

THE EFFECTS OF THE NATURE AND CONCENTRATIONS OF α - Al_2O_3 PRECURSORS ON SIMULTANEOUS SILICA-ALUMINA TRANSFORMATIONS

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Received 10. 2. 1994

The effect of heating on the phase transformations in binary mixtures of amorphous SiO_2 and different precursors of α - Al_2O_3 (gibbsite, boehmite and γ - Al_2O_3) at the temperature of 1000 °C was studied. The influence of alumina precursors on the phase transformations has been explained by their thermal history.

Key words: precursors of α - Al_2O_3 , Hedvall effect, topotactical effect, phase transformations, silica – alumina crystallization

INTRODUCTION

The inorganic materials, based on silica and alumina, are convenient and usual supports of heterogeneous catalysts and can determine their characteristics, phase transformations of supports, change their behaviour and can affect the catalyst performance differently. It is known that the phase transformations are determined by several factors, which are often in very complex mutual interactions, and because of that they can influence the phase compositions differently. So these transformations of silica and alumina supports can be facilitated by their interactions with other components of the catalyst and represent one of the significant factors of catalyst aging [1, 2, 3]. They can noticeably change the physical properties of the catalyst [4, 5, 6, 7], the state of the primary component [8, 9, 10, 11] or the way of the simultaneous transformations of the components of the catalyst [12, 13]. The mutual interactions of support components can also affect the phase composition significantly and therefore the behaviour of the supports. The investigations of mutual interactions and their influence on the phase compositions and the nature of interactions in the systems of silica and aluminas whose numerous modifications are stable at different temperature intervals, possessing different physico-chemical properties, have always been an existing problem not only in the field of catalysis, but in other fields of inorganic chemistry too. Consequently, this system has been undoubtedly mostly investigated.

In this work, one of the examples of these effects was studied in mixed silica – alumina supports with different α - Al_2O_3 precursors in a broad interval of concentrations. The stable α - Al_2O_3 form was used for the comparison with the given precursors. The nature and intensity of reciprocal influences of silica and alumina phases on phase compositions of silica-alumina supports were investigated after the prolonged thermal treatment in the air.

The results of these investigations elucidate the complex changes in this multi-component catalyst support, the role of the particular components, the conditions of different phase formations, the nature and intensity of components interactions in the system under the given conditions.

EXPERIMENTAL

Binary model systems studied in this work were composed of commercial amorphous SiO_2 (40 μm) and gibbsite, boehmite and γ - Al_2O_3 (63–71 μm) respectively. Gibbsite and boehmite were synthesized from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ using the known procedure [14]. γ - Al_2O_3 was prepared by thermal degradation of gibbsite in two steps for 2 hours at 180 °C in vacuum and for 4 hours at 450 °C in air, and the α - Al_2O_3 by thermal treatment of boehmite at 1115 °C, for 72 hours in air [15].

The mixtures containing 5–70 wt % of dry Al_2O_3 residues were prepared by mechanical mixing of powders. The pure components, as well as their mixtures, were heated for 24 hours at 1000 °C in air before further analyses.

Identification and semiquantitative analysis of crystalline phases was done by XRD, using Philips PW 1050 apparatus. The x-ray for semiquantitative analysis was performed with the same quantity of all samples and under the identical conditions and therefore, the surface areas of x-ray lines, which are proportional to the formed crystalline phases, were comparable [16]. These results are shown in the figure 1, as relative intensities in mm of α -cristobalite and α - Al_2O_3 x-ray lines $d = 0.404$ and $d = 0.2085$ nm respectively, calculated from their surface areas. In order to compare the degrees of silica and alumina crystallizations in the samples with different contents of the components, the relative intensities of XRD lines were calculated on the weight units of silica and

Table I

Crystalline modifications in alumina-silica mixtures after thermal treatment

G – gibbsite; B – boehmite; S – silica;
 α – α -Al₂O₃; γ – γ -Al₂O₃; θ – θ -Al₂O₃; c – α -cristobalite
 A – amorphous state, * – small quantity; + indition;

