Korean J. of Chem. Eng., **14**(3), 153-161 (1997)

REVIEW

HYDROCARBON-AMMONIA MOULDING-A NEW TECHNOLOGY FOR PRODUCTION OF COMBUSTION CATALYSTS

Zinfer R. Ismagilov, R. A. Shkrabina and Natalia A. Koryabkina†*

Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva, 5, Novosibirsk, Russia, 630090

(Received 2 April 1997 • accepted 9 May 1997)

Abstract – Fluidized bed catalytic combustion has proved to be very promising for industrial application. The milestone problem is development of support and catalyst with high mechanical and thermal stability. We have developed a new technology for production of alumina supports with desired spherical shape, texture and structure. Properties of spherical granules depend on the method of granulation and most attention has been paid to development and optimization of hydrocarbon-ammonia moulding to produce uniform alumina spheres. Optimization of high quality spheres production focused on study of effect of initial hydroxide properties and molding conditions on properties of final product. Modification of spherical alumina with oxides of Mg, La, Ce, and Si proved to be effective to substantially improve the mechanical and thermal stability. This effect is most pronounced when pairs of these dopes are introduced simultaneously.

Key words: *Spherical Alumina, Hydrocarbon-ammonia Moulding, Mechanical Strength, Thermal Stability, Modification by Mg, La, Ce, Si*

INTRODUCTION

Catalytic oxidation, including the combustion of fuels, is one of the main direction of R&D of the Institute of Catalysis. Combustion of fuel-air mixtures that are closed to stoichiometric is a high exothermic process, and fluidized bed catalytic reactors [Ismagilov and Kerzhenzev, 1990], the so-called catalytic heat generators (CHG) have been proposed to use.

It is known that oxidation catalysts which operate under fluidized bed conditions may change considerably during use, which is connected with the sintering of the support. Phase transformations and mechanical decomposition of the catalyst granules also occur under these conditions. For this reason, CHG used for the fuel combustion impose severe demands to the catalyst. One of most requirement is high mechanical strength and thermal stability. It should retain its activity and resistance to attrition in the fluidized bed where local thermal shocks occur. Apparently, the properties of the catalysts are determined by the mechanical strength and thermal stability of the support. The main demands to the catalysts and supports to be used in CHG have been formulated [Ismagilov and Kerzhenzev, 1990]. At first time, support granules should have a regular spherical shape and be 1-3 mm in size with a narrow partical size distribution (1.0-1.4, 1.6-2.0, 2.0-2.5, etc.) to avoid the catalyst losses due to mechanical attrition and uptake caused by the non-uniform partical size distribution. Support and catalyst granules should be strong enough to avoid cracking during the operation. The average strength of spherical granules should be not less than 18 MPa. Support and catalyst should retain their key properties during the operation when local overheating up to 1000 °C occurs on the catalyst granules.

It is known that γ-alumina obtained from pseudoboehmite is the most thermally stable alumina since its transformation to α-Al_2O_3 starts at the highest temperature (1200 °C). Taking all of these requirements into account we have concentrated on development of spherical supports for CHG on the basis of γ-Al_2O_3.

1. Production of Pseudoboehmite

Pseudoboehmite differs from boehmite by having additional water molecules inserted into the interlayer space roughening the structure [Lippens and Strgerda, 1970]. Monohydrate is highly dispersed and chemically active hydroxide. It has higher specific surface area and can produce soluble basic salt in reaction with acids, which serves as good binders in moulding.

The most industrially recognised method for synthesis of pseudoboehmite aluminum hydroxide is a periodic precipitation from the solutions of sodium aluminate with acids or from solutions of aluminum salts (nitrates, sulfates) with alkali (NaOH, NH_4). In both cases gibbsite used as raw material to obtain the solutions of aluminum compounds [Trimm and Stanislaus, 1986]. Regarding the precipitation temperature, one distinguishes the so-called "cold" (about 20 °C) and "hot" (100 °C) precipitation. In industry the so-called "mixed" pseudoboehmite hydroxide are used. The hydroxide of the cold and hot precipitation are mixed usually in ratio of 1 : 3 to provide better filtering and washing from impurities.

Recently continuous precipitation methods have been recognized. The precipitation is conducted in a single flow at 40-50 °C followed by aging at 30-35 °C.

Precipitation conditions including pH, temperature, time and temperature of precipitate aging and other process parameters determine the properties of hydroxide such as porous structure (at 110 °C), dispersity, arrangement of primary particles in secondary aggregates, etc.

Pseudoboehmite synthesis via gibbsite amorphization and processing has recently become quite popular. The process of gibbsite amorphization in the catalytic heat generators has been de-

---

† To whom correspondence should be addressed.

*Present address: Korea Institute of Energy Research, 71-2, Jang-dong, Yusung-Gu, Taejon 305-343, Korea veloped at Boreskov Institute of Catalysis (BIC) and commercialized in Russia [Shkrabina et al., 1990; Ismagilov et al., 1995]. The further processing of the obtained thermal decomposition product (TDP) of gibbsite yields hydroxide of the pseudoboehmite structure. Fig. 1 is schematic presentation of the pseudoboehmite hydroxide production according to the new CHG technology in comparison with the traditional one.

2. Properties of Pseudoboehmite Aluminum Hydroxide

Variety of methods used for the pseudoboehmite hydroxide production lead to different properties of samples which are compared in Table 1.

Note that pseudoboehmite's morphology is also different. The packing of the primary particles into the secondary aggregates and the morphology of samples 1-3 have been studied using TEM [Shepeleva et al., 1986, 1988, 1991]. Sample 4 obtained via salt precipitation consisted of the roughly packed secondary aggregates formed by fibers made of thin (~40 nm) needles. Pseudoboehmite produced by continuous precipitation (sample 5) was an assembly of small needles 2-3 nm thick in fibers ~1500 nm long. Large shapeless aggregates were scarce (unlike in sample 1). Therefore, morphologically this type of pseudoboehmite is similar to the ordinary one containing needles packed in fibers [Lippens and Steggerda, 1970]. Pseudoboehmite produced from TDP (sample 5) was similar by its morphology to that produced by the mixed precipitation method (sample 3). It consisted of needles and almost spherical particles packed in large aggregates as plates larger than 100 nm.

