Modification of γ -Alumina by Barium and Lanthanum, and the Consequential Effect on the Reducibility and Dispersibility of Nickel

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The influence of modifiers such as barium and lanthanum on the physical properties of γ -alumina has been studied. Calcination of the modified alumina at 723 K for 5 h does not result in any compound formation as evidenced from X.r.d. *Ca.* 8–9 wt % nickel was prepared by impregnation method using this modified alumina. Ba and La modifiers improve the reducibility of nickel and the metal area measured by hydrogen adsorption. It is presumed that the oxide layers over the surface of alumina prevent the interaction between nickel and γ -Al₂O₃, making more nickel available on the surface. The activity and turnover number (TON) for benzene hydrogenation vary directly with the available metal area, irrespective of the modifier.

Although alumina is widely used as an oxide support, its surface area significantly decreases accompanied by phase transformation at high-temperature operation conditions. It is equally important to maintain the surface area of the support without sintering as in the case of the active metal. It has been shown¹⁻⁴ that the addition of foreign cations as modifiers to alumina-based catalysts controls the properties of support as well as the active metal phase deposited on the modified support. However, only a few studies have focussed attention on the effect of additives or modifiers on the nature of the active metal component and its dispersion over the support.¹⁻⁵ The influence of modifiers on reduction and dispersion of the active metal depends on the order and method of addition, concentration of modifiers and calcination temperature.

In our earlier publications^{5,6} we have reported the influence of calcination and lithium modifier on alumina and on the reduction and dispersion of nickel. As a part of a systematic study on the nickel–alumina system, we report the influence of barium and lanthanum modifiers on alumina and the consequential effect on the reducibility and dispersibility of nickel over the support. The use of barium and lanthanum⁷⁻¹⁰ seems to prevent sintering of alumina at elevated temperatures. McVicker *et al.*¹¹ reported that when CaO-, SrO- and BaO-modified aluminas are used as supports, they inhibit oxidative sintering of irridium at temperatures up to 923 K. Lanthanum oxide has recently been used as a support for Pd and was found to undergo reduction and behave like TiO₂, resulting in the suppression of hydrogen adsorption.^{12,13} The use of La³⁺ ions as a surface modifier for alumina is a new concept and it improves the thermal stability of alumina.^{8-10,14,15}

The nickel-alumina catalyst is generally prepared either by coprecipitation or by a deposition precipitation method. The modifier incorporated onto this nickel-alumina is found to increase the thermal stability and catalytic activity. The method of preparation of modified nickel-alumina reported in this study is different from the procedure described in the literature.^{8-10, 14-19} The aim of this study is to modify the alumina support itself with barium and lanthanum and use this modified support for loading nickel as a part of the general investigation on the infuence of various modifiers on the reducibility and dispersibility of nickel.

Experimental

Harshaw alumina Al 111-61E (1000–1400 μ m) was used as the support. Barium- and lanthanum-modified aluminas were prepared by incipient wetness of the support, using appropriate concentrations of the metal nitrate solutions, dried at 393 K and calcined in air at 723 K for 5 h. The total intrusion volume, total surface area and average pore diameter were measured by mercury-penetration porosimetry.

Nickel catalysts (ca. 8–9 wt %) were prepared by impregnating alumina and modified aluminas with nickel nitrate solution of appropriate concentrations, dried at 393 K overnight. The catalysts were then calcined at 723 K for 5 h, reduced in hydrogen at the same temperature for 5 h and passivated at room temperature in a mixture of inert gas and air, following the procedure of Bartholomew and Farrauto.²⁰ These catalysts were further reduced for 2 h at 723 K before adsorption experiments were performed. Hydrogen and oxygen uptake measurements were carried out in a constant-volume adsorption system capable of achieving 1×10^{-5} Torr.[‡] The metal area, percentage reduction, dispersion and metal crystallite size were calculated as described earlier.⁵

Benzene hydrogenation at 423 K was carried out in a vertical fixed-bed tubular reactor at atmospheric pressure.^{5,21} Hydrogenation of benzene in terms of activity and turnover number (TON) was calculated and correlated with the metal area, which is directly related to hydrogen chemisorption. The activity is defined as the number of moles of benzene converted to cyclohexane per unit time per unit weight of the catalyst. The turnover number (TON) is defined as the number of molecules of benzene converted to cyclohexane per atom of exposed nickel per second.

X.r.d. patterns of the samples were taken using a Philips PW 1051 diffractometer with nickel-filtered Cu K_{α} radiation ($\lambda = 1.5405$ Å). Metal contents were estimated by atomic absorption spectroscopy.

