JOURNAL OF MATERIALS SCIENCE 26 (1991) 6479–6486

Application of lanthanum to pseudo-boehmite and γ-Al_2O_3

I. I. M. TIJBURG*, J. W. GEUS
Department of Inorganic Chemistry, University of Utrecht, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

H. W. ZANDBERGEN
Laboratory of Metallurgy, Delft University of Technology, Rotterdamseweg 137, 2626 AL Delft, The Netherlands

Elements such as lanthanum, zirconium, thorium and cerium are known to raise the thermostability of γ-Al_2O_3. Among these elements lanthanum is the most effective. Three procedures have been used to apply lanthanum homogeneously to the surface of pseudo-boehmite and γ-Al_2O_3, namely, incipient wetness impregnation, deposition–precipitation from a homogeneous solution, and specific adsorption of a La(EDTA)-complex. The latter procedure results in supports covered homogeneously with lanthanum. The minimum amount of lanthanum required to render the catalyst supports thermostable, depends on the procedure to apply the lanthanum. The specific adsorption procedure offers the possibility to obtain thermostable supports with loadings as low as 0.5 wt % La.

High-resolution electron microscopy was used to assess the mechanism of the stabilization by application of foreign metal ions in amounts less than a monolayer. It appeared that addition of foreign metal ions brings about crystallization of the amorphous surface layer of γ-Al_2O_3.

1. Introduction

Many catalytic processes require catalysts based on supports which combine a high surface area with a high stability at elevated temperatures, even in the presence of water vapour. Additionally, the internal surface of the support must be easily accessible for reactants and products, which implies that pores must not be too narrow. Examples of processes in which thermostable catalysts must be used are steam-reforming and combustion of natural gas. The support that best meets with these demands is γ-Al_2O_3 of acicular elementary particles. Already at temperatures above 600 °C sintering of γ-Al_2O_3 is a severe problem. At temperatures above 1000 °C formation of α-Al_2O_3, the thermodynamically most stable form, results in a dramatic drop in surface area.

Elements such as lanthanum, zirconium, thorium, and cerium are known to raise the thermostability of γ-Al_2O_3. Among these elements lanthanum is the most effective. Schaper [1] extensively investigated the sintering of γ-Al_2O_3 either or not stabilized by addition of lanthanum. Addition of 3 to 15 wt % La resulted in a remarkable increase in thermostability. Schaper attributes the raised thermostability to formation of a surface layer of $LaAlO_3$, in which the mobility of mainly surface-oxygen ions is lower. Vereshchagin *et al.* [2], however, performed the same experiments and concluded that addition of lanthanum accelerated transformation of γ-Al_2O_3 to α-Al_2O_3. Matsuda *et al.* [3] studied coprecipitation of aluminium nitrate and lanthanum nitrate. They describe the higher thermostability to formation of lanthanum β-aluminate ($La_2O_3 \cdot 11\ Al_2O_3$) at low, and to $LaAlO_3$ at higher loadings of lanthanum.

Burtin *et al.* [4] impregnated γ-Al_2O_3 with salts of various elements. These authors measured the thermostability by assessing the amount of α-Al_2O_3 formed during heat treatment. Lanthanum and thorium appeared to have the greatest retarding effect on the transformation to α-Al_2O_3. Using either the incipient wetness impregnation or coprecipitation technique to apply the stabilizing agent, rather high loadings are required to obtain supports of a sufficiently high thermostability, due to the inhomogeneous distribution of lanthanum over the surface of the support.

This paper deals with the effect of the distribution of lanthanum ions over the surface of γ-Al_2O_3 on the thermal stability. To be able to establish a homogeneous distribution over the alumina surface, the alumina must have an internal surface area situated at wide pores, which can be easily covered. We, therefore, studied pseudo-boehmite and γ-Al_2O_3 produced from pseudo-boehmite; both supports contain essentially non-porous acicular elementary particles. The surface of the acicular particles can be covered relatively easily.

Three different procedures were used to homogeneously apply lanthanum ions, namely, incipient

---

*Present address: AKZO Chemicals B.V., Research Centre Amsterdam-Noord, PO Box 26223, 1002 GE Amsterdam, The Netherlands.

wetness impregnation, deposition–precipitation from a homogeneous solution, and specific adsorption of the [La(EDTA)]$^-$ complex. The distribution of lanthanum on a rough scale was assessed by scanning electron microscopy combined with element detection. On a smaller scale, distribution of lanthanum was obtained from transmission electron micrographs of thermally treated samples. Where locally lanthanum was absent, reaction of α-Al_2O_3, which can be easily distinguished in the microscope, proceeds.

2. Experimental procedure

2.1. Materials

Preparation of the thermostable supports was carried out with pseudo-boehmite (Al 4170, Engelhard De Meern B.V., The Netherlands) and γ-Al_2O_3 (Al 4172), produced by dehydration of pseudo-boehmite at 600 °C. Purity and texture of these supports have been described in detail elsewhere [5]. All other chemicals were obtained from Merck and were of p.a. quality.

2.2. Procedures

Application of lanthanum to AlOOH and γ-Al_2O_3 was performed by the following procedures:

(a) incipient wetness impregnation;

(b) deposition–precipitation from a homogeneous solution;

(c) specific adsorption of a lanthanum complex.