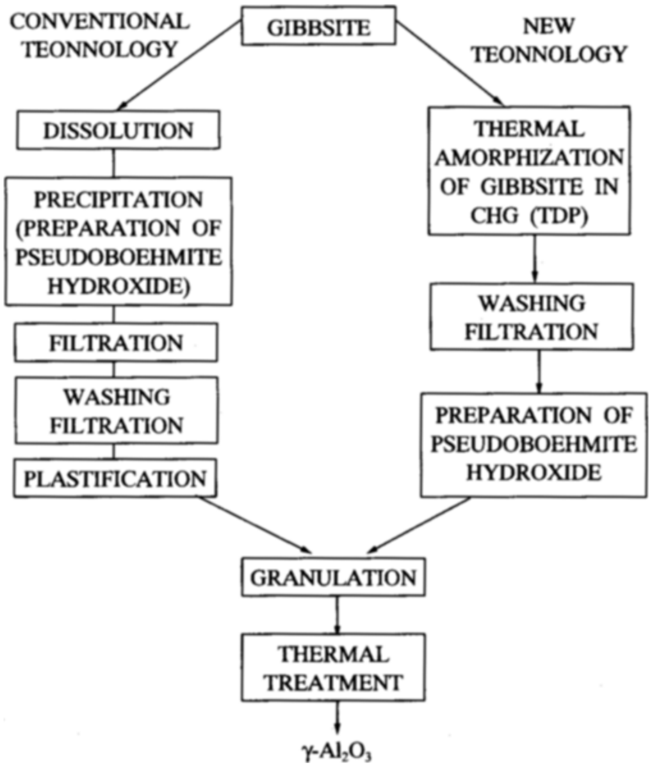

Fig. 1. Two schemes of preparation of γ-Al_2O_3.

3. Methods of the Preparation of Spherical Granules and Property Control

Detail information about the methods of granulation used to produce spherical granules can obtain [Shubert, 1975; Klassen and Grishaev, 1982]. Let us consider the peculiarities of different granulation methods.

3-1. Rotating Pan Granulation

A round dish rotating is one of the most known method to produce spherical granules. Oxide or hydroxide powders in the presence of water or binding solutions are fed into the dish and the small rotating particles develop layer by layer into larger spherical granules. Rotating of wet extrudates, whose height and diameter are approximately the same, is also used to produce spherical shape of granules. The letter method does not allow to obtain a narrow size distribution, and the particle diameter is as rule larger than 2 mm. Besides, alumina granule strength does not exceed 10 MPa. Theses disadvantages make it impossible to use such granules in the moving or fluidized bed.

3-2. Gas Phase Granulation (Spray Drying)

This method is a suitable technique to produce microspherical particles not exceeding 0.1 mm. In a spray dryer a hydrogel or a sol (solid content less than 25 wt%) is sprayed through nozzles into a heated zone. However, these microspherical granules can hardly be used in the fuel combustion at high linear rates.

3-3. Liquid Phase Moulding

In this method spherical die plates with cylindrical holes are used to produce drops of the aluminum hydroxide sol, which

Table 1. Effect of preparation conditions on the properties of pseudoboehmite hydroxide

N	Preparation procedure	Preparation conditions		H_2O, cont., wt%	S_{BET}, m^2/g	Primary particle size, nm	V_Σ	Pore structure	
		pH	T					$V_{r<4}$	$V_{r4\text{-}100}$ sm^3/g
1	reprecipitation (cold)	8.5	20	85	270	~3	0.572	0.322	0.075 (>100, 0.175)
2	reprecipitation (hot)	8.5	100	59	110	15-17	0.945	0.125	0.235 (>100, 0.585)
3	mixed hydroxide (cold : hot=1 : 1)	-	-	75	220	5; 15	0.460	0.270	0.190 0.790
4	acid precipitation	7	70	81	290	~4; 12	1.410	0.210	(>100, 0.410) 0.058
5	continuous	8.5	40	80	250	3-4	0.314	0.154	(>100, 0.102) 0.210
6	gibbsite thermal decomposition in CHG	3-4	130	75	200	5; 15	0.480	0.270	

then gets into the oil layer on top of the column and thus the spherical shape due to the surface tension. Further on, these granules congeal during their falling down through the gelating media layer (gel formation). Two technologies are distinguished depending on the congealing condition: oil and hydrocarbon-ammonia molding.

3-4. Oil molding

In this case, spherically shaped sol [containing e.g. hexamethylenetetramine (HMTA) or an organic monomer] is introduced into a hot oil (~90°C). Congealing of the sol occurs due to HMTA decomposition (or monomer polymerization). The method provides formation of uniform spherical granules. But the use of the hot oil and necessity to keep the sol drops for quite a long time (>10 min) under such severe conditions to complete HMTA decomposition or polymerization are obvious drawbacks.

3-5. Hydrocarbon-ammonia Molding

Figs. 2 and 3 present the main stages and a principal schematic view of the hydrocarbon-ammonia molding (HAM).

Aluminum hydroxide (AH) is treated by an acid-peptizer to obtain a flowing (plastic) sol. Then the sol drops through a die plate into the liquid hydrocarbon layer on top of the moulding column, where it takes spherical shape due to the surface tension. Further on, sol spherical granules fall down into the ammonia solution. The sol transforms to gel in the coagulant media, and thus granules are congealed. Then the spherical granules of the gel are dried and calcined to produce spherical alumina.

Colloidal processes occurring at the plastisizing stage, namely how the pseudoboehmite morphology (aggregation degree) and amount of acid affect the texture of both hydroxide and spherical alumina, were studied by Shepeleva et al. [1986, 1988, 1990, 1991] and Ismagilov et al. [1991]. The type of contact between the primary particles has been shown to play the important role in the process of the interaction of hydroxides with acid. In cold and continuous precipitation hydroxides (samples 1 and 5, Table 1, respectively) the primary particles are bound by electrostatic or van der Waals forces. Both types of contacts are present in mixed (samples 4 and 6, Table 1, respectively), acid-precipitation or TDP-originated hydroxides (samples 4 and 6, Table 1, respectively). Therefore, these hydroxides can be used to produce the plastic mass by the acid treatment. Contacts between the primary particles in the hot-precipitation pseudoboehmite (sample 2, Table 1) belong to the crystallization type due to chemical interactions, and this hydroxide can not be peptized by acid to produce the sol for HAM.