Sample	Weight % of dry Al ₂ O ₃ residue						
	0	5	10	20	50	70	100
G – S	A	A	A	θ	θ, α, c	θ, α, c	θ
B – S	A	A	$\theta, * \alpha, c$	θ, α, c	θ, α, c	θ, α, c	$\theta, * \alpha$
γ – S	A	θ	$\theta, * \alpha, c$	$\theta, * \alpha, c$	$\theta, + \alpha, + c$	θ	θ
α – S	A	α	α	α	α	α	α

alumina contents in the studied samples. The represented results do not show the absolute amounts, but they are convenient to follow the relative rates of the phase formations. SEM analyses of surface morphology were done by JEOL JSM-35. BET surface areas were determined by LTNA using Sorptometer 212D Perkin-Elmer-Shell.

RESULTS AND DISCUSSION

The results of x-ray analyses (Table I) show that under the applied experimental conditions crystallization of pure SiO₂ into α -cristobalite does not take place. On the other hand, in the binary systems the crystallization occurs, which suggests that the crystallization is facilitated in comparison to pure silica. Under the same conditions of the thermal treatment, the α -cristobalite formation is registered in the G-S, B-S and γ -S systems at the following concentration intervals: 50–70 wt % of gibbsite, 10–70 wt % of boehmite and 10–50 wt % γ -Al₂O₃. These results show that the transition of amorphous silica into α -cristobalite are influenced not only by temperature but by the other factors too. The comparison of relative rates of phase transitions of aluminas shows that α -cristobalite formation is connected with the transformation of different aluminas into α -Al₂O₃ (Table I). The phenomenon of higher reactivity of the solids during the phase transformations are well known as Hedvall effect [17], and this phenomenon can cause the accelerated crystallization of silica. But Hedvall effect cannot be the only cause of the accelerated crystallization of silica into α -cristobalite, because, if it had been in this case, the appearance of α -cristobalite would have taken place in the systems with 20 wt % of gibbsite and 5 and 70 wt % of γ -Al₂O₃ respectively.

Namely, the alumina transformations have been registered in these samples too up to θ form of Al₂O₃. It is very important to point out that the accelerated transformations of amorphous silica have been noticed only in those samples where the phase transformations of different aluminas gave the stable α -form (Table I). So the crystallization of amorphous silica takes place depending on the nature of aluminas, the concentrations of samples and only when α -Al₂O₃ is formed (Table I).

Parallel appearance of α -cristobalite and α -Al₂O₃ in silica – alumina mixtures, observed at various concentrations of α -Al₂O₃ precursors, can provide the role of topotactical effect in these interactions, based on similarity in crystal lattices [18, 19]. In topotactical reactions the structure of each product is determined by the structure of another product or by the participant in the system, formed in situ during the chemical reactions or physico-chemical transformations, when the two-dimensional similarity of their crystal surfaces exists. In this case of α -cristobalite and α -alumina the two-dimensional similarity is present between the 0.497 × 0.497 nm (ASTM-11-695) and 0.491 × 0.491 nm (ASTM-10-173) respectively, and the topotactical effect enables and favours the crystallization of amorphous silica into α -cristobalite.

In the model system, with α -Al₂O₃ as the initial component, the crystallization of SiO₂ has not been detected. This indicates the different behaviour of α -Al₂O₃ as the initial component in relation to the formed one in the simultaneous phase transformations. This confirms the importance of the phase transformations because the prerequisite of the observed topotaxy is the activation of phases during the transition, known as the Hedvall effect.

The alumina phase transformations show the reciprocal influence of SiO_2 too (Table I). Under the given experimental conditions the formation of $\alpha\text{-Al}_2\text{O}_3$ from pure gibbsite and boehmite does not occur or occurs slightly, whereas in the presence of silica its occurrence is apparent. The rate of its formation grows in line with the increase of gibbsite or boehmite concentrations, (Figure 1), i.e. the line diagrams present the XRD results of semiquantitative analyses.