2.2.1. Incipient wetness impregnation

10 g of powdered support material were kept in rough vacuum (2×10^3 Pa) for at least 3 h in order to remove air from the pores. The alumina powder thus evacuated was impregnated to incipient wetness with an aqueous solution of $La(NO_3)_3 \cdot 6\,H_2O$. The amount of $La(NO_3)_3 \cdot 6\,H_2O$ corresponded with loadings of 1 to 8.5 wt% La, calculated as

$$\frac{\text{wt La}}{\text{wt La} + \text{wt } Al_2O_3} \times 100\%$$

Incipient wetness impregnation experiments were also performed using a solution of the complex formed by La^{3+} and EDTA (ethylene diamine tetra-acetic acid). The [La(EDTA)]$^-$ complex was prepared using the following procedure. 1.95 g EDTA was dissolved in 50 ml of demineralized water by raising the pH from 3 to 5 by addition of concentrated ammonia. An equimolar amount of $La(NO_3)_3 \cdot 6\,H_2O$ was dissolved into 10 ml of demineralized water and slowly added to the EDTA solution. To prevent precipitation of EDTA, the pH was kept at a value greater than 4 by addition of diluted ammonia. Finally, the volume of the solution was raised to that required for pore volume impregnation. The volume required was established by measuring the take-up of liquid water by the sample.

Subsequently, the [La(EDTA)]$^-$ solution was added to the alumina powder previously evacuated. The impregnated sample was allowed to dry under vacuum at room temperature for 20 h.

2.2.2. Deposition–precipitation from a homogeneous solution

Geus has described deposition–precipitation from a homogeneous solution in detail [6]. Precipitation experiments of lanthanum onto pseudo-boehmite and γ-Al_2O_3 were carried out in a standard precipitation set-up shown in Fig. 1. The vessel was equipped with a powerful stirring motor and baffles to ensure homogeneity of the contents.

Titration experiments can provide important information about the interaction between a support material and a catalytically active compound. Titration curves in which the pH is plotted as a function of the amount of alkali added, were recorded for water, a lanthanum nitrate solution, a suspension of pseudo-boehmite or γ-Al_2O_3 in water and in a lanthanum nitrate solution. The chemicals were suspended in 700 ml of demineralized water at a temperature of 30 °C. Lanthanum nitrate was added in an amount corresponding with the desired loading. The initial pH was set at 4.0 by addition of nitric acid. The pH of the solution or suspension was raised homogeneously by injection of a 1 M NaOH solution through a capillary tube under the level of the vigorously agitated suspension. The rate of injection was 0.28 mmol OH^- min^{-1}. After 20 h the suspension was filtered, washed with demineralized water, and dried overnight at 60 °C. The lanthanum concentration in the filtrate was measured with atomic absorption spectrometry (AAS).

2.2.3. Specific adsorption

Adsorption of metal ions and organometallic complexes onto the surface of solids depends, among other

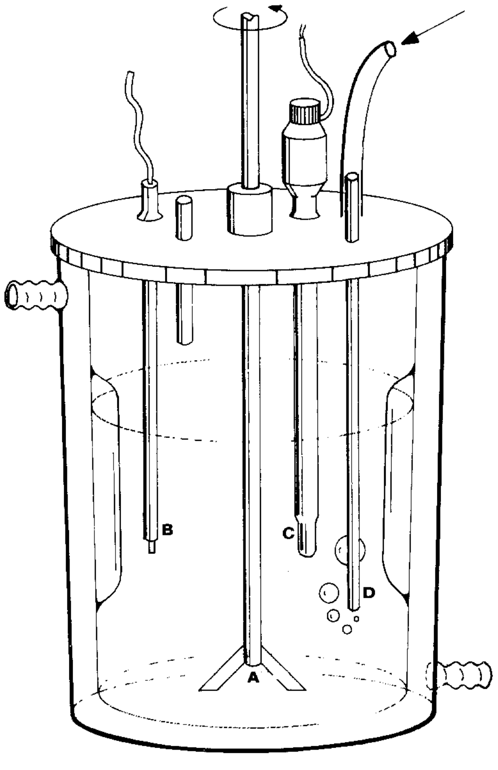

Figure 1 Schematic representation of the standard precipitation set-up A: stirrer; B: injection tube: C: pH-electrode; D: nitrogen injection tube.

things, on the electrical charge of the surface. The pH at which the surface of a solid placed in an electrolyte is electrically neutral is called the isoelectric point (IEP). At pH values lower than the IEP, the surface is charged positively due to formation of OH_2^+ groups and adsorption of negatively charged ions and complexes takes place. At pH values higher than the IEP, the opposite process proceeds due to the presence of O^- groups at the surface [7]. The IEP of pseudo-boehmite and γ-Al_2O_3 was determined using the procedure described by Jiratova [7]. As the IEP depends on the temperature of the suspension [8], an adsorption experiment was also performed at 70 °C.

Adsorption of metal ions and organometallic complexes onto the surface of oxidic supports thus strongly depends on the pH of the suspension. The following experiments were performed to investigate the dependence of the adsorption of the $[La(EDTA)]^-$ complex on the pH. In addition to pseudo-boehmite and γ-Al_2O_3 (Al 4172), also γ-Al_2O_3 calcined for 2 h at 800 °C (Al 4173) was used.