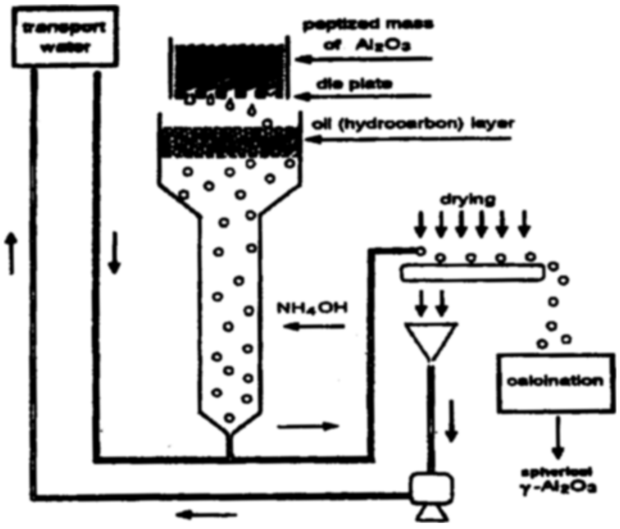

Fig. 2. Principal scheme of hydocarbon-ammonia moulding technology.

The stage of the peptization influences the porous structure of the spherical hydroxide, and thus of alumina. The later depends also on the raw hydroxide properties. Thus, for the cold-precipitation samples (sample 1, Table 1) the sol formed during peptization loses its macropores since the large secondary aggregates decompose. The gel after coagulation also does not contain macropores and, therefore, the spatial arrangement of coagulation contacts in the gel is not uniform enough.

The stage of the sphere formation includes two steps:

– spherical granules formation in a hydrophobic medium of liquid hydrocarbon layer by means of surface tension;

– congealing of the spheres.

There is an optimal height of the hydrophobic liquid layer because the residence time affects the shape and uniformity of granules. The residence time in the coagulant-NH_4OH solution, its concentration and temperature influence the rate of coagulation, uniformity of coagulant diffusion into granule affect the properties of the spherical alumina produced also [Shepeleva et al., 1990].

In general, HAM allows to produce spherical γ-Al_2O_3 granules from the aluminum hydroxide of pseudoboehmite structure containing coagulation contacts between the primary particles. But properties of γ-Al_2O_3, e.g. mechanical strength, thermal stability, depend on the morphology and pore structure of the raw hydroxide.

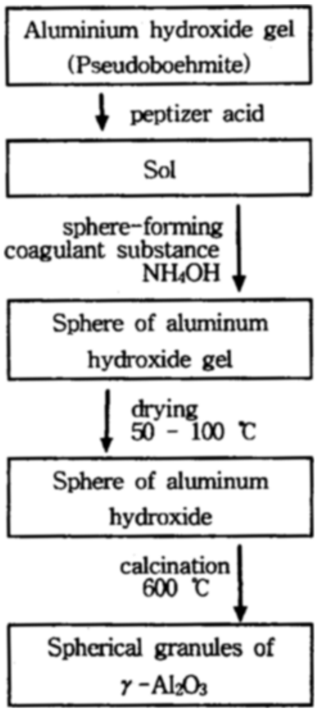

Fig. 3. The main stages of hydrocarbon-ammonia moulding.

4. Methods to Estimate Mechanical Strength of Granules

High mechanical strength is one of the demands to γ-Al_2O_3-supported catalysts for CHG apparatus with the fluidized catalyst bed. There are variety of method to determine this key parameter and it is important to choose the most appropriate method, which adequately reflects mechanical impact on the spherical granules in the fluidized bed of the CHG apparatuses.

Apparently, the term "mechanical strength" includes different characteristics such as resistance to crushing and to attrition, resistance to thermal and mechanical shock, etc.

As regards testing conditions, static and dynamic methods are used. We used the following strength measurements [Ismagilov et al., 1996]:

- crushing strength;
- attrition strength;
- impact strength.

These methods to determine the strength were compared in our work [Ismagilov et al., 1996]. Based on the results obtained we chose crushing as a test method.

Sample strength according to this method (Pav, MPa) was calculated as the arithmetic mean from values determined for 30 granules. The maximum and minimum sample strength were determined as the arithmetic mean for 5 granules possessing the minimum (P_{min}) or maximum (P_{max}) strength. Since the granules of minimum strength were the first to be crushed, it was important to fix this particular parameter, P_{min}.

5. Effect of Initial Hydroxide Properties on the Support Mechanical Strength

Table 2 presents the main properties of spherical γ-Al_2O_3 obtained from pseudoboehmite as in Table 1. Numbering of samples corresponds to that of Table 1. Note, that as it is not possible to obtain spherical γ-Al_2O_3 via HAM from the hot-precipitation hydroxide (sample 2, Table 1), there is no data for the alumina from this hydroxide. Pseudoboehmite synthesis from TDP is described elsewhere [Shkrabina et al., 1990].

One can see that the properties of the parent hydroxide determine the porous structure and mechanical strength. Therefore, the character of contacts between the primary particles in aluminum hydroxide not only plays the key role in HAM but also affects the structure and mechanical properties of γ-Al_2O_3.

Dispersing is a well known way to change the crystal structure and energy states of solids. Using the AH milling, one can change the contact character and thus affect the mechanical strength of granules. Table 2 presents the properties of γ-Al_2O_3 (sample 7) obtained from the milled AH with mixed contacts between the secondary aggregates (sample 3, Table 2). In the case of spherical γ-Al_2O_3 preparation from the milled TDP (sample 8) the milling reduces the polydispersity of the TDP fractional composition to a minimum and increased its chemical activity thus reducing the optimal autoclave operation time and acid consumption. As in the case of reprecipitated hydroxide, we obtained a strong alumina with a monodisperse structure.

Table 2. Properties of spherical γ-Al_2O_3 (granule diameter 2-3 mm)

N	Bulk density, g/cm^3	S_{BET}, m^2/g	V_Σ, cm^3/g	Volume of pores with radius				Mechanical strength, P, MPa		
				4-10	10-100	100-1000	>1000	P_{av}	P_{max}	P_{min}
1	0.86	290	0.40	0.39	0.01	-	-	21	25	14
3	0.67	240	0.44	0.18	0.05	0.21	-	8	9	5
4	0.39	280	1.59	0.78	0.35	0.098	0.37	7	8	5
5	0.75	250	0.36	0.35	0.01	-	-	20	22	16
6	0.51	230	0.63	0.41	0.22	-	-	7	9	6
7*	0.81	230	0.35	0.35	-	-	-	25	46	15
8**	0.80	225	0.40	0.40	-	-	-	24	42	14

*after grinding hydroxide

** from milled TDP

Using X-ray analysis we have shown that the granules consists of separate weakly bound fragments which form a mosaic structure. There are inner cavities and cracks also. All of these can be attributed to the large (micron scale) defects. The curves of Al K_α irradiation intensity with typical for each sample oscillations were obtained for the inner cuts of granules [Ovsyannikova et al., 1989]. Scanning of the weaker samples showed that the irradiation intensity oscillated intensively indicating numerous defects and microcracks which reduced the granule strength. The higher the strength the smaller the intensity oscillations amplitude.