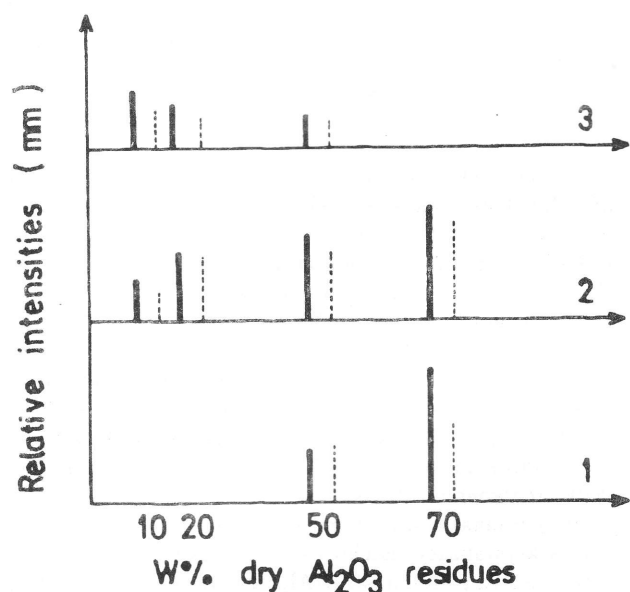


Fig. 1. Relative intensities of characteristic α -cristobalite (full line) and $\alpha\text{-Al}_2\text{O}_3$ (dash line) X-ray lines after thermal treatment of mixture: gibbsite- SiO_2 (1); boehmite- SiO_2 (2); $\gamma\text{-Al}_2\text{O}_3$ - SiO_2 (3).

The noticeable increase of the amount of $\alpha\text{-Al}_2\text{O}_3$ has been detected at the same intervals of gibbsite and boehmite concentrations which are characterized by the increased crystallization of SiO_2 into α -cristobalite, 50–70 wt % and 10–70 wt % respectively. The crystallization of $\gamma\text{-Al}_2\text{O}_3$ into $\alpha\text{-Al}_2\text{O}_3$, which under the given experimental conditions does not occur in pure state, proceeds faster in the presence of silica. However, its rate declines with the growth of the concentration of $\gamma\text{-Al}_2\text{O}_3$ (Figure 1, Table I). Figure 1 shows that the rate of the crystallization of amorphous silica in binary systems takes place with different intensity and also depends both on the nature and the concentrations of present alumina phases. The following order of the facilitating effect on the silica crystallization for the examined $\alpha\text{-Al}_2\text{O}_3$ precursors has been established in the applied concentration range of precursors: boehmite > gibbsite > $\gamma\text{-Al}_2\text{O}_3$ > $\alpha\text{-Al}_2\text{O}_3$ (Fig. 1). The specific effect of precursor concentrations has been observed. In the mixtures of gibbsite or boehmite with SiO_2 the rates

of silica crystallization have increased with the increase of gibbsite or boehmite concentrations. This is especially visible at the intervals of 50–70 wt % of gibbsite and 10–70 wt % of boehmite (Fig. 1). In the case of $\gamma\text{-Al}_2\text{O}_3$ the trend is opposite, so that in the sample with 70 wt % of $\gamma\text{-Al}_2\text{O}_3$ the presence of α -cristobalite has not been detected after thermal treatment.

Table II

Surface area, m^2/g after thermal treatment

G – gibbsite; B – boehmite; γ – $\gamma\text{-Al}_2\text{O}_3$; S – silica;

Sample	Weight % of dry Al_2O_3 residue				
	5	10	20	50	70
G – S	3.80	12.50	28.50	75.02	90.57
B – S	20.85	20.50	19.20	50.25	75.45
γ – S	3.20	16.20	19.57	20.50	20.45
α – S	1.50	3.20	4.60	7.20	12.80

The influence of the concentrations is similar in the samples with gibbsite and boehmite, but different in the samples with $\gamma\text{-Al}_2\text{O}_3$. This can be explained by LTNA and SEM data. In the mixtures with higher gibbsite and boehmite concentrations an evolution of pore structure results in noticeable increase of BET surface during the thermal treatment (Table II, Fig. 2). This contributes to the better contact between silica and alumina phases and facilitates their interaction. At higher concentrations of $\gamma\text{-Al}_2\text{O}_3$ the interaction with silica is inhibited by unsuitable texture formed during the thermal treatment. The closed compact structure of the sample with 70 wt % $\gamma\text{-Al}_2\text{O}_3$ (Fig. 2) and significantly lower surface area (Table 2) indicate insufficient contacts between silica and alumina phases and explain the absence of both α -cristobalite and $\alpha\text{-Al}_2\text{O}_3$ in the samples.