20 g of support material were suspended in 750 ml of demineralized water in the thermostatted vessel described above. The pH of the suspension was set at the desired value by addition of concentrated nitric acid or ammonia. The pH levels at which the adsorption of $[La(EDTA)]^-$ was studied, ranged from 4 to 9. A solution containing 0.06 mole l^{-1} $[La(EDTA)]^-$ was prepared as described above. The pH of this solution was set at the same value as that of the suspension. The $[La(EDTA)]^-$ solution was added to the vigorously stirred suspension, and the pH was kept constant at an adjusted value between 4 and 9 by automatic injection of dilute nitric acid or a dilute NaOH solution, depending on the pH at which adsorption took place. Temperature of the suspension was 25 °C. After 1 h the suspension was filtered, and washed with demineralized water. The lanthanum concentration in the filtrate was determined by AAS. The loaded support was dried at 60 °C overnight.

2.2.4. Sinter experiments

After drying, loaded samples of 2 g were placed into an electric furnace and calcined at 550 °C for 5 h in order to decompose the lanthanum complex. After cooling down to room temperature the temperature was raised at 15 °C min^{-1} to 1050 °C and samples remained at this temperature for up to 145 h. For comparison, non-stabilized alumina supports were treated in the same way.

2.2.5. Characterization

BET surface area measurements were performed after outgassing the samples in vacuum at 200 °C overnight. The specific surface area was calculated from the extent of nitrogen sorption at -195 °C at relative pressures from 0.05 to 0.35. For the surface area per nitrogen molecule a value of 0.162 nm^2 was assumed. Measurements were performed with a Carlo Erba Sorptomatic type 1800.

Transmission electron microscopy (TEM) was performed within a Philips EM 420 electron microscope operated at 100 kV. TEM samples were ground in an agate mortar, suspended in ethanol and submerged in an ultrasonic bath for 1 min to ensure homogeneity of the suspension. Drops of this suspension were applied to a holey carbon film supported by a copper grid. Selected area electron diffraction (SAED) patterns were taken at the same accelerating voltage. Calibration was performed with evaporated gold films. High-resolution transmission microscopy (HREM) was carried out within a JEOL microscope of the University of Antwerp, Belgium (RUCA).

The lanthanum distribution over the supports was studied with scanning electron microscopy (SEM) using a Cambridge S 150 electron microscope. For elemental analysis (EDX, Energy Dispersive analysis of X-rays) a LINK system was attached to the scanning electron microscope. SEM samples were mounted on aluminium tables with carbon glue, and covered with a thin film of carbon in an Edwards vacuum evaporator.

Powder X-Ray diffraction (XRD) was performed with a Guinier camera equipped with a Johansson monochromator (CuK_{α_1} radiation) in combination with a microdensitometer (Jenoptik MD 100), and a Philips diffractometer PW 1050 ($CuK_{\alpha_{1,2}}$ radiation).

3. Results and discussion

3.1. Incipient wetness impregnation

With almost all metals, EDTA virtually instantaneously forms water-soluble complexes. The pK of the complex formed by lanthanum and EDTA is 14.7. According to Perrin [9], the concentration of a complex between lanthanum and EDTA displays a maximum at pH 10.1.

UV-spectrometry of an aqueous solution of $[La(EDTA)]^-$ (0.06 mole l^{-1}) showed a strong absorption band at 290 nm. In this range of wavelengths an aqueous solution of EDTA alone showed no absorption at all. The band at 290 nm was situated at the same position as the band in the UV-spectrum of an aqueous lanthanum nitrate solution of 0.06 mole l^{-1}. Due to the resemblance of the spectra of $[La(EDTA)]^-$ and lanthanum nitrate, it is difficult to provide evidence for the formation of the $[La(EDTA)]^-$ complex in a solution containing nitrate. The sharp decrease in absorption at 260 nm in the spectrum of an aqueous EDTA solution, which was absent in the spectrum of a lanthanum nitrate solution, was, however, an indication for the formation of the $[La(EDTA)]^-$ complex.

Impregnation of pseudo-boehmite and γ-Al_2O_3 with a lanthanum nitrate solution resulted in a higher thermostability. Loadings higher than 3.5 wt % did not further improve the thermostability. The surface area of samples containing 3.5 to 8.5 wt % La was about 80 $m^2 g^{-1}$ after 145 h sintering at 1050 °C in stagnant air. The surface area of an untreated sample (γ-Al_2O_3 Al 4172) was 45 $m^2 g^{-1}$ after the same heat treatment. SEM investigations showed the lanthanum distribution to be very inhomogeneous. Fig. 2 shows a SEM micrograph of a sample containing 4.3 wt % of