6. Influence of Moulding Conditions on the Mechanical Strength

The type of raw hydroxide and its ability to disaggregate in acids determines specific surface area, porous structure and the strength of the granules. Meanwhile, molding in hydrocarbon liquid as well as granule solidification in the coagulant solution mostly affect the defectness of the shape, inner cavities, tensions and other factors that essentially determine the granule strength.

It has been shown Shepeleva et al. [1990] that the deepness of the plastic sol (PS) interaction with the coagulant (NH_4OH solution) depends on its concentration and time of the granule stay in ammonia. In the same paper one can find the data on how the PS aging time, acid module, acid type and hydrocarbon layer height influence the granule mechanical strength, shape and fractional composition. Effect of Al_2O_3 concentration in the PS, ammonia solution and PS temperature have also been studied. Water amount in the plastic sol appears to have a less drastic effect than the ratio of capillary compression and skeleton rigidity. In the systems with weak skeletons (poorly crystallized or mechanically activated AH), capillary forces provide dense and strong γ-Al_2O_3 granules even if comparatively large water amounts are removed. On the apposite, in the systems with rigid skeletons (roughly disperse AH) macropores resist

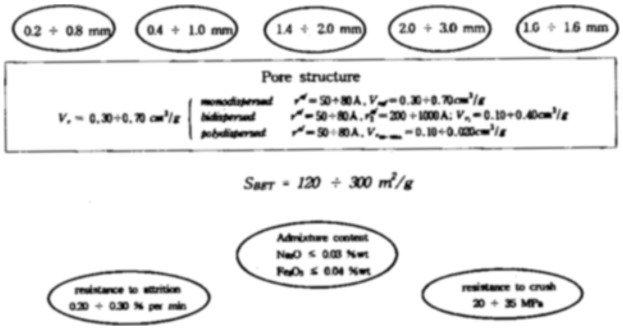

Fig. 4. Basic feature of the obtained spherical supports.

drying and calcination resulting in the decrease the granule strength.

As for spherical γ-Al_2O_3 used as the support for catalysts working in the moving or fluidized beds, the above results show that in the framework of operating technology of hydrocarbon-ammonia moulding the spherical supports with desired properties can be produced (see Fig. 4).

7. Alumina Modification as Method to Regulate Its Main Properties

The interest in high-temperature catalyst application, such as jet engines or gas turbines, methane steam reforming has evolved in recent years. In this application, goal temperatures will be in the range of 1000-1400 °C. Therefore, it is still necessary to improve these supports since the high temperature processes impose more and more severe demands to supports and catalysts. It is evident that one of the crucial problems is how to suppress sintering of the oxide support in a high temperature combustion catalyst.

γ-Al_2O_3 obtained from pseudoboehmite or boehmite is the most thermally stable alumina since its transformation to α-phase starts at the highest temperature [Lippens and Steggerda, 1970].

$$\gamma\text{-}Al_2O_3\text{~}1000\,^{\circ}C \rightarrow \delta\text{-}Al_2O_3\text{~}1200\,^{\circ}C \rightarrow \alpha\text{-}Al_2O_3$$

Generally, the final transformation was pointed out to be the main cause for the loss of surface area [Kuklina et al., 1971; Gagarina et al., 1972; Imato et al., 1975]. It is known that in the low temperature alumina Al^{+3} occupies tetrahedron and octahedron vacancies, whereas in α-Al_2O_3 it occupies only the octahedron ones. Therefore, transition of alumina into α-phase involves the Al^{+3} diffusion into the octahedron vacancies and is accompanied by the lattice rearrangements. It was reported that a neck region, i.e. contact point among primary particles was an origin for phase transformation. Particle growth occurs by successive elimination an adjacent particles, close to an area contact. With the progress of the dehydroxylation, there are necks formed between particles and, finally, small particles grow to larger ones accompanied by significant surface area loss.

There are two approach to solve this problem. The first is to develope novel method of preparation. The hypothesis refered was tested by a novel preparation of alumina aerogel [Horiuchi et al., 1994] in which the number of the necks is decreased and as a result phase transformation is suppressed. Synthesis of alumina by the thermal decomposition of alkoxide in nonpolar organic solvents was proposed by Kominami et al., [1992]. This alumina was stable and maintained a surface area above 100 m^2/g until its transformation at 1150 °C to α-Al_2O_3.

Another approach is chemical modification of alumina by various doping to improve the properties of the final product.

Table 3 presents the main properties of modified alumina.

7-1. La_2O_3-, CeO_2-, SiO_2-Al_2O_3 systems

It is known that the addition of La_2O_3, CeO_2, SiO_2 is effective in retaining large surface areas of alumina. Note, however, that data on the role of modifiers on the alumina properties are contradicting.

In the papers [Koryabkina et al., 1996; Shkrabina et al., 1996] the role of lanthanum and cerium in the increase of thermal stability is discussed where the X-ray study of these systems was carried out to establish dependencies on the method of introduction, type of alumina and amount of additives. Lanthanum introduction procedure has the drastic effect on the change of the thermal stability. Thus, the incipient wetness impregnation of oxide granules is more efficient as compared with the introduction of the lanthanum salt into aluminum hydroxide granules. Lanthanum effect at the same introduction procedure is determined by the type of alumina used. The stabilizing effect of lanthanum was assumed to result from the formation of intermediate X-ray amorphous compounds with the transient Al_2O_3 forms.