CONCLUSION

Topotactical effect which governs phase transformations of silica and alumina in their mixtures submitted to high temperatures is strictly conditioned by the activation of phases during the transition of themselves (the Hedvall effect). An additional prerequisite of the observed interactions provides a good contact between silica and alumina phases. This explains the influence of the nature and concentration of alumina precursors by determining textural changes they control the contacts between phases.

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Submitted in English by the authors

VLIV DRUHU A KONCENTRACÍ PREKURZORŮ
 α -Al₂O₃ NA SOUČASNÉ PŘEMĚNY OXIDŮ
 KŘEMIČITÉHO A HLINITÉHO

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V práci byl sledován vliv fázové interakce na fázové přeměny binárních směsí SiO₂ s 5–70 hmot.% gibbsitu, boehmitu, γ -Al₂O₃ a α -Al₂O₃. Tyto anorganické látky se běžně používají jako nosiče heterogenních katalyzátorů. Jejich fázové přeměny mohou výrazně změnit fyzikální vlastnosti příslušného katalyzátoru [4, 5, 6] a stav primární složky, a mohou být proto příčinou stárnutí katalyzátoru [1, 2, 3]. Identifikace a semikvantitativní analýzy byly prováděny pomocí rentgenové difrakční analýzy, morfologie povrchu byla hodnocena řádkovací elektronovou mikroskopií a specifický povrch metodou BET. Výsledky rentgenové difrakční analýzy ukazují, že krystalizace SiO₂ v binárních systémech probíhá snadněji ve srovnání s krystalizací čistého oxidu křemičitého, a dochází k ní pouze za přítomnosti α -Al₂O₃ (tab. I). Rychlost této krystalizace závisí na morfologii a koncentraci oxidu hlinitého. Bylo stanoveno pořadí vlivu prekurzoru na krystalizaci oxidu hlinitého. Bylo stanoveno následující pořadí vlivu prekurzoru na krystalizaci oxidu křemičitého: boehmit > gibbsit > γ -Al₂O₃ > α -Al₂O₃. Ve směsích gibbsitu nebo boehmitu s oxidem křemičitým se rychlost krystalizace oxidu křemičitého zvyšuje s koncentrací oxidu hlinitého. V případě γ -Al₂O₃ je tato závislost opačná (obr. 1). Přítomnost oxidu křemičitého rovněž stimuluje fázové přeměny oxidu hlinitého (tab. I). U směsí α -cristobalitu s různými podíly α -Al₂O₃ se projevuje topotaktický efekt prekurzorů. Nepřítomnost α -cristobalitu ve vzorcích připravených s α -Al₂O₃ potvrzuje význam Hedvallova efektu. Zpomalování krystalizace SiO₂ při větších koncentracích γ -Al₂O₃ lze vysvětlit nedostatečným kontaktem mezi oxidem křemičitým a γ -Al₂O₃, způsobeným nevhodnou texturou vytvořenou během tepelného zpracování (obr. 2, tab. II), a tím také inhibicí vzniku α -Al₂O₃.

Obr. 1. Relativní intenzity charakteristických difrakčních linií α -cristobalitu (plné) a α -Al₂O₃ (přerušované) po tepelném zpracování směsí: gibbsit-SiO₂ (1), boehmit-SiO₂ (2), γ -Al₂O₃-SiO₂ (3).

Obr. 2. Elektronové mikrofotografie vzorků hlinitokřemičitanů s obsahem 70 hmot.% Al₂O₃.