Results and Discussion

Effect of Barium

In this section, the role of barium as a modifier is discussed in order to understand its influence on the reducibility and dispersibility of Ni/Al₂O₂ catalysts. Table 1 summarizes the physical properties of alumina and barium-modified aluminas. With the addition of barium, the total intrusion volume, the total surface area and the average pore diameter of alumina increase. This is in contrast to what was observed for lithium-modified alumina.⁶ For lithium additions of 0.5 to 3.0 wt % the total surface area and intrusion volume decreased after a small increase and the average pore diameter increased. The differences in the influence of lithium and barium on the physical properties of alumina may be attributed to the extent of interaction between the modifier and the support. Lithium, being small (atomic radius 0.68 Å) compared to barium (atomic radius 1.29 Å), diffuses into the pores of alumina more easily and interacts more strongly than barium. This is also reflected in the X.r.d. patterns of lithium-modified alumina and bariummodified alumina. In fig. 1, the X.r.d. patterns of lithium-modified aluminas are compared with those of Ba- and La-modified aluminas and unmodified aluminas calcined at 723 K for 5 h. The alumina support became crystalline with the addition of 0.5 to 3.0 wt % of lithium. However, barium showed no influence on the crystallinity of alumina. X.r.d. patterns of Ba/Al₂O₃ calcined at 723 K do not reveal any evidence of compound formation between barium and alumina. The unreactive BaO itself may contribute to the increase in surface area. It is likely that barium forms only a surface oxide layer on alumina, thereby preventing the interaction between the metal and support. This would help the reducibility of nickel but not the dispersion, since easy reducibility can also contribute to agglomeration of metal particles. The total acidity of barium-modified alumina is somewhat less than the acidity of alumina alone. This

† 1 Torr = 101 325/760 Pa.

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properties	Al ₂ O ₃	Ba/Al ₂ O ₃	Ba/Al_2O_3	
modifier/wt % Ba total intrusion volume/cm ³ g ⁻¹ total surface area/m ² g ⁻¹ average pore diameter/nm acidity/meguiy. n-butylamine	0.0 0.481 265 7.4 0.431	0.5 1.186 322 14.7 0.343	3.0 1.060 296 14.3 0.322	

Table 1. Effect of barium on the physical properties of alumina



Fig. 1. X.r.d. patterns of alumina and modified aluminas: (1) alumina, (2) 0.5 La, (3) 2.0 La, (4) 0.5 Ba, (5) 3.0 Ba, (6) 0.5 Li, (7) 3.0 Li.

Table 2. Effect of barium on adsorption properties of nickel-alumina catalysts

properties	Ni/Al_2O_3	$Ni/Ba/Al_2O_3$	$Ni/Ba/Al_2O_3$	
modifier/wt % Ba	0.0	0.5	3.0	
nickel/wt %	8.5	9.1	8.9	
H _a uptake/ μ mol g ⁻¹ Ni	200	824	775	
O_{a}^{\prime} uptake/ μ mol g ⁻¹ Ni	718	3462	4270	
O_{a}/H_{a}	3.6	4.2	5.5	
$metal area/m^2 g^{-1} Ni$	15.3	64.8	60.7	
reduction (%)	9	42	51	
dispersion (%)	27	23	18	
crystallite size/nm	3.7	4.4	5.8	

decrease in acidity may be due to the direct contribution from barium oxide rather than from barium aluminate.

The chemisorption properties of nickel-alumina catalysts are summarised in table 2. Barium addition increased the reducibility of nickel ions nearly five times and the metal area by fou. times. The crystallite size and dispersion have not been altered substantially, indicating the absence of any large agglomeration of metallic particles in spite of the easy reducibility of nickel ions due to barium addition. The increase in oxygen and hydrogen uptake as well as the increase in O_2/H_2 ratio indicate that more bulk and surface metallic nickel is available in the barium-modified nickel-alumina compared with the unmodified

Modification of y-Alumina by Ba and La



Fig. 2. Variation of hydrogenation activity of modified nickel-alumina catalysts with metal area. Temperature = 423 K; WHSV = 0.43 mol h⁻¹ g⁻¹; H/HC = 3.6. (----) Turnover number, (----) activity; \Box , without modifier; \triangle , 0.5 wt % Ba; \triangle , 3.0 wt % Ba; \bigcirc , 0.5 wt % La; \bigcirc , 2.0 wt % La.

nickel-alumina. There is no measurable oxygen and hydrogen uptake by Ba/Al_2O_3 at the experimental conditions of 673 K, indicating that barium modifier does not contribute to any O_2 uptake on its own in the absence of nickel. Barium, when used as modifier to alumina, only helps the reduction of nickel and increases hydrogen and oxygen uptake in the case of Ni/Ba/Al_2O_3 compared to Ni/Al_2O_3 without barium.

The variation of benzene hydrogenation activity with metal area over barium- and lanthanum-modified nickel alumina catalysts is shown in fig. 2. The activities of these catalysts also corroborate the observed chemisorption properties. Nickel-alumina without barium has a low reducibility and hydrogen adsorption capacity and shows negligible benzene hydrogenation activity, whereas the barium-modified nickel-aluminas with improved reducibility and hydrogen adsorption capacity show definite catalytic activity.