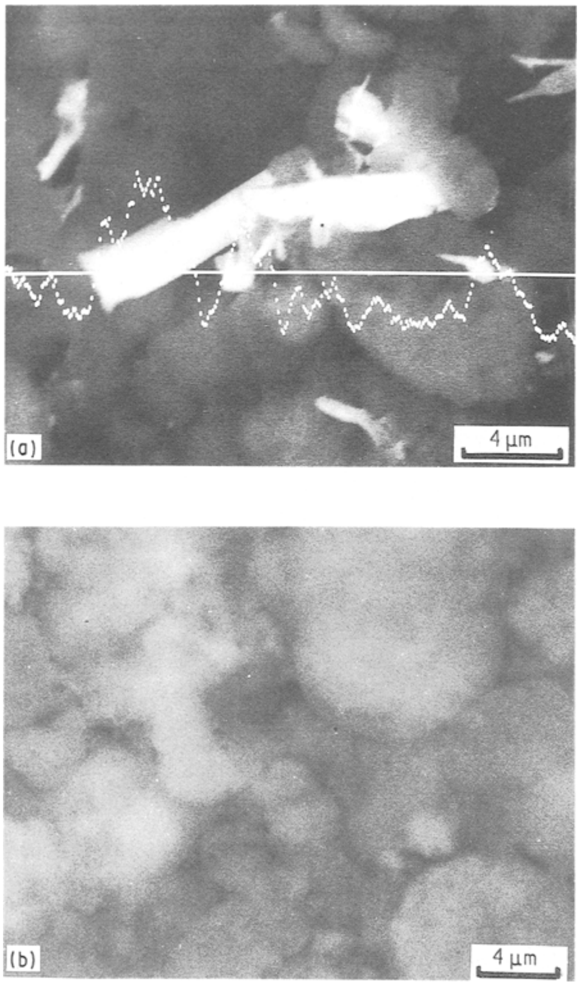

Figure 2 SEM micrograph of a sample impregnated with a lanthanum nitrate (top) and with a $[La(EDTA)]^-$ solution (bottom) after calcination at 550 °C for 5 h. Both samples contain 4.3 wt % La on γ-alumina.

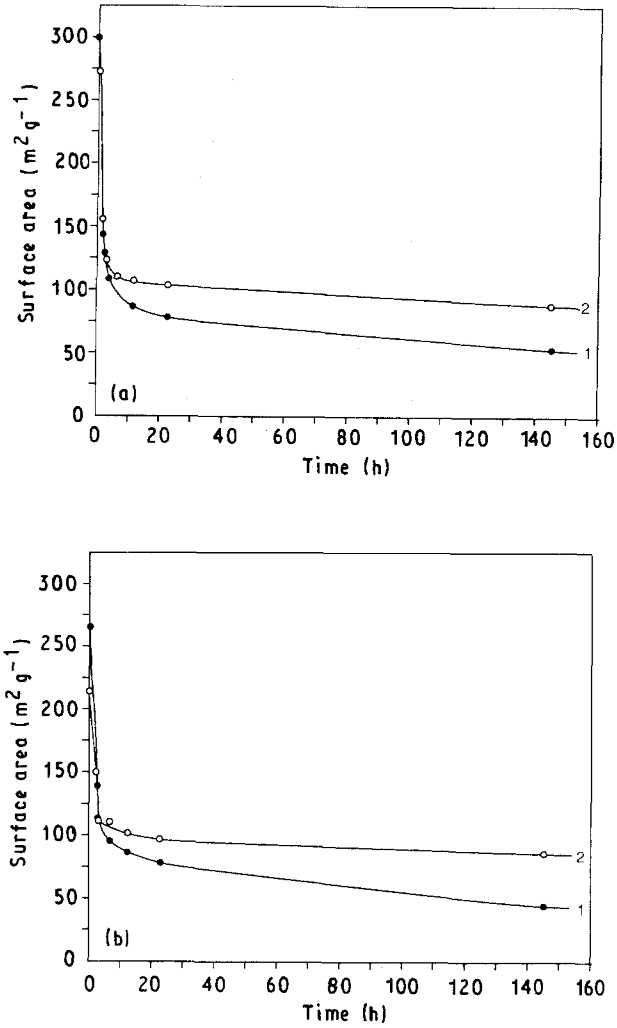

Figure 3 Surface area-versus-time plots obtained at 1050 °C in air (a) for pseudo-boehimite (Al 4170) and (b) γ-alumina Al 4172. ● before impregnation, ○ after impregnation with $[La(EDTA)]^-$ solution.

lanthanum after calcination at 550 °C for 5 h. The micrograph was taken from the back-scattered electrons providing element contrast. White areas show the presence of La_2O_3. The lanthanum EDX signal was recorded along the horizontal line.

When pseudo-boehmite (Al4170) and γ-Al_2O_3 (Al4172) were impregnated with an aqueous solution of $[La(EDTA)]^-$, and dried by the appropriate heating cycle, the thermostability of these support materials increased remarkably. In Fig. 2b a SEM micrograph (back-scattered electrons) is presented of γ-Al_2O_3 (Al4172) impregnated with a $[La(EDTA)]^-$ solution. The loading of the sample was 4.3 wt % of lanthanum after calcination of 550 °C for 5 h. The absence of white spots in the micrograph of the sample impregnated with a $[La(EDTA)]^-$ solution indicates a homogeneous distribution of lanthanum.

In Fig. 3 resulting surface areas are plotted as a function of heating time for pseudo-boehmite and γ-Al_2O_3 (Al4172). Sinter experiments were performed at 1050 °C in air.

