Kinetics and Catalysis, Vol. 41, No. 3, 2000, pp. 394–398. Translated from Kinetika i Kataliz, Vol. 41, No. 3, 2000, pp. 433–438.

Study of the Catalysts for Fuel Combustion Reactions: XIX. Thermal Stability of Alumina Promoted with Lanthanum and Silicon

R. A. Shkrabina, V. A. Ushakov, N. A. Koryabkina, and Z. R. Ismagilov

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Received October 30, 1998

Abstract—X-ray diffraction analysis and data on the strength and specific surface area are used to study the thermal stability of a La–Si/Al_2O_3 system depending on the concentration of introduced additives and calcination temperature. The mechanisms of interactions of these elements and alumina are discussed. Silicon and lanthanum cations begin to interact at low temperatures (~500°C). The authors assume that silicon and lanthanum cations occupy tetrahedral and octahedral positions, respectively, in the γ-alumina lattice and thus significantly enhance its thermal stability. Up to 50% of γ-Al_2O_3 is retained at 1200°C, and α-Al_2O_3 starts to form in the ternary system only at 1300°C.

INTRODUCTION

This article continues our studies of the effect of the modification of alumina with Mg, La, Ce [1–3], La–Mg [4, 5], and Ce–Mg [6] cations on the properties of this support. Here, we consider alumina systems simultaneously modified with lanthanum and silicon.

EXPERIMENTAL

Silicon, either in the form of a silica sol or powder was introduced into the sol of pseudoboehmite aluminum hydroxide prior to the formation of spherical granules. Aluminum hydroxide was of the pseudoboehmite structure prepared by the procedure described in [7]. Lanthanum was introduced into the samples by incipient-wetness impregnation of spherical γ-Al_2O_3 granules 2–3 mm in diameter using a lanthanum nitrate solution. Spherical granules were formed by the hydrocarbon–ammonia method [8]. Granules were dried at 110°C and calcined at 550–1300°C (for 2 or 4 h at each temperature).

Samples were analyzed by XRD on an HZG-4 diffractometer using the procedure similar to that described in [1–3].

The specific surface area (S_{sp}) of the samples was determined by the thermal desorption of argon using the BET method.

The mechanical strength of granules was measured on an MP-9S instrument using a standard procedure. The strength was averaged over at least 30 granules (P_{av}).

RESULTS AND DISCUSSION

Table 1 summarizes the results of studies of the effect of silicon ions on the structural and mechanical properties of alumina during its thermal treatment. An increase in the concentration of SiO_2 added as a silica sol results in a decrease in the concentration of α-Al_2O_3 at 1200°C. At a SiO_2 concentration of 33 wt % (sample 4), the product of its interaction with Al_2O_3 (mullite) is observed. Note that α-SiO_2 is formed along with mullite in this sample at 1300°C. This fact points to the limited interaction of SiO_2 with alumina. The crystallizing effect is not observed if silicon is introduced as a cristobalite (samples 5 and 6). Table 2 presents the phase composition of the silica system obtained by the calcination of silica sol for comparison. It is seen that the silica system is an X-ray-amorphous phase up to 900°C, and only the cristobalite phase is detected already at 1000°C. Note that no cristobalite phase is observed at 1000°C in the alumina–silica systems into which SiO_2 was introduced as a sol.

Our results demonstrate a mutual stabilizing effect of aluminum and silicon cations in aluminum–silicon oxides and suggest that this effect is due to the interaction of oxides.

Note that a mechanical stability is enhanced together with a thermal stability with an increase in the concentration of SiO_2 added as a sol. The strength of granules containing 33 wt % SiO_2 at 1200°C is 5 times higher than that of a pure α-Al_2O_3 (Table 1).

We studied the effect of the calcination temperature and time on the thermal stability in detail for the samples containing 2.5 wt % SiO_2. A prolonged thermal treatment for 24 h showed that the stability of these samples was significantly higher than that of pure Al_2O_3 samples. A decrease in S_{sp} because of sintering upon calcination is 8% (at 1000°C), ~6% (at 1100°C), and 12% (at 1200°C) for the samples containing 2.5 wt % SiO_2. These changes are 30% (at 1000°C),

0023-1584/00/4103-0394$25.00 © 2000 MAIK "Nauka/Interperiodica"

Table 1. Effect of SiO_2 additives on the properties of spherical alumina (d = 2–3 mm)