Table 3. Properties of spherical alumina

N	dope	S_{BET} m^2/g	Strength, MPa	Phase composition
				550 °C
1		200	24	γ-Al_2O_3
2	La	180	26	γ^*-Al_2O_3
3	Si	210	22	γ-Al_2O_3
4	Ce	185	21	γ-Al_2O_3
5	Mg	180	44	γ^*-Al_2O_3
6	La-Si	190	32	γ^*-Al_2O_3
7	La-Mg	160	38	γ^{**}-Al_2O_3
8	Ce-Mg	180	38	γ^*-Al_2O_3+CeO_2
				1200 °C
1		7	28	α-Al_2O_3
2	La	30	35	α-Al_2O_3+$LaAlO_3$+$La_2O_3 \cdot 11Al_2O_3$
3	Si	40	28	δ-Al_2O_3+40 % α-Al_2O_3
4	Ce	14	35	α-Al_2O_3+CeO_2
5	Mg	10	60	α-Al_2O_3+$MgAl_2O_4$
6	La-Si	80	38	γ^*-Al_2O_3+50 % δ-Al_2O_3
7	La-Mg	27	60	γ^{**}-Al_2O_3+$MgAl_{11}LaO_{19}$+α-Al_2O_3(traces)
8	Ce-Mg	23	60	α-Al_2O_3+CeO_2+$MgAl_2O_4$
				1300 °C
1		6	28	α-Al_2O_3
2	La	12	44	α-Al_2O_3+$LaAlO_3$+$La_2O_3 \cdot 11Al_2O_3$
3	Si	12	30	α-Al_2O_3
4	Ce	8	36	α-Al_2O_3+$MgAl_2O_4$ CeO_2
5	Mg	6	65	α-Al_2O_3
6	La-Si	26	48	θ-Al_2O_3+$La_2O_3 \cdot 11Al_2O_3$+α-Al_2O_3(traces)
7	La-Mg	24	70	γ^{**}-Al_2O_3+$MgAl_{11}LaO_{19}$+α-Al_2O_3(traces)
8	Ce-Mg	10	65	α-Al_2O_3+CeO_2+$MgAl_2O_4$

γ^* -Al_2O_3-solid solution of Me cation on the base of γ-Al_2O_3

γ^{**}-Al_2O_3-continuous number of low temperature solid solutions of La and Mg cations.

Unlike La_2O_3-Al_2O_3 system, the method of cerium introduction has no influence on the thermal stability of alumina. The thermal stability of Al_2O_3 was shown to increase only at low content of CeO_2 and only a part of cerium introduced was found to interact with alumina.

Specific surface area of doped alumina was shown to be stabilized at the temperatures ranging from 900-1000 °C. Thus at 1100 °C specific surface area of La-modified alumina was 3-6 time larger (depending on the alumina preparation procedure and dope amount) than that of "pure" alumina [Koryabkina et al., 1996]. The most pronounced stabilization effect was observed for the samples prepared form TDP and containing 5 wt% of La_2O_3. It related to the stronger interaction of the dope with alumina, as the latter contained χ-Al_2O_3 beside γ-Al_2O_3 due to peculiarities of its preparation. Most probably not only γ-Al_2O_3 but also χ-Al_2O_3 interacts with doped ions. The latter is more defective and disordered.

Specific surface area of Ce-modified alumina exceeded that of the "pure" alumina only by a factor of 1.2-2 within the 900-1200 °C range independently of the alumina preparation conditions.

Note that the S_{BET} stabilization effect was also more pronounced in the system La_2O_3-Al_2O_3 then in CeO_2-Al_2O_3 at T> 1200°C (see Table 3). The reason is the presence of lanthanum hexaaluminate, $La_2O_3 \cdot 11Al_2O_3$. Hexaaluminate is known [Arai and Machida, 1996] to have a layered structure that retains its large surface at high temperatures. In the CeO_2-Al_2O_3 system no cerium hexaaluminates were registrated.

In the paper [Koryabkina et al., 1996] study of structural-mechanical properties of modified supports in prolonged time calcination have been investigated. The sharpest change of S_{BET}, occurred for all the samples in the first 2 hours of calcination (see Fig. 5). A longer calcination decreased S_{BET}, of non-modified samples but not of La-containing samples prepared from gibbsite TDP (series 11). These samples had the largest specific surface area after the 30 h calcination. For Ce-samples S_{BET}, stabilization after 30 h calcination at 1000 °C did not depend on the way of the alumina preparation.

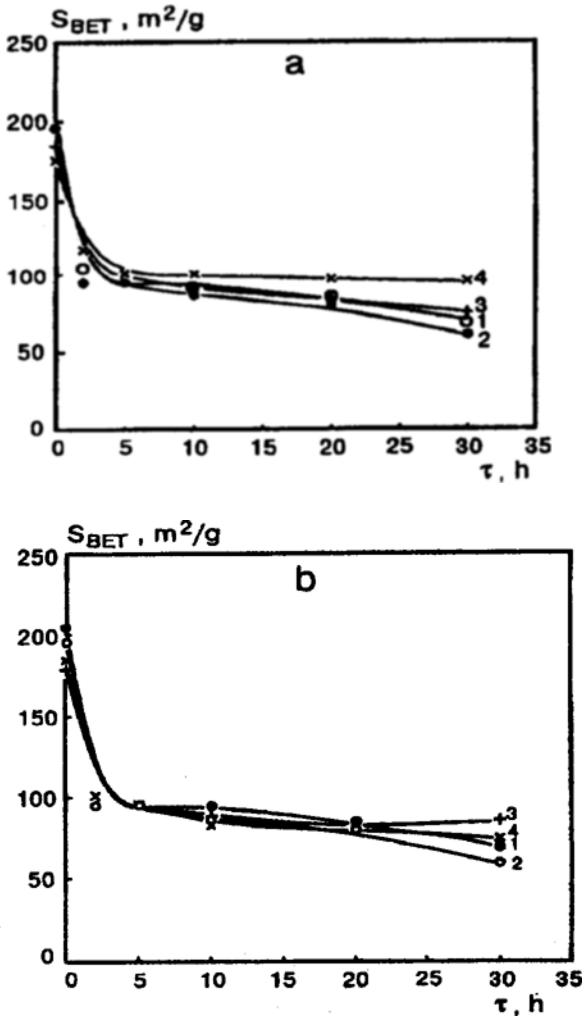

Fig. 5. Influence of calcination time at 1000 °C on S_{BET} of alumina.

1-Al_2O_3 obtained form grinding hydroxide (series 1);
2-Al_2O_3 from milled TDP (series 11);
3-MeO_x/Al_2O_3, series 1;
4-MeO_x/Al_2O_3, series 11;
a) with 5 % La_2O_3
b) with 5 % CeO_2

Note that the modified samples did not lose their strength during a long time calcination and were mechanically stable. The granule strength of La-doped samples of series 1 and 11 after the 30 h calcination at 1000 °C was 58.5 and 33 MPa. In the Ce-doped samples it was 54 and 30 MPa, respectively.