The rapid initial decrease in surface area is similar for all samples. The surface area against time curves of the impregnated samples show a steep drop in the rate of decrease in surface area after about 6 h. The surface area against time curves for pure pseudo-boehmite and γ-Al_2O_3 exhibit a more gradual decrease in surface area after a strong initial decrease. The initial decrease can be attributed to sintering of large fibrils of pseudo-boehmite and γ-Al_2O_3 (length 70 to 80 nm and width 5 to 6 nm) to rods with a length of 50 to 60 nm and a width of 7 to 8 nm [5]. This change in morphology is accompanied by a transformation of γ-Al_2O_3 to θ-Al_2O_3. The gradual decrease in surface area after 6 h for the pseudo-boehmite and γ-Al_2O_3 samples can be attributed to the formation and growth of nuclei of α-Al_2O_3 in a transition alumina matrix [4]. No differences between the pseudo-boehmite and γ-Al_2O_3 samples were observed. This is due to the fact that already during heat treatment at 550 °C, transformation of pseudo-boehmite to γ-Al_2O_3 takes place.

XRD and SAED showed that addition of lanthanum resulted in stabilization of θ-Al_2O_3. Transformation of θ-Al_2O_3 to α-Al_2O_3 is retarded. These results agree very well with those of Schaper [1]. He tested the thermostability of γ-Al_2O_3 samples impregnated with an aqueous solution of lanthanum nitrate. Raising the loading to 15 wt % La resulted in an increase in thermostability, while still higher loadings resulted in a decrease in surface area after sintering, due to blocking of small pores. Schaper suggests that a certain amount of sintering of the θ-Al_2O_3 matrix is required before phase transformation to α-Al_2O_3 can take place. The temperature at which the transformation to α-Al_2O_3 proceeds is raised by 100 °C by addition of 3.5 wt % La.

XRD patterns of samples impregnated with a lanthanum nitrate solution (3.5 wt % La) showed the presence of La_2O_3 as well as $LaAlO_3$ after sintering at 1050 °C in stagnant air. Samples impregnated with a $[La(EDTA)^-$ solution showed neither $LaAlO_3$ nor La_2O_3 after the sinter experiments.

In our opinion the inhomogeneous distribution of lanthanum caused by impregnation with lanthanum nitrate leads to local formation of lanthanum oxide after drying and calcination. After prolonged heating at temperatures higher than 800 °C, $LaAlO_3$ is formed. Isothermic experiments during 24 h were performed by Ropp and Carrol [10] in order to study the reaction between alumina and lanthanum oxide. They found that formation of $LaAlO_3$ starts at 400 °C and is completed at 800 °C. When alumina is impregnated with a solution of $[La(EDTA)]^-$, transport and crystallization during drying is prevented due to a large interaction between the lanthanum complex and the alumina surface. The lanthanum complex is a badly crystallizing compound. Meima [11] succeeded in applying thin films of tin(IV) oxide to α-Al_2O_3 by impregnating the support with organometallic tin complexes, like tin(II)EDTA, tin(II)citrate and tin(II)formate.

SEM micrographs made by detection of backscattered electrons showed the presence of white spots on a grey background for samples impregnated with lanthanum nitrate. With EDX these spots could be identified as a lanthanum containing compound. The absence of white spots in the micrograph of the sample impregnated with a $[La(EDTA)]^-$ solution indicated that these samples were loaded much more homogeneously with lanthanum. Since the resolution limit of the scanning electron microscope is about 100 nm, lanthanum compounds with smaller particle sizes could not be detected. Neither with TEM nor with high resolution TEM was evidence found for the presence of inhomogeneously distributed lanthanum.

3.2. Deposition-precipitation from a homogeneous solution

Titration curves of demineralized water, a solution of $La(NO_3)_3 \cdot 6\,H_2O$, a suspension of γ-Al_2O_3 in water and in a lanthanum nitrate solution are plotted in Fig. 4.

The curve of γ-Al_2O_3 in a lanthanum nitrate solution is situated below the theoretical sum curve, which implies that the consumption of hydroxyl ions exceeds the theoretically calculated value over a large pH range. The difference between the experimental and theoretically calculated curve points to a large interaction between lanthanum species and γ-Al_2O_3. The same results were obtained for a system in which pseudo-boehmite was used instead of γ-Al_2O_3.

Samples prepared by homogeneous deposition–precipitation of lanthanum on pseudo-boehmite and γ-Al_2O_3 were sintered at 1050 °C in the standard sinter experiments described above. After 145 h at 1050 °C, surface areas were 80 $m^2\,g^{-1}$ for samples loaded with 3.5 wt % La and 90 $m^2\,g^{-1}$ samples loaded with 8.5 wt % La.