Effect of Lanthanum

In fig. 3 the variation in the physical properties of alumina due to lanthanum addition is shown. Both the intrusion volume and average pore diameter increase with lanthanum concentration up to 1 wt %, and with further addition they decrease but the change is not significant in the case of total intrusion volume. The total surface area, on the other hand, decreases significantly for the first addition of 0.5 wt % lanthanum and further addition causes an increase in the surface area. The increase in the average pore diameter and decrease in total area for a small addition of lanthanum may be due to the blocking of narrow pores. Further addition of the modifier would probably start filling the large pores without interacting with the support. The non-reactive La_2O_3 may also contribute to the increase in surface area, since the compound formation, if it takes place, will result in surface area decrease. X.r.d. patterns of modified alumina which are calcined at



Fig. 3. Effect of lanthanum on physical characteristics of alumina: ○, total intrusion volume; average pore diameter; ▲, total surface area.

Fable 3. Effect of lanthanu	n on adsorption	properties of n	nickel-alumina catalysts
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properties	Ni/Al_2O_3	Ni/La/Al ₂ O ₃	Ni/La/Al ₂ O ₃	
 modifier/wt % La	0.0	0.5	2.0	
nickel/wt %	8.5	8.7	8.6	
H _a uptake/ μ mol g ⁻¹ Ni	200	276	1138	
O_{a}^{2} uptake/ μ mol g ⁻¹ Ni	718	1356	4209	
O_{s}^{2}/H_{s}	3.6	4.9	3.7	
metal area/m ² g ⁻¹ Ni	15	22	88	
reduction (%)	9	16	51	
dispersion (%)	27	20	26	
crystallite size/nm	3.7	5.1	3.9	

723 K do not give any clue to compound formation (fig. 1) even though LaAlO₃ has been reported²² at 1073 K with characteristic peaks at 2θ values of 34.45 and 41.25°. Schaper *et al.*⁹ have showed that γ -Al₂O₃ sinters by a surface diffusion mechanism and lanthanum prevents sintering by the formation of lanthanum aluminate layer on the surface.

Chemisorption properties of nickel-alumina catalysts are given in table 3. Lanthanum addition certainly improves hydrogen and oxygen uptake, indicating the increased availability of surface and bulk metallic nickel. This is a reflection of the easy reducibility of nickel oxide on lanthanum-modified alumina, as evidenced by the percentage of reduction and the metal area. This is similar to the observation on barium-modified alumina. It is likely that La_2O_3 also forms only a surface oxide layer over alumina as in the case of Ba/Al_2O_3 , preventing interaction between metal and support. In

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Fig. 4. Variation of hydrogenation activity of lithium-modified nickel-alumina with metal area. Temperature = 423 K, WHSV = 0.09 mol $h^{-1} g^{-1}$, H/HC = 6.4. \bigcirc , Activity; \triangle , turnover number.

lanthanum-nickel-zeolite systems, the difficulty in reduction was explained on the basis of formation of La—O—Ni inside the supercages.²³ The improvement in the reducibility of Ni²⁺ ions with lanthanum-modified alumina as support also confirms the absence of any compound formation between metal and modifier which would retard reduction. Dispersion and crystallite size do not show much variation.

Gelsthorpe *et al.*¹⁹ found, on the other hand, a decrease in the metal area, as measured by hydrogen and CO adsorption, and an increase in the methanation activity due to lanthanum addition. The promotional effect of lanthanum in methanation activity is explained on the basis of activity per nickel site or improved turnover number, rather than increased metal area. It should however be remembered when comparing these two observations on hydrogen adsorption, that Gelsthorpe *et al.*¹⁹ used coprecipitated Ni–Al–La material in their studies, whereas we have used impregnated samples. We prepared La/Al₂O₃ first and then impregnated it with nickel. As mentioned by Gelsthorpe *et al.*¹⁹ lanthanum added during coprecipitation becomes more evenly distributed through the samples and its effect on the surface properties is rather less than that of La incorporated by impregnation. The preparation procedure would probably account for the enhanced hydrogen adsorption of nickel observed on lanthanummodified alumina.

When La_2O_3 is used as support for transition metals^{12,13} such as Pd, hydrogen chemisorption is suppressed after reduction above 673 K. It is therefore clear from the foregoing observation, that La_2O_3 as a modifier plays different roles depending on the method of preparation and concentration.

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As can be see from fig. 2 the benzene hydrogenation activity improves significantly when nickel is loaded onto lanthanum-modified (2 wt %) alumina. There is a smooth variation of TON with metal surface area of nickel-alumina catalysts. It is interesting to compare the benzene hydrogenation activity of lithium modified alumina catalysts with the activity of barium- and lanthanum-modified nickel-alumina. Lithium addition up to 2 wt % improves the reducibility and the available metal area for hydrogen chemisorption and hydrogenation activity.⁶ In fig. 4 the variation of hydrogenation activity at lithium-modified nickel-alumina with metal area is shown. It can be derived from fig. 2 and 4 that irrespective of the type and the amount of modifier used, the TON and activity vary smoothly with metal area, even though the mechanism by which each modifier affects the reducibility of nickel may be different.

Conclusions

Modification of γ -alumina by incorporating barium and lanthanum before loading nickel ions improves the reducibility and metal area of nickel-alumina.

In the case of both barium and lanthanum, there was no evidence of any compound formation at the experimental conditions. It is presumed that they form oxide layers on alumina, thereby preventing the interaction between metal and support.

Benzene hydrogenation activity is improved by the addition of the modifier and with the metal area.

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