Sample number	SiO_2, %	S_{sp}, m^2/g	P_{av}, MPa	Phase composition
		550°C, 4 h*		
1	0	240	19	γ-Al_2O_3
2	2.5 (sol)	240	19	γ-Al_2O_3
3	14.5 (sol)	240	22	γ-Al_2O_3
4	33.0 (sol)	250	17	γ-Al_2O_3 + amorphous phase
5	2.0 (cristobalite)	210	19	γ-Al_2O_3
6	14.5 (cristobalite)	220	16	γ-Al_2O_3
		1200°C, 4 h*		
1	0	8.6	26	α-Al_2O_3
2	2.5 (sol)	40	29	40% α-Al_2O_3 + δ-Al_2O_3
3	14.5 (sol)	44	51	30% α-Al_2O_3 + δ-Al_2O_3
4	33.0 (sol)	30	130	2% α-Al_2O_3 + δ-Al_2O_3 + traces of mullite
5	2.5 (cristobalite)	10	29	α-Al_2O_3 + α-SiO_2
6	14.5 (cristobalite)	12	14	α-Al_2O_3 + α-cristobalite
		1300°C, 2 h*		
1	0	6	34	α-Al_2O_3
2	2.5 (sol)	7.9	29	α-Al_2O_3
3	33.0 (sol)	6.5	135	α-Al_2O_3 + α-SiO_2 + mullite
		1400°C, 2 h*		
1	0	2.9	38	α-Al_2O_3
2	2.5 (sol)	3.0	31	α-Al_2O_3
3	33.0 (sol)	4.0	145	α-Al_2O_3 + α-SiO_2 + mullite

* Conditions of the thermal treatment of modified alumina.

~70% (at 1100°C), and 40% (at 1200°C) for the samples of pure alumina.

The thermal stability of pure Al_2O_3 support the previously reported data on a drastic change in the properties of alumina obtained from the product of the thermal decomposition of gibbsite at 1100°C [1–3]. Because of an inhomogeneity in the phase composition of a low-temperature oxide, which contains the χ-phase along with γ-Al_2O_3, S_{sp} drastically decreases together with the mechanical strength of granules.

Based on the results obtained, we chose the following composition for the synthesis and study of alumina system modified with La and Si cations: 2.5% SiO_2 + 5% La_2O_3 + 92.5% Al_2O_3.

The main properties of this system are compared in Table 3 with those of pure Al_2O_3 and alumina containing only SiO_2 (2.5 wt %) or only La_2O_3 (5 wt %). The data in Table 3 show that the introduction of both lanthanum and silicon results in a significant retardation of phase conversions in alumina and in the ensuing retention of a rather high specific surface area during high-temperature treatment. The maximum effect of the thermal stabilization is observed at $T > 1000$°C. Thus, S_{sp} for the sample containing both La and Si was almost twice as high as that for the La/Al_2O_3 and Si/Al_2O_3 systems at 1100°C. A substantial difference in the specific surface areas of these two systems is retained up to 1200°C. At 1300°C, S_{sp} for the La–Si/Al_2O_3 system is 3–4 times higher than that for La/Al_2O_3, Si/Al_2O_3, and pure Al_2O_3. For these systems, specific surface areas become less pronounced. This is because the phase composition of the systems is essentially different. The α-Al_2O_3 phase in the La–Si/Al_2O_3 sample appears only at 1300°C and only in trace amounts. In contrast to the La/Al_2O_3 system [2], the phase of lanthanum aluminate in the La–Si/Al_2O_3 system is not observed after high-temperature ($T > 1000$°C) treatments. Lanthanum hexaaluminate appears only at 1300°C. Note also that the products of the interaction between lanthanum and

Table 2. Temperature dependence of the phase composition of the silica system obtained from a sol

Calcination temperature, °C	Phase composition
550	X-ray-amorphous phase
900	X-ray-amorphous phase, which is better crystallized than that calcined at 550°C
1000	Cristobalite