The surface area against time plots are similar to those recorded for samples prepared by incipient wetness impregnation with either a lanthanum nitrate or a $[La(EDTA)]^-$ solution. XRD patterns could not provide evidence for the presence of lanthanum compounds. A possible explanation is the particle size of the lanthanum compound deposited on the surface being too small. Another explanation is the formation of a thin lanthanum containing surface layer that cannot be detected by XRD, because it is amorphous or too thin. SAED revealed no information about the presence of La_2O_3 particles, because the alumina support itself is polycrystalline and displays a strong electron diffraction pattern with d spacings close to those of La_2O_3. SEM micrographs showed a homogeneous distribution of lanthanum. Samples were also studied with TEM after the sinter experiments. The number of α-Al_2O_3 nuclei formed during heat treatment seemed to be higher if compared with samples made by incipient wetness impregnation. This is confirmed by BET surface area measurements as the α-form has a very low surface area in comparisoon with γ-Al_2O_3 and transition aluminas. Shape and

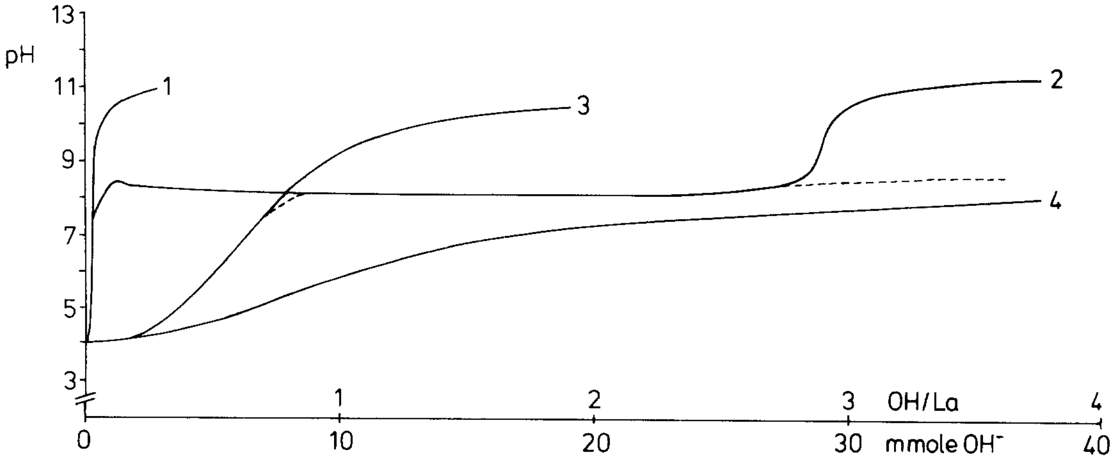

Figure 4 Titration curves of water (1), lanthanum nitrate (2), γ-alumina (Al 4172) (3) and γ-alumina in a solution of lanthanum nitrate (4). The dashed line is the sum curve of 1, 2 and 3.

average size of the transition alumina rods after the sinter experiments are equal to those formed in sinter tests of samples prepared by incipient wetness impregnation.

It can be concluded that deposition–precipitation of lanthanum onto alumina results in a homogeneous distribution of lanthanum over the support. As the elementary alumina particles are present in clusters, however, transport of hydroxyl ions and lanthanum ions therein, is rather difficult. As a result, a small part of the support is not loaded with lanthanum and nucleation of α-Al_2O_3 is very likely to take place there.

3.3. Specific adsorption experiments

Results of measurements of the IEP for different supports are presented in Table I.

Specific adsorption of $[La(EDTA)]^-$ was carried out with samples of pseudo-boehmite (Al 4170), γ-Al_2O_3 (Al 4172) and γ-Al_2O_3 (Al 4173). Results of these experiments are plotted in Fig. 5.

As can be seen in Fig. 5, adsorption of $[La(EDTA)]^-$ is a function of the pH of the suspension and of the support. As the three support materials have different surface areas, the adsorbed amount of lanthanum was calculated per square metre.

Huang and Lin [12] studied adsorption of $[Co(\text{III})EDTA]^-$ at the surface of γ-Al_2O_3. They propose a model in which $[Co(\text{III})EDTA]^-$ is adsorbed below the IEP at the surface of Al_2O_3 by hydrogen-bridge formation between surface OH_2^+ groups and carboxyl groups of EDTA. Between pH 5 and 7 formation of these surface complexes is suppressed because the density of OH_2^+ groups on the surface has decreased. Theoretically, two other surface complexes can be formed at higher pH levels, where the surface of γ-Al_2O_3 contains a considerable number of OH and O^- groups. Surface complexes formed by interaction between [Co(III)EDTA] and surface OH groups or surface O^- groups are not, however, stable. Other Co(III)EDTA complexes are responsible for adsorption at higher pH levels.

Our results for the adsorption of $[La(EDTA)]^-$ agree very well with those found by Huang and Lin for $[Co(\text{III})EDTA]^-$. Due to the fact that La^{3+} just as Co^{3+} is octahedrally surrounded by EDTA the structure of $[La(EDTA)]^-$ can be compared with that of $[Co(\text{III})EDTA]^-$. Additional evidence for this mechanism is found from the fact that the surface hydroxyl-group density of γ-Al_2O_3 (Al4172 and Al4173) at 30 °C, as determined in the IEP experiments, is 2.2×10^{-6} mole OH m^{-2}. The maximum amount of $[La(EDTA)]^-$ that can be adsorbed at the alumina surface (at pH 5) is 0.7×10^{-6} mole La m^{-2}. Hence, three surface hydroxyl groups are required for the adsorption of one $[La(EDTA)]^-$ ion. This is in agreement with the proposed adsorption mechanism. Because of the low stability of metal–EDTA complexes having one or more water molecules or hydroxyl groups as ligands, these have not been taken into account in the mechanism, but it is likely that at higher pH values a significant contribution of these species is present. In order to get a complete understanding of the adsorption mechanism, a more elaborate study, involving spectroscopic techniques and NMR, will be required.

