THE EFFECT OF Ni-Al RATIO ON THE PROPERTIES OF COPRECIPITATED NICKEL-ALUMINA CATALYSTS WITH HIGH NICKEL CONTENTS

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ABSTRACT
A series of nickel-alumina catalysts with a Ni/Al ratio between 3 and 20 has been prepared by coprecipitation. The calcination and reduction of these samples have been studied by thermogravimetry and their structures after calcination and reduction at different temperatures has been examined by X-ray diffraction. The methanation activities of the final catalysts have been determined by differential scanning calorimetry. Whereas the alumina present in the samples with Ni/Al = 3 stabilises the catalysts against crystalline growth during both calcination and reduction, the effect is much less pronounced with higher nickel contents. The resultant catalysts for Ni/Al = 6, 9 and 20 were found to have activities comparable with those with Ni/Al = 3 as long as the calcination and reduction are carried out at relatively low temperatures. A model of the catalysts is proposed.

INTRODUCTION
Coprecipitated nickel-alumina catalysts with relatively high nickel contents (Ni/Al molar ratios between 2 and 3) derive their high activities and stabilities from the fact that a single precursor precipitate contains both the nickel and aluminium ions in close proximity within the "brucite" layers of a hydrotalcite structure. The properties of the precipitates, and of the calcined and reduced materials derived from them, have been studied in considerable detail [1-8]. Most work to date has been restricted to the composition range corresponding to the stability of the layer structure [1] but some has also been done with lower nickel contents [7] corresponding to the composition of the spinel NiAl2O4. The most satisfactory model of the catalyst is one in which the reduced material consists of two separate phases, the first being nickel-rich (paracrystalline with dissolved Al ions [7]), the second being alumina-rich and determining the physical appearance and texture of the catalysts; the alumina-rich phase effectively acts as a support for the paracrystalline nickel crystallites [5,6].

One of the consequences of the strong interaction of the nickel- and aluminium-containing phases is that the catalyst requires temperatures up to 600°C for complete reduction. The resultant material has high stability and has a high residual methanation activity even after prolonged exposure to water-hydrogen mixtures at 700°C [6]. For many purposes in which nickel catalysts are used, however, such high
stabilities are not necessary, for example in the methanation of traces of CO prior to the synthesis step in ammonia plants or in the hydrogenation of unsaturated molecules, where the temperatures are not likely to be much above 300°C. In such applications, the high reduction temperature is likely to be undesirable as in situ reduction will be difficult to perform. Because prior reduction is not required for Raney nickel catalysts, these are frequently used for hydrogenation purposes; however, the stability of Raney nickel is limited, sintering occurring at relatively low temperatures [9].

The aim of the present programme of work is to examine the structure and properties of coprecipitated nickel-alumina catalysts with higher nickel ratios than those which we have previously studied. We hope that by studying the behaviour of samples with Ni/Al ratios above three we shall learn more about the way in which aluminium stabilises the catalysts and also establish whether or not catalysts with higher nickel contents have adequate activities and stabilities for use in relatively low-temperature processes. We wish to ascertain how a variation of the Ni/Al ratio affects the distribution of the Al between the nickel- and aluminium-rich phases; is the change in composition similar in both phases or is it more pronounced in the alumina-rich phase? In this paper, we present results of thermal analysis studies of the calcination and reduction of materials with Ni/Al ratios of 6, 9 and 20, comparing these with the behaviour of a sample with Ni/Al = 3 of the type studied previously [1-3]. We also give results for the phase analysis of the various samples before and after calcination and reduction at a variety of temperatures and for the methanation activities of the resultant catalysts. On the basis of these results, we propose a model for the structure of the catalysts studied here.

EXPERIMENTAL

Catalyst preparation

The catalyst precursors were made by coprecipitation using the constant pH method which has been described previously [1]. Precipitation was carried out at 80°C at a pH of 7.0 by the simultaneous addition of a solution containing a total of about 0.9 mol of Ni(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O in known proportions per dm³ of water and one of sodium carbonate (about 1 mol per dm³) to deionised water (150 cm³) maintained in a Pyrex vessel. After precipitation, the precipitate was thoroughly washed with 1 dm³ of deionised water at 80°C and was then dried in an oven at between 120°C and 130°C overnight. This was followed by a second washing and drying cycle; although one washing was sufficient to give low sodium contents for most samples, the second washing lowered the sodium content below 0.01 wt%.

Calcination of the samples was carried out in a flow of nitrogen in a Stanton Redcroft tube-furnace maintained at a temperature of 350, 450, 525 or 600°C after an initial temperature increase at a rate of 2°C min⁻¹ (Stanton Redcroft tempera-
ture programmer); the time at the final temperature was 3 h for the upper three temperatures but 21 h was used for calcination at 350°C to ensure complete decomposition of the precipitate structure. Each sample was then reduced in a stream of hydrogen (50%) in nitrogen, final temperatures of 300, 400 or 600°C being maintained for 15, 5 and 3 h respectively, in order to ensure that a constant composition was achieved at that temperature; the temperature was raised from room temperature to the final reduction temperature at a rate of 2°C min⁻¹. After reduction, the samples were passivated in a stream of nitrogen saturated with water vapour (P = 20 Torr, 1 Torr = 133.3 N m⁻²) at a temperature of 70°C. The degree of reduction of the samples prereduced in the tube-furnace could be determined using thermogravimetry (see below): the passivated material was re-reduced in the thermobalance at a temperature no higher than the original reduction temperature but sufficiently high to bring about complete re-reduction and was then re-oxidised to constant weight at a temperature of 400°C, the uptake of oxygen being a measure of the degree of reduction which had originally been achieved.