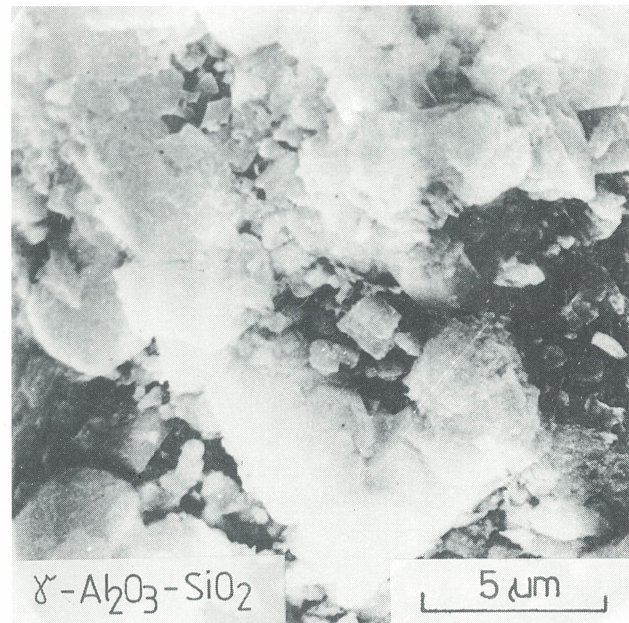
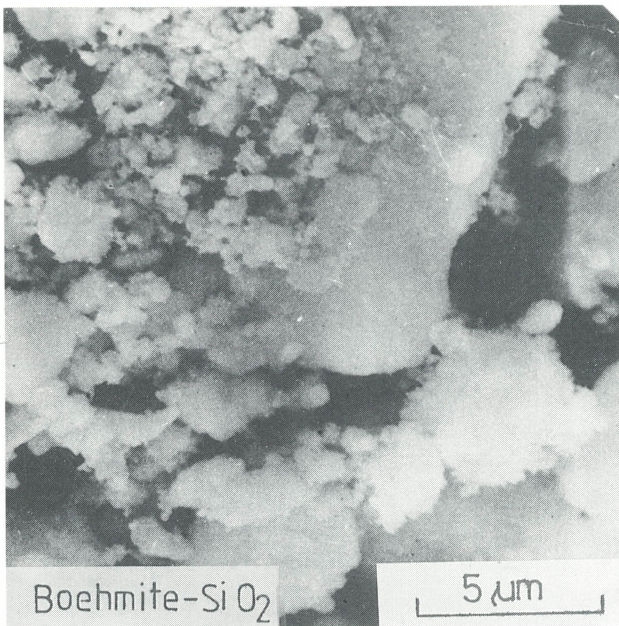
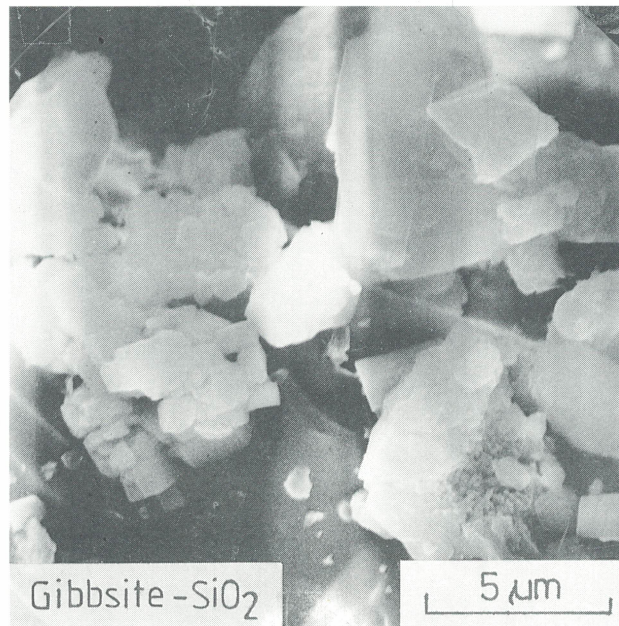


Fig. 2. SEM pictures of alumina-silica samples with 70 wt% of dry Al₂O₃ residue.