15)
50	960	158 (102)	129 (88)	76 (**)
100		214	170	156

*The numbers in parentheses represent the surface area contributed by the matrix phase in the composite (calculated using Eq. 1).

**The calculated value is negative, because there is an appreciable destabilization of the alumina phase by titania when the temperature is above 700°C (see the text).

Table 3 gives the surface area and the anatase-to-rutile transformation temperature from DSC data of TiO_2-Al_2O_3 nanocomposites containing different amounts of alumina. DSC transformation temperature increased with an increase in the alumina content. It should be noted that a transformation temperature of 960°C does not mean that the material contains only anatase below this temperature. In isothermal calcinations, the amount transformed depends on the temperature and soaking time. Theoretically, rutile should be stable at all temperatures above absolute zero. However, the DSC transformation temperature gives us a good comparison for transformation extension and the pore structure stability associated with it.

Pure titania lost all of its surface area after calcination at 600°C for 8 h (Kumar et al., 1992). With the increase in alumina content, the absolute surface area value increased. This increase is not simply due to the surface area contributed by the alumina second phase. To have a clear understanding, the surface area contributed by the titania phase was calculated using a simple mixture rule

$$S_T = [1/(1-n)]\,(S_{TA} - nS_A) \qquad (1)$$

where S_T is the surface area of the titania phase in the composite containing alumina, S_{TA} is the measured surface area of the titania-alumina nanocomposite, S_A is the measured surface area of pure alumina, and n is the volume fraction of alumina present in the composites, $n = 0.03$, 0.06, 0.09, and 0.5. The above equation is valid only if the presence of titania in the composite does not affect the textural properties of the alumina phase. In fact titania destabilizes the alumina second phase. That means, for a given temperature, the actual surface area of alumina in the composite is smaller than the surface area of pure alumina. This will result in an underestimate of the surface area (S_T) contributed by titania in the composite when using Eq. 1.

Surface area of titania phase of composites containing different amounts of alumina has been calculated using Eq. 1 from the data given in Table 3 and presented within the parenthesis. At 600°C and 700°C, the calculated surface area of the titania phase in the composite shows a clear increase with the increase in the alumina content. Even though the Al_2O_3-TiO_2 phase diagram does not indicate any solid solution formation, there is still some possibility of extremely small amounts of alumina dissolving in titania and modifying the surface of titania particles and thereby retarding sintering (surface area reduction). In any case the total amount of alumina dissolved in titania is much less than 3 vol. %, because the 3 vol. % alumina containing nanocomposite showed alumina second phase in the electron micrograph. XRD of samples heated above 1,100°C gave clear indication of the presence of α-alumina. If the chemical modification (by dissolution) of titania by alumina is the only retarding mechanism which is operating in the present case, then the surface area of the titania phase in the composite should not increase with the increase in the amount of alumina. Therefore, it is reasonable to assume that the increase in the surface area contributed by the titania phase in the composite with increase in alumina content is at least partly due to the decrease in the subcoordination number of titania particles. In other words, with increase in alumina content the effective contribution of subcoordination in retarding sintering will increase. At lower alumina contents, the effect due to chemical modification of titania by alumina might dominate the process of retardation. The same reasoning can be applied to explain the increase in the anatase-to-rutile transformation temperature (decrease in the transformation rate) with increase in alumina content.

Figure 2 provides the field emission scanning electron micrographs (FE-SEM) of pure titania and the composites containing 3 and 9 vol. % titania heated at 700 and 800°C. Pure titania is completely dense, and there is a gradual grain growth, from about 100 nm (700°C) to 150 (800°C) nm. Pure titania becomes completely rutile already at 600°C. Therefore, from 700 to 800°C no drastic grain was observed.

Both the 3 and 9 vol. % alumina containing composites retained a considerable amount of porosity even after calcining at 800°C for 8 h. In the precursor gel, titania particles were equiaxed with an average diameter of 5 to 6 nm and alumina particles were needle shaped with a diameter of 4 to 5 nm. The microstructure of the nanocomposites heated at 700°C looks more or less like a single-phase material. It is impossible to distinguish between the titania matrix phase and the alumina second phase. This is possibly due to the small size difference between the primary particles of the two phases. Note that there is a drastic increase in the grain size when the sample was heated at 800°C. The large crystallites are titania (matrix) particles and the small particles are alumina (second phase). This drastic grain growth of titania (matrix) phase can be attributed to the enhanced mass transport during the anatase-to-rutile phase transformation. Even the 700°C heated samples of the nanocomposite contained only less than 25% rutile, whereas after heat treatment at 800°C, 3 and 9 vol. % samples contained more than 90% and 60% rutile, respectively. At 700°C, the difference in primary particle size between 3 and 9 vol. % samples is insignificant, whereas at 800°C the average grain size is larger for the composite containing 3 vol. % of alumina. There is practically no difference in grain size between pure titania and the nanocomposite containing 3 vol. % alumina, whereas the samples containing 9 vol. % alumina have smaller average grain size. However, in both the cases the nanocomposites retained a porosity of about 20 to 30%. Figure 3 gives the FE-SEM pictures of titania 50 vol. % alumina nanocomposites heated at 800°C. The larger crystallites are titania. The average size of it is much smaller than that present in the composites containing 3 and 9 vol. % of alumina. The extent of stabilization increases with the amount of the alumina second phase.