It is known that silica introduced into alumina may substantially improve its thermal stability [Imato et al., 1975; Beguin et al., 1991; Kominami et al., 1992]. We have studied the influence of content and additive form (sol, powder of SiO_2) on the thermal stability of Al_2O_3 [Koryabkina et al., 1988] and shown that only introduction of sol SiO_2 into the mass before moulding allowed to increase the thermal stability of alumina (see Table 3). Alumina content 2-3 wt% of silica maintained a large surface area at 1200°C (see Table 4). We proposed that SiO_2 is in the neck region, i.e., contact point among primary particle as a glassy phase and results in the suppression of phase transformation and maintaining a large surface area.

Comparison of the efficiency of La_2O_3, CeO_2, and SiO_2 (characterized by change in S_{BET}) shows that up to 1100 °C the best additives is La_2O_3, and SiO_2 promotor is the most effective at 1200 °C. The data are presented in Fig. 6. The S_{BET} of alumina content 2-3 wt% SiO_2 after sintering at 1200 °C increases 3-4 times in comparison with "pure" Al_2O_3.

The results obtained show that modified spherical alumina properties depend on the method of the introduction of chemical compounds. This is connected with the different nature of the interaction between aluminium compounds and modifying additives.

7-2. MgO-Al_2O_3 System

Mechanical strength and mechanical stability is one of the main properties of the granular catalysts working in the fluid-

Table 4. Influence of silica additive on the properties of spherical alumina

N	SiO_2, wt%	S_{BET} m^2/g	P_{AV}, MPa	V_{Σ}, sm^3/g	Phase composition
				550 °C	
1		240	20	0.45 (r~50 Å)	γ-Al_2O_3
2	2(sol)	240	20	0.48 (r~45 Å)	γ-Al_2O_3
3	7(sol)	240	22	0.55	γ-Al_2O_3
4	14(sol)	250	17	0.57	γ-Al_2O_3+amorph.
5	2(kristob)	210	19	0.38	γ-Al_2O_3
6	14(kristob)	220	16	0.56	γ-Al_2O_3
				1200 °C	
1		7	26	0.28	α-Al_2O_3
2	2(sol)	36	29	0.36	40 % α-Al_2O_3+δ-Al_2O_3
3	7(sol)	40	51	0.30	30 % α-Al_2O_3+δ-Al_2O_3
4	14(sol)	30	130	-	α-SiO_2(tr)+δ-Al_2O_3 +α-Al_2O_3(tr)
5	2(kristob)	10	29	-	α-Al_2O_3+α-SiO_2
6	14(kristob)	12	14	-	α-Al_2O_3+α-SiO_2

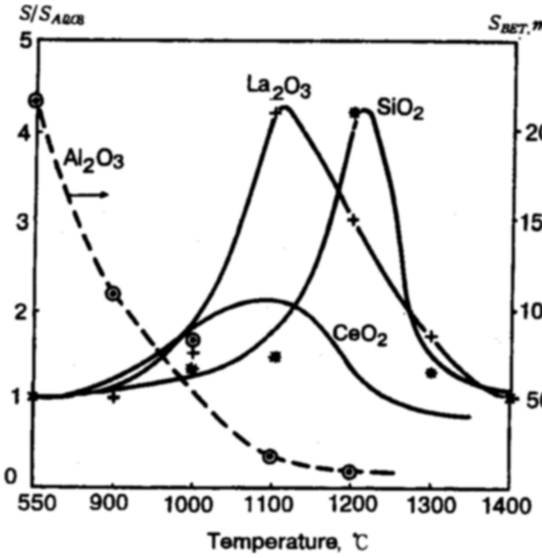

Fig. 6. The efficiency of various additives at different temperatures.

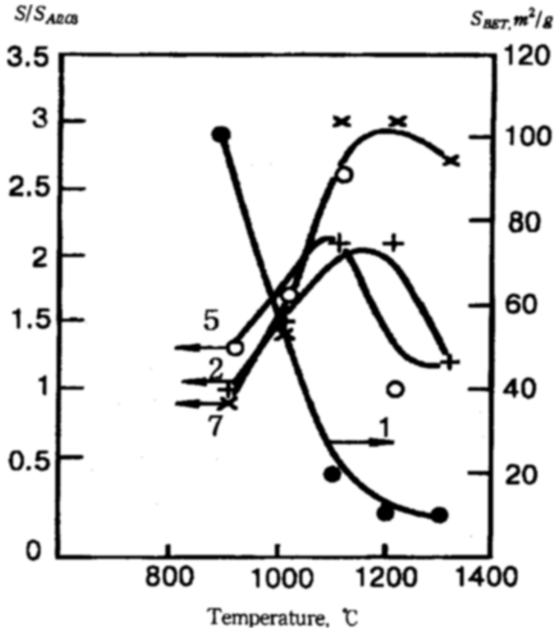

Fig. 7. Specific surface areas of the doped samples relative to that of alumina as function of the calcination temperature. The numbers of samples are the same as in Table 3.

ized bed. Such elements as Ca and Mg are known to increase sufficiently the strength of alumina at the temperature exceeding 1000 °C. The data on the strengthening the low temperature alumina with above elements are not available.

We have studied the possibility to increase the strength of low temperature alumina via chemical modifying and have designed original impregnation procedure. We have shown [Koryabkina et al., 1991] that magnesium introduction to aluminium hydroxide granules (independently of how the letter are prepared) allows to increase sharply the strength of granules (1.5-2.0 times) in comparison with pure alumina after calcination at 550 °C (Table 3, samples 5 and 2 correspondently). The dependence of mechanical strength of spherical granules on the MgO content at different temperature have been shown by Ismagilov et al. [1995]. To explain the reasons for strengthening of γ-Al_2O_3 with magnesium oxide the physico-chemical processes that occur in aluminum-magnesium system have been studied by method of X-ray phase analysis, thermal analysis, electron microscopy, X-ray spectral microanalysis and adsorption methods [Ovsyannikova et al., 1989; Koryabkina et al., 1991, 1993]. Introduction of magnesium does not cause support texture to change. It was shown that the increase in durability of modified low-temperature support is due to component interaction [Koryabkina et al., 1991] and to the decrease of granules defectiveness [Ovsyannikova et al., 1989].