Table 3. Properties of spherical alumina modified with different cations

Sample number	Modifying additive	S_{sp}, m^2/g	P_{av}, MPa	Phase composition
			550°C	
1	–	200	24	γ-Al_2O_3
2	La	180	26	γ^*-Al_2O_3
3	Si	240	19	γ-Al_2O_3
4	La–Si	190	32	γ^{**}-Al_2O_3
			900°C	
1	–	100	20	γ-Al_2O_3 + κ-Al_2O_3 + δ-Al_2O_3
2	La	100	25	γ^*-Al_2O_3 + 50% δ-Al_2O_3
3	Si	125	20	γ-Al_2O_3 + δ-Al_2O_3
4	La–Si	120	35	γ^{**}-Al_2O_3
			1000°C	
1	–	60	26	50% α-Al_2O_3 + κ-Al_2O_3 + δ-Al_2O_3
2	La	110	25	γ^*-Al_2O_3 + 50% δ-Al_2O_3
3	Si	95	25	γ-Al_2O_3 + δ-Al_2O_3
4	La–Si	110	35	γ^{**}-Al_2O_3
			1100°C	
1	–	11	27	α-Al_2O_3
2	La	64	23	[γ- + δ- + α- (tr)] Al_2O_3 + $LaAlO_3$ (tr) + $La_2O_3 \cdot 11Al_2O_3$ (tr)
3	Si	50	28	[δ- + α- (tr)]Al_2O_3
4	La–Si	100	37	γ^{**}-Al_2O_3
			1200°C	
1	–	7	28	α-Al_2O_3
2	La	29	35	$LaAlO_3$ (tr) + α-Al_2O_3 + $La_2O_3 \cdot 11Al_2O_3$
3	Si	40	29	40% α-Al_2O_3 + δ-Al_2O_3
4	La–Si	80	38	γ^{**}-Al_2O_3 + δ-Al_2O_3 (~50%) (better crystallized)
			1300°C	
1	–	6	30	α-Al_2O_3
2	La	8	44	$LaAlO_3$ + α-Al_2O_3 + $La_2O_3 \cdot 11Al_2O_3$
3	Si	8	29	α-Al_2O_3
4	La–Si	26	48	α-Al_2O_3 (tr) + θ-Al_2O_3 + $La_2O_3 \cdot 11Al_2O_3$ (tr)

* γ is the solid solution of La^{3+} in γ-Al_2O_3;
** γ is the amorphous γ-Al_2O_3; tr denotes trace amounts.

silicon oxides were not detected. The phase of γ-Al_2O_3 is present even at 1200°C, although in a more crystallized form than in the sample calcined at 550°C.

It is interesting that the stabilizing effect for the La–Si/Al_2O_3 system is much more pronounced than that for the Mg–La/Al_2O_3 system. Thus, at a La_2O_3 concentration of 5 wt % in these samples treated at 1200°C, 15% α-Al_2O_3 is formed in the Mg-containing system [5] and its S_{sp} is almost four times lower than that for the Si-containing system for which no α-Al_2O_3 phase was detected (Table 3, sample 4). Only α-Al_2O_3 (in addition to a mixed solid solution of magnesium and lanthanum in alumina [5]) is present in the Mg–La/Al_2O_3 system at 1300°C, whereas the α-Al_2O_3 phase is detected only in trace amounts in the La–Si/Al_2O_3 sample.

In ^{29}Si NMR spectra of the 2.5% SiO_2–Al_2O_3 (sol) sample calcined at 550 and 900°C, no signal with the shift typical of silicon atoms bound to aluminum through an oxygen bridge is observed. This is probably due to a low concentration of such bonds (Si–O–Al). However, the small deviations of chemical shifts cannot be unambiguously explained by the interaction

between aluminum and silicon cations, but they allow us to assume the probability of such an interaction.[1]

Therefore, the NMR and XRD data cannot be used to confirm the interaction between the components in the Si–Al and La–Si–Al systems. Nevertheless, the following indirect evidence suggest this interaction:

(1) The formation of an X-ray-amorphous oxide at 550°C and mullite at 1200°C in the 33% SiO_2–Al_2O_3 system (Table 1), whereas pure X-ray-amorphous SiO_2 transforms into cristobalite already at 1000°C (Table 2) and

(2) the formation of amorphous γ-Al_2O_3, which is stable up to 1200°C, when alumina is simultaneously modified by silicon and lanthanum (Table 3).

In our opinion, the stabilization of γ-Al_2O_3, as well as the magnesium–lanthanum system, at high temperatures can be explained on the basis of the hydroxy–oxide model for the structure of low-temperature aluminas and analysis of the pathways for changing the structures of solid solutions based on these oxides during their thermal treatment [9, 10].

According to the above-mentioned model, η- and γ-Al_2O_3 have a protospinel structure described by the formula

$$A^*_{x_1}A^*_{x_2}B^*_{y_1}B^*_{y_2}O_{32-z}(OH, \ldots)_z,$$

where A and B are the spinel tetrahedral and octahedral cationic sites and A* and B* are the protospinel cationic positions, which are defects in the spinel structure. The hydroxyl groups present in the anionic framework stabilize this structure. The overall aluminum cation content is ~18.5 instead of 24 as in spinel. Low-temperature solutions based on protospinel are generally close their structures but differ in x, y, and z coefficients.