TABLE I IEP of pseudo-boehmite (Al 4170), γ-Al_2O_3 (Al 4172) and γ-Al_2O_3 (Al 4173)

Support	IEP
AlOOH (Al 4170)	7.5
γ-Al_2O_3 (Al 4172)	7.6
γ-Al_2O_3 (Al 4173)	8.1

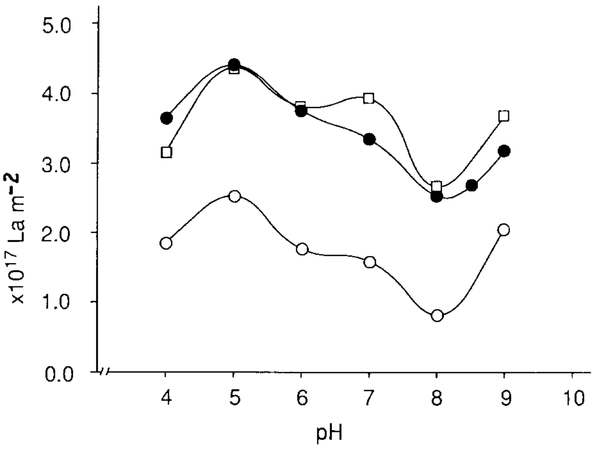

Figure 5 Adsorption against pH curves for pseudo-boehmite (Al 4170) (○), γ-alumina (Al 4172) (●) and γ-alumina (Al 4173) (□).

Adsorption of non-complexed lanthanum was negligible at pH 6 or lower. At higher pH levels the adsorption increased, but this was probably due to precipitation onto the support as $La(OH)_3$ or a related species, rather than real adsorption.

Raising the temperature of the suspension from 30 to 70 °C resulted in an increase in adsorption of 40% for pseudo-boehmite at pH 6. This can be explained with the results obtained by Akratopulu *et al.* [8], who studied the effect of the temperature on the IEP. The increase in IEP at higher temperatures, due to the higher concentration of OH_2^+ groups at the surface, is responsible for the increase in adsorption. An extension of the time of adsorption from 1 to 2 h at 30 °C showed no increase in adsorption. Actually the adsorption takes place in the first minutes after addition of the $[La(EDTA)]^-$ solution to the suspension of the support. It can be concluded, therefore, that the adsorption is not kinetically controlled.

Sinter experiments for 145 h at 1050 °C in air with samples made by specific adsorption of $[La(EDTA)]^-$ onto pseudo-boehmite and γ-Al_2O_3 resulted in surface areas between 90 and 100 $m^2 g^{-1}$. Surface area against time plots were similar to those discussed above.

It is remarkable that the thermostability remains high at very low loadings. This is in contrast with the impregnation and precipitation experiments in which loadings lower than 3.5 wt % La resulted in a decrease in thermostability. Schaper [1] ascribed the increase in thermostability by addition of lanthanum to the formation of a surface layer of $LaAlO_3$ after heat

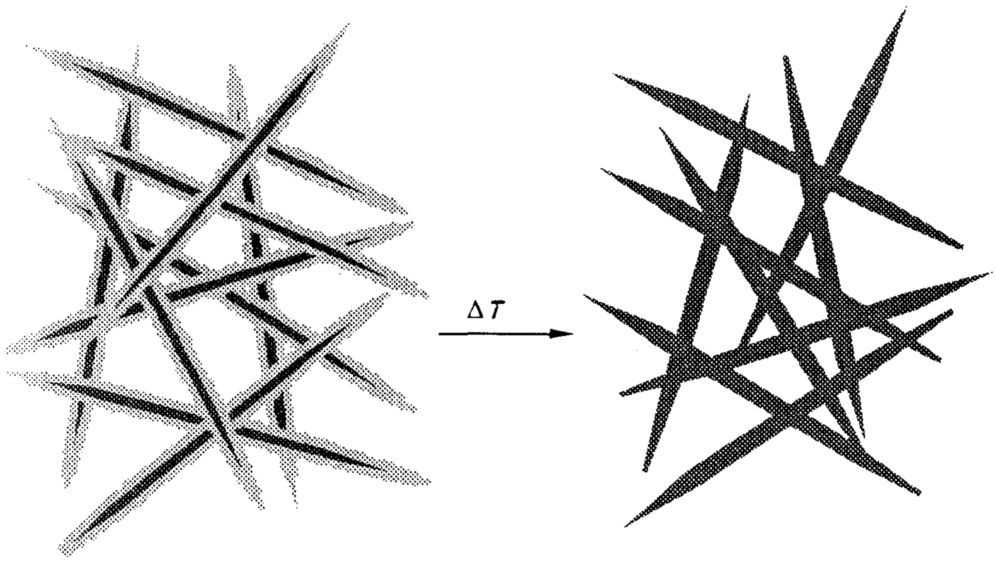

Figure 6 Schematic drawing of the lanthanum-induced crystallization process.

treatment. The amount of lanthanum, however, in our experiments is much too small to form a stoichiometric layer of $LaAlO_3$. At pH 8 the loading of the pseudo-boehmite sample is only 0.5 wt % La. Results obtained with high resolution TEM showed that the amorphous alumina layer, which was present at the surface of every γ-Al_2O_3 or pseudo-boehmite fibril, crystallized under influence of small amounts of lanthanum.