8. Alumina Modified Simultaneously by Two Additives

8-1. Mg-La/Al_2O_3 System

The understanding of the mechanism of strengthening upon Mg^{+2}-doping and phase stabilization upon La^{+3} doping allows to suggest the special procedure of double modification of support with Mg and La cations for the preparation of alumina support with unique properties (see Table 3, sample 7) [Koryabkina et al., 1996]. The introduction of magnesium increases the mechanical strength of granules by factor 1.5-2.0 in comparison with pure alumina. The introduction of the second cation-lanthanum results in the increase of P_{av} at high temperature (1200-1300 °C). At the same time, introduction of lanthanum preserves thermal stability with additional increase of efficiency at high temperatures. In Fig. 7 the surface area of doped samples is presented relative to that of the undoped alumina as afunction of the calcination temperature. The X-ray studies [Ushakov et al., 1996] show that Mg^{2+} and La^{3+} ions simultaneously present in alumina stabilize the solid solution, based on γ-Al_2O_3 the structure. The co-existence of Mg and La that favor to occupy different cation positions (tetrahedral and octahedral respectively) in oxygen anion lattice in the γ-Al_2O_3 based solid solution hinders the Al ion diffusion yielding the high temperature oxides.

8-2. Mg-Ce/AL_2O_3 System

Fig. 8 shows how the specific surface area of modified alumina changed with the calcination temperature. For comparison, data for "pure" alumina are presented on the same figure. Apparently, aluminas containing both Mg and Ce had the largest specific surface area at 900-1100 °C (see Fig. 8). S_{BET} of aluminas modified with Mg and "pure" alumina decreased in the above temperature range. Ce-doped alumina retained its developed surface up to 1000 °C.

Ce and Mg ions present in alumina increase its thermal stability in comparison to the CeO_2/Al_2O_3 system but does not increase in comparison to Mg-La/Al_2O_3 system. This effect is due to only small part of Ce introduced is able to interact with the support to stabilize as Ce^{+3} and improve the thermal stability. The mechanical strength of these samples increases with temperature.

All the data obtained for the Mg-La/Al_2O_3 and Mg-Ce/AL_2O_3 systems prove that two and three-valent cations both present in alumina increase effects of each other and allow to improve the thermal and mechanical stability of alumina.

8-3. Si-La/AL_2O_3 System

Table 3 shows the main properties of modified samples with temperature growth. Thus specific surface area retained large. The best stabilization effect are observed at 1200 °C. At this temperature, S_{BET} of the samples containing La and Si are twice

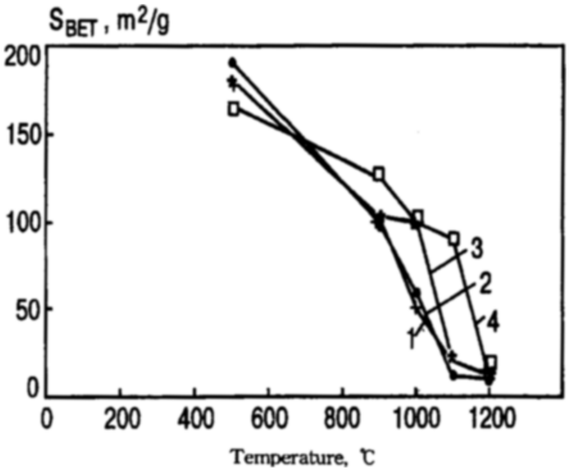

Fig. 8. Dependence of S_{BET} of alumina on temperature.
1-pure Al_2O_3,
2-2.5 % MgO/Al_2O_3,
3-5 % CeO_2/Al_2O_3,
4-$Mg-Ce/Al_2O_3$

higher than that of La/Al_2O_3, Si/AL_2O_3 and $Mg-La/Al_2O_3$. Calcination at 1573 K removed the difference between La/Al_2O_3, Si/AL_2O_3, while $Si-La/AL_2O_3$ are 3-4 times higher. Only a traces of α-Al_2O_3 are present in $Si-La/AL_2O_3$ at 1300 °C.

Silica addition produces a glassy surface layer in the point of contact among primary particles, which prevents the phase transformation to α-Al_2O_3. Simultaneously lanthanum ions fill octahedral positions, their presence in transient structure creates additional limitations for structural rearrangement with the formation of α-phase. The present of both additives (La and Si) in alumina increases effects of each other and improves the thermal stability alumina.

CONCLUSIONS

The data obtained in the fundamental studies allowed us to suggest a technological solution for the synthesis of spherical alumina with high mechanical strength and thermal stability.

Such alumina supports for the catalysts operating in the moving-or fluidized bed reactors can be prepared via the hydrocarbon-ammonia moulding of pseudoboehmite aluminum hydroxide.

We suggested a new technology to produce pseudoboehmite aluminum hydroxide based on the thermal decomposition of gibbsite in the catalytic heat generator.

The results obtained show that modified spherical alumina properties depend on the method of the introduction of chemical compounds. This is connected with the different nature of the interaction between aluminum compounds and modifying additives. The optimal conditions were chosen to prepare strong and thermally stable modified alumina supports.

New spherical supports with unique properties were synthesized by modifying alumina with two dopes simultaniously.

REFERENCES

Amato, I., Martorana, D. and Silengo, B., "Sintering of Pelleted Catalysts for Automotive Emission Control", Kuczunski, G. C. ed., Plenum, New York, 1975.

Arai, H. and Machida, M., "Thermal Stabilization of Catalyst Supports and Their Application to High-Temperature Catalytic Combustion", *Appl. Catal.*, **138**, 161 (1996).

Beguin, B., Garbovskii, E. and Primet, M., "Stabilization of Alumina toward Thermal Sintering by Silicon Addition", *J. Catal.*, **127**, 595 (1991).

Gagarina, V. A., Kuklina, V. N., Khomyakova, L. G., Ione, K. G., Rizhak I. A. and Levitskii, E. A., "Sintering of Alumina", *Kinet Catal.*, **12**, 963 (1972).

Horiuchi, T., Sago, T., Osaki, T., Sugiyama, T., Masida, H., Horio M., Suzuki, K. and Mori, T., "High Perfomance of Pd Catalyst Supported on Alumina Aerogel for Combustion of Methane", in Proc. Inter. Workshop on Catal. Comb., April 18-20, Tokyo, Japan, 38 (1994).

Ismagilov, Z. R. and Kerzhenzev, M. A., "Combustion in a Fluidized Bed Reactor", *Catal. Rev.-Sci. Eng.*, **32**(1&2), 51 (1990).

Ismagilov, Z. R., Shepeleva, M. N., Shkrabina, R. A. and Fenelonov, V. B., "Interrelation between Structural and Mechanical Characteristics of Spherical Alumina Granules and Initial Hydroxide Properties", *Appl. Catal.*, **69**, 65 (1991).