As the temperature increases, protons are removed and the cubic anionic lattice becomes more perfect because the cationic sites are packed more and more closely. There may be different mechanisms for this process:

(1) The occupation of octahedral sites is preferable and it increases, but the occupation of defective sites decreases. As a result, the stoichiometric AB_2O_4 spinel is formed. This route is typical of the system containing magnesium.

(2) The occupation of tetrahedral cationic sites is preferable, and it increases. In this case, new cationic positions, which are not characteristic of the spinel and low-temperature forms of alumina, are filled. As temperature increases, the δ- and θ-alumina or solid solutions based on them are formed. This mechanism of restructuring is typical of alumina and the lanthanum-containing system. It results in the transformation of a close-packed cubic oxygen anionic lattice to a hexagonal structure with the formation of α-Al_2O_3, its solid solutions, or hexaaluminates.

It is known that, depending on the coordination, the ionic radii of cations mentioned in the paper are 0.053 (Al^{3+}), 0.040 (Si^{4+}) and 0.106 (La^{3+}) nm for the octahedral environment and 0.039 (Al^{3+}) and 0.026 (Si^{4+}) nm for the tetrahedral environment [11]. Aluminum ions can easily be replaced by smaller ions, for example, silicon ions. The close cubic packing of oxygen allows the ions with radii of at most 0.075 nm to be introduced without distorting the lattice.

The introduction of silicon into alumina leads to a new situation caused by the properties of silicon (the 4+ charge and the preference of the tetrahedral oxygen environment). If the structure of the low-temperature form of oxide is preserved, the substitution of silicon for aluminum should not result in the appearance of an excess positive charge of a cationic sublattice, which can be decreased by removing a part of protons, the most labile structural elements. At the same time, the removal of protons from the anionic sublattice of protospinel and the ensuing disturbance of molecular electroneutrality are a driving force for the structural rearrangement of the transition forms of alumina and alumina-based solid solutions with an increase in the temperature. Thus, the replacement of aluminum ions by silicon ions and the removal of protons make the structural rearrangement of the low-temperature oxide unnecessary when the temperature increases. Correspondingly, the content of cations should remain virtually unchanged, and the structure of the low-temperature oxide should be "frozen."

This manifests itself in XRD as a virtually unchanged diffraction pattern for the low-temperature form of alumina. When the substitution is rather high, the structure is distorted, and probably loses symmetry, but it virtually retains the cubic anionic lattice. This shows itself in the smearing of a diffraction pattern.

The substitution of silicon for aluminum in the structure of the low-temperature form of alumina has two limiting factors: the number of hydroxyl groups and the number of tetrahedral positions occupied by aluminum; evidently, the former factor is determining. This means that the composition of the product of interaction between SiO_2 and Al_2O_3 will be determined by the rates of two competitive processes silicon substitution for aluminum and hydroxyl group removal to form anionic vacancies because these processes both increase the positive charge in a cell.

The final result of thermal conversions of the product of interaction between SiO_2 and Al_2O_3 is mullite. Although the formula $Al_6Si_2O_{13}$ is assigned to mullite, the structural studies show that it corresponds to the formula $Al_{6-x}Si_xO_z$, where (according to different data) x = 1.016–1.48 and z = 9.0508–9.74. If we consider a triple mullite cell whose volume is almost identical to that of the spinel cell, the difference in the occupations of cationic and anionic sublattices can be evaluated for

[1] The authors are grateful to A.V. Nosov for the helpful discussions of the results.

the structure of a pure low-temperature form of alumina and mullite. Such a triple cell approximates to the formula $Al_{14}Si_4O_{29}$. According to our model, γ-Al_2O_3 has a protospinel structure described by the formula $A^*_{1.75}A_{6.75}B^*_{1.0}B_{9.0}O_{23.5}(OH)_{8.5}$. The comparison of these formulas demonstrates that the occupation degree of the cationic sublattice is preserved in agreement with the above discussion. The loss of protons from the anionic framework is compensated in part by the replacement of half the aluminum ions in tetrahedral sites by silicon ions and in part by the removal of anions with the formation of anionic vacancies when the temperature of a thermal treatment increases. The replacement of aluminum ions with silicon ions and the removal of almost 10% of the anions from the cubic anionic framework finally resulted in the distortion of the structure, namely, in the transformation from cubic to orthorhombic symmetry.