After calcination, the alumina displayed a well crystallized surface. The presence of this crystallized surface was responsible for the high thermostability, because nucleation of α-Al_2O_3 was more difficult. This is schematically represented in Fig. 6. High resolution TEM micrographs of fresh γ-Al_2O_3, and γ-Al_2O_3 treated at 1050 °C for 23 h are shown in Fig. 7a and b.

4. Conclusions

By applying lanthanum homogeneously to the surface of pseudo-boehmite and γ-Al_2O_3 by deposition–precipitation from a homogeneous solution or by impregnation and adsorption of $[La(EDTA)]^-$, supports with a very high thermostability were prepared. For heating times up to 145 h at 1050 °C in air, surface areas of more than 90 $m^2 g^{-1}$ were obtained for the commercial acicular alumina.

The minimum amount of lanthanum required, depends on the procedure used to apply lanthanum. When deposition–precipitation from a homogeneous solution or incipient wetness impregnation are used, loadings of 3.5 wt % La are required to obtain a sufficiently thermostable support. With the specific adsorption procedure thermostable supports can be prepared with loadings as low as 0.5 wt %. Under influence of lanthanum ions crystallization of the alumina surface takes place. The mobility of surface oxygen ions is lower in this crystalline layer, resulting in an increased thermostability. Since less than a monolayer of lanthanum ions already brings about crystallization, low loadings of lanthanum are sufficient for thermal stabilization, provided the distribution of lanthanum over the alumina surface is completely homogeneous.

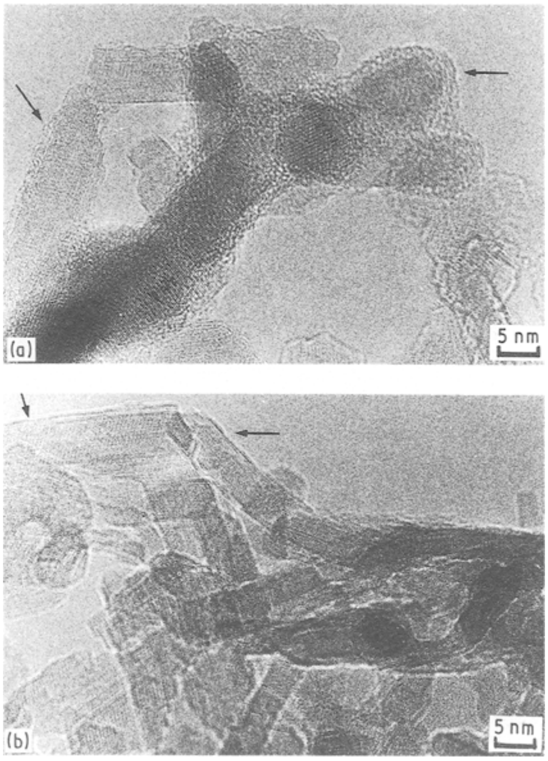

Figure 7 (a) High resolution TEM micrograph of fresh γ-alumina (Al 4172) showing acicular alumina particles. Arrows show the amorphous alumina layer. (b) High resolution TEM micrograph of lanthanum-coated γ-alumina (Al 4172) treated for 23 h at 1050 °C in air. Arrows show the crystalline alumina layer.

References

1 H. SCHAPER, PhD Thesis, University of Technology Delft, The Netherlands (1984)

2 V. I. VERESHCHAGIN, V. YU. ZELINSKII, T. A. KHABAS and N. N. KOLOVA, *J. Appl. Chem. USSR* **55** (1982) 1792.

3. S. MATSUDA, A. KATO, M. MITSUMOTO and H. YAMASHITA, in Proceedings of 8th International Congress on Catalysis, Berlin, 1984 (Verlag Chemie, Weinheim) p. 879.

4. P. BURTIN, J. P. BRUNELLE, M. PIJOLAT and M. SOUSTELLE, *Appl. Catal.* **34** (1987) 225.
5. I. I. M. TIJBURG, PhD Thesis, University of Utrecht, The Netherlands (1989).
6. J. W. GEUS, in "Preparation of Catalysts III, Scientific Bases for the Preparation of Heterogeneous Catalysts", edited by B. Delmon, P. Grange, P. Jacobs and G. Poncelet (Elsevier, Amsterdam, 1982) p. 1.
7. K. JIRATOVA, *Appl. Catal.* **1** (1981) 165.
8. K. Ch. AKRATOPULU, L. VORDONIS and A. LYCOURGHIOTIS, *J. Chem. Soc., Faraday Trans. I* **82** (1986) 3697.
9. D. D. PERRIN, "Masking and Demasking of Chemical Reactions" (Wiley Interscience, New York, 1970).
10. R. C. ROPP and B. CARROL, *J. Amer. Ceram. Soc.* **63** (1980) 416.
11. G. R. MEIMA, PhD Thesis, University of Utrecht, The Netherlands, (1987).
12. C. P. HUANG and Y. T. LIN, in "Adsorption from Aqueous Solutions", edited by P. H. Tewari (Plenum, New York, 1981) p. 61.

Received 20 September 1990
and accepted 7 March 1991