Ismagilov, Z. R., Shkrabina, R. A., Kerzhnzev, M. A. and Barannik, G. B., "New Catalysts and Processes for Environmental Protection," *React. Kinet. Catal. Lett.*, **55**(2), 480 (1995).

Ismagilov, Z. R., Shkrabina, R. A., Koryabkina, N. A. and Kaptein, F., "Synthesis of Mechanically Strong and Thermal Stable Spherical Alumina Catalysts for the Process of Methane Dimerization in a Fluidized Bed", *Catal. Today*, **24**, 2 (1995).

Ismagilov, Z. R., Shkrabina, R. A. and Koryabkina, N. A., "New Technology for Production of Spherical Supports for Fluidized Bed Combustion", *Catal. Today*, in press, (1997).

Klassen, P. V. and Grishaev, I. G., "The Basis of Granulation Methods", Chimiya, Moscow, 1982.

Kominami, H., Inoue, M. and Inui, T., "Synthesis of Material for Catalyst by Thermal Decomposition of Alkoxides in Nonpolar Organic Solvents", *Shokubai*, **34**, 372 (1992).

Koryabkina, N. A., Ismagilov, Z. R., Shkrabina, R. A., Moroz, E. M. and Ushakov, V. A., "Influence of the Method of Alumina Modification on Formation of Low-temperature Solid Solutions in Magnesia-Alumina Systems", *Appl. Catal.*, **72**, 63 (1991).

Koryabkina, N. A., Litvak, G. S., Shkrabina, R. A. and Ismagilov, Z. R., "Investigation on Magnesia-Alumina System Using Thermogravimetric Methods", *Kinet. Catal.*, **34**, 354 (1993).

Koryabkina, N. A., Shkrabina, R. A. and Ismagilov, Z. R., "Stabilization of Alumina at High Temperature by Silica Modification", in Proc. of Conference on the Problem of Catalysts Deactivation, 13-18-June, Ufa, Russia, Part 1, 57 (1989).

Koryabkina, N. A., Shkrabina, R. A., Ushakov, V. A. and Ismagilov, Z. R., "Synthesis of a Mechanically Strong and Thermal Stable Alumina Support for Catalysts Used in Combustion Processes", *Cat. Today*, **29**, 427 (1996).

Koryabkina, N. A., Shkrabina, R. A., Ushakov, V. A., Lausberg, M. and Ismagilov, Z. R. "Influence of Lanthanum and Cerium on Structural-Mechanical Properties of Spherical Alumina", *Kinet. Catal.*, in press, 1997.

Koryabkina, N. A., Shkrabina, R. A., Ushakov, V. A., Moroz, E. M., Lausberg, M. and Ismagilov, Z. R., "Thermostable of

CeO_2-Al_2O_3 System", *Kinet. Catal.,* **37**, 124 (1996).

Kuklina, V. N., Pluasova, L. M., Kefeli, L. M. and Levitskii, E. A., "Influence of Thermal Treatment on Phase Transformation on Alumina", *Kinet. Catal.,* **12**, 963 (1971).

Lippens, B. C. and Steggerda, J. J., "Physical and Chemical Aspects of Adsorbents and Catalysts", Academic Press, New York, 1970.

Ovsyannikova, I. A., Goldenberg, G. I., Koryabkina, N. A., Shkrabina, R. A. and Ismagilov, Z. R., "Study of the Mechanical Properties of Spherical Alumina Using X-Ray Microprobes", *Appl. Catal.,* **55**, 75 (1989).

Shepeleva, M. N., Fenelonov, V. B., Shkrabina, R. A. and Moroz, E. M., "Influence of Hydroxide Aggregation on the Structural-Mechanical Properties of Alumina", *Kinet. Catal.,* **27**, 1202 (1986).

Shepeleva, M. N., Shkrabina, R. A., Okkel, L. G., Fenelonov, V. B. and Ismagilov, Z. R., "Formation of Texture Pseudoboehmite under the Liquid Mould Granulation of Spherical Supports for the Catalysts Used in CHG", *Kinet. Catal.,* **29**, 195 (1988).

Shepeleva, M. N., Shkrabina, R. A. and Ismagilov, Z. R., "Improvement of the Hydrocarbon-Ammonia Granulation Method for Production of Spherical Alumina with Variable Properties", *Technology Today,* **3**, 150 (1990).

Shepeleva, M. N., Shkrabina, R. A., Fenelonov, V. B. and Ismagilov, Z. R., "Production of Spherical Granules of Alumina with Controlled Porous Structure", *Appl. Catal,* **78**, 175 (1991).

Shepeleva, M. N., Shkrabina, R. A., Ismagilov, Z. R. and Fenelonov, V. B., "Preparation of Strong Alumina Supports for Fluidizied Bed Catalysts", in Proc. 5th Symp. Preparation of Catalysts, Pocelet, G., Jacobs, P. A. and Delmon Eds., Elsevier, Amsterdam, 583 (1991).

Shkrabina, R. A., Ismagilov, Z. R., Shepeleva, M. N., Lohokari S. R., Vaidya, M. C. and Sane, D. R., "Comparative Study of a Spherical Alumina Supports Prepared from ρ-Al_2O_3", in Recent Developments in Catalysis. Theory and Practice. Proc 10th Nat. Symp. on Catalysis, Madras, December 18-21(1990), New Delhi, Vistmanthan, B. and Pilai, C. N. Eds, Part 11, 30 (1990)

Shkrabina, R. A., Koryabkina, N. A., Ushakov, V. A., Moroz, E. M., Lausberg, M. and Ismagilov, Z. R., "Thermostable of La_2O_3-Al_2O_3 System", *Kinet. Catal.,* **37**, 116 (1996).

Shkrabina, R. A., Koryabkina, N. A., Ismagilov, Z. R., Ushakov, V. A., Tsykoza, L. T. and Arendarskii, D. A., "Thermal Stability of Alumina Modified with Silica and Lanthanum Simultaneously", in Proc. 7th Nordic Symp. and Catalysis, Book of Abstr., Turku, Finland, 2-4 June, 31 (1996).

Shubert, H., "Uber Grendsflachenvorgange in der Aglomerationsteehnik", *Chem. Ing. Techn.,* **47**, 86 (1975)

Trimm, D. I. and Stanislaus, A., "The Control of Pore Size in Alumina Catalyst: A Review", *Appl. Catal.,* **21**, 215 (1986).