The appearance of lanthanum in the alumina structure leads to significant distortions of the lattice, because the size of the cation is rather large. The solubility of lanthanum even in α-Al_2O_3 is at most 10 mol %. We believe that the loose structure of γ-Al_2O_3, in which defects of anionic sublattice can be formed, favors the limited lanthanum solubility, which is sufficient for the enhancement of the total thermal stability of the system.

As in the case of magnesium–lanthanum system, the presence of lanthanum in the alumina system favors the incorporation of silicon ions into the support structure and imposes additional diffusion limits on the rearrangement of the structure of a solid solution at high temperatures.

Thus, the promotion of alumina supports with two cations, silicon and lanthanum, allowed us to stabilize the structure of the low-temperature forms of alumina by the formation of a stable solid solution.

In one work known to us [12], a phase was observed that was the product of interaction between SiO_2 and Al_2O_3. The authors showed that the method of preparation of mixed Si- and Al-containing xerogels affected the formation of phases of mullite precursors. If xerogels were formed by a fast hydrolysis, a spinel phase with a composition close to $SiO_2 \cdot 6Al_2O_3$ was observed. The mullite phase was crystallized from the spinel phase during thermal treatment. The spinel phase was also mentioned in [13], where the authors studied the products of the mechanical activation of kaolinite after their thermal treatment. Above 900°C, in the mechanically activated kaolinite, the authors detected spinel traces whose fraction increased after the calcination at 1000°C. A further increase in the temperature resulted in an increase in the fraction of mullite.

Thus, the XRD studies carried out in this work and the available literature data suggest the low-temperature interaction of alumina and silica. Moreover, our early understanding of the mechanism of γ-Al_2O_3 stabilization upon introducing lanthanum [2, 4–6] is now confirmed. Lanthanum and silicon cations in the La–Si/Al_2O_3 system have a synergetic effect on the stabilization of the alumina structure.

REFERENCES

1. Koryabkina, N.A., Ismagilov, Z.R., Shkrabina, R.A., *et al.*, *Appl. Catal.*, 1991, vol. 72, no. 1, p. 63.
2. Shkrabina, R.A., Koryabkina, N.A., Ushakov, V.A., *et al.*, *Kinet. Katal.*, 1996, vol. 37, no. 1, p. 116.
3. Koryabkina, N.A., Shkrabina, R.A., Ushakov, V.A., *et al.*, *Kinet. Katal.*, 1996, vol. 37, no. 1, p. 124.
4. Koryabkina, N.A., Shkrabina, R.A., Ushakov, V.A., *et al.*, *Kinet. Katal.*, 1997, vol. 38, no. 1, p. 128.
5. Ushakov, V.A., Shkrabina, R.A., Koryabkina, N.A., and Ismagilov, Z.R., *Kinet. Katal.*, 1997, vol. 38, no. 1, p. 133.
6. Ismagilov, Z.R., Shkrabina, R.A., and Koryabkina, N.A., *Alyumooksidnye nositeli: proizvodstvo, svoistva i primenenie v katalitricheskikh protsessakh zashchity okruzhayushchei sredy* (Alumina Supports: Manufacturing, Properties, and Applications in Environmental Catalytic Processes), Novosibirsk: Nauka, 1998.
7. Shkrabina, R.A., Ismagilov, Z.R., Shepeleva, M.N., *et al.*, *Proc. 10th National Symp. on Recent Developments in Catalysis, New Delhi*, 1990; part II, p. 30.
8. Shepeleva, M.N., Shkrabina, R.A., Okkel', L.G., *et al.*, *Kinet. Katal.*, 1988, vol. 29, no. 1, p. 195.
9. Ushakov, V.A. and Moroz, E.M., *Kinet. Katal.*, 1985, vol. 26, no. 4, p. 968.
10. Ushakov, V.A., Moroz, E.M., and Levitskii, E.A., *Kinet. Katal.*, 1985, vol. 26, no. 5, p. 1200.
11. Cook, L.P., *Alumina Chemicals: Science and Technology*, Hart, L.D., Ed., Westerville: Am. Ceram. Soc., 1990, p. 49.
12. Okada, K. and Otsuka, N., *J. Am. Ceram. Soc.*, 1986, vol. 69, no. 9, p. 652.
13. Muller, D., Gessner, W., Behrens, H.-J., and Schler, G., *Chem. Phys. Lett.*, 1981, vol. 799, no. 1, p. 59.