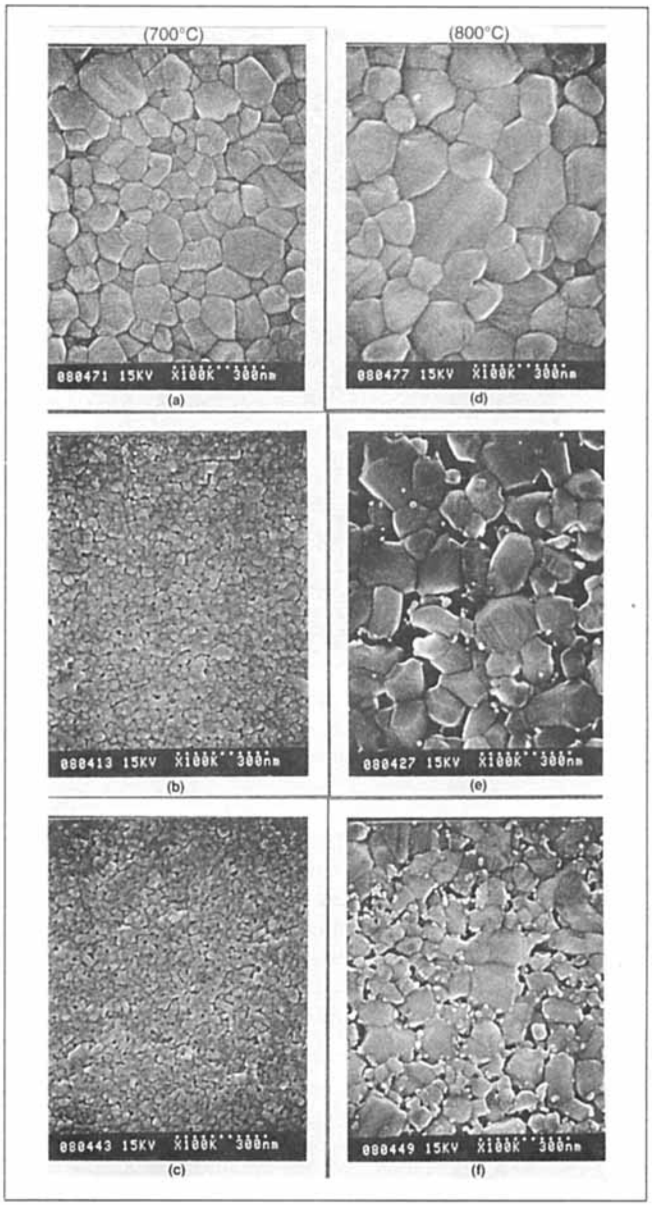

Figure 2. FE-SEM micrographs of titania containing (a) pure titania; (b) 3 vol. % alumina; (c) 9 vol. % alumina after heating at 700°C for 8 h; (d), (e) and (f) are the ones heated at 800°C for 8 h, respectively.

Magnification, 100,000 times.

Conclusion

Strategies to develop high-temperature catalyst supports and ceramic membranes are introduced. The importance of

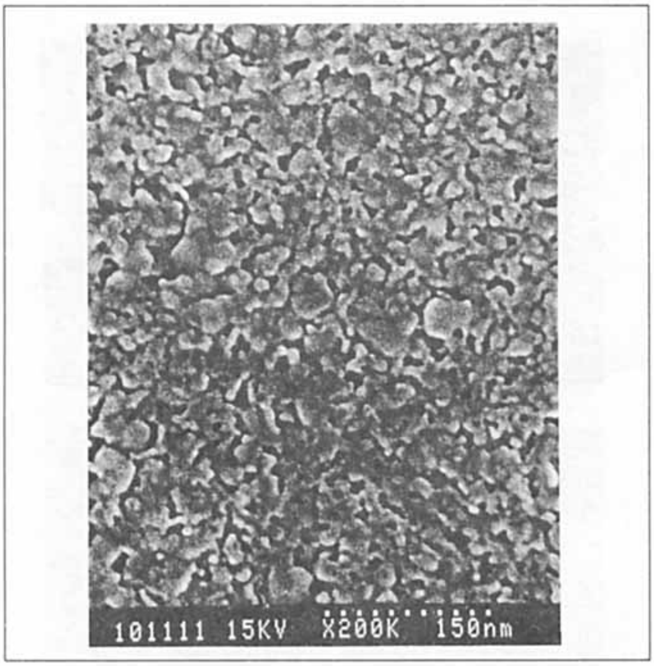

Figure 3. FE-SEM micrograph of titania-50 vol. % alumina after heating at 800°C for 8 h.

Magnification, 200,000 times.

phase transformation and particle packing in controlling sintering is demonstrated. Both avoiding and retarding the phase transformation can be effective in stabilizing the pore structure of metastable nanostructured oxides. Porous nanocomposite formation is an effective way to stabilize the pore structure of the matrix phase. The techniques discussed here can be extended to other oxide and mixed oxide systems.

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