Thermogravimetric studies of the calcination and reduction of the materials was carried out with a DuPont system (990 control unit, 951 TG systems). The heating rate for calcination was 20°C min⁻¹ and for reduction was 10°C min⁻¹. The gases used were identical to the ones mentioned above.

Phase analysis and particle size measurements

Phase analysis measurements on the precipitates and on the calcined and reduced materials were carried out by X-ray diffraction using a Philips PW 1370 diffractometer (using Ni-filtered CuKα radiation). X-ray line broadening calculations of particle size of the oxidic and reduced phases were carried out using the Scherrer equation applied to the following diffraction lines: calcined material, (220) line of NiO-rich phase, occurring between 1.46 and 1.48 Å, depending on composition; reduced material, (200) line of Ni-rich phase, occurring between 1.75 and 1.76 Å.

Activity measurements

Activity measurements were carried out using differential scanning calorimetry (DSC; DuPont 910 unit with a high pressure cell) using a procedure described previously [11]. The passivated samples were re-reduced in a flow of hydrogen at 400°C (or at 300°C in cases when the prereduction was at 300°C) in the DSC cell prior to carrying out the activity measurements. The samples were cooled to 200°C and then CO was added to the hydrogen flow so that the H₂/CO ratio was 3 and the total flow rate was 40 cm³ (STP) per minute. Activities were obtained at a range of temperatures from about 200 to 300°C but only the activities at 300°C are quoted. Repeat measurements carried out with duplicate samples were generally within 10% of the average values for that sample composition.
RESULTS AND DISCUSSION

The precipitates

Phase analysis of the precipitates showed that the hydrotalcite structure [1] was the main phase present in samples with Ni/Al ratios of 3, 6 and 9; see Figure 1. The precipitate with a Ni/Al ratio of 20 was much less crystalline and contained no discernable hydrotalcite phase. Although there was no evidence for the presence of nickel hydroxide phases in any of the samples, we cannot exclude the possibility that these exist with particles too small to give rise to observable diffraction lines. However, after hydrothermal ageing, phase separation was clearly discernable for samples with an Ni/Al ratio higher than 3 [1].

Analyses of the sodium contents of the precipitates by atomic absorption spectroscopy showed that there was no problem of removal of the sodium ions introduced during the precipitation stage of the catalyst preparation. After washing with 1 dm$^3$ of water (80°C) immediately following precipitation, a sodium content of up to 1 wt% was found; however, after drying in air (120-130°C) overnight and further washing, hardly any sodium was left (below 0.01 wt%) as long as the sample was re-washed after the drying stage as described in the Experimental section. This washing procedure has previously been shown to be necessary for samples of Ni-Al coprecipitates formed at pH = 10 [12] and for samples containing lanthanum ions [10].

Calcination

Figure 2 gives DTG results for the decomposition of three of the precipitates studied. The results show that increasing the Ni/Al ratios leads to an increasingly easier decomposition of the layer structure. There is no indication from these
results that more than one phase exists in the precipitate. However, this is not totally conclusive as the hydrothermally aged precipitate referred to above, which contains two phases, exhibited decomposition behaviour similar to that of the unaged sample. It should also be noted that the shape of the first peak in Figure 2 changes with increasing nickel content, the shoulder at about 200°C not being visible for Ni/Al = 9 and 20. This indicates that the latter samples contain much less water of crystallisation than is found with the Ni/Al = 3 sample [1].

The calcined material
The X-ray diffraction patterns of the calcined materials corresponded in all cases to those of nickel oxide and there was no evidence for the presence of alumina-rich phases, as has previously been observed for samples with Ni/Al less than about 3.0 [2,3,10]. The table gives the lattice spacings observed for the NiO(200) and (220) reflections of each of the samples as a function of the calcination temperature and the results for the Ni/Al ratio of 3 are included to allow a comparison with those reported in previous work. The NiO (200) and (220) lattice spacing for pure NiO [13] for comparison purposes are 2.088 and 1.476 Å respectively. The results show that whereas the spacing for the Ni/Al ratio of 3.0 indicates a deviation from that of pure NiO, due probably to aluminium ions dissolved within the NiO lattice, as observed before [2,3,6], the samples with higher nickel contents were essentially indistinguishable from those of pure NiO.
TABLE
X-Ray lattice spacings in Å for the (200) and (220) reflections of NiO for samples with different Ni/Al ratios calcined at a series of temperatures.

<table>
<thead>
<tr>
<th>Ni/Al ratio</th>
<th>Lattice spacing Å</th>
<th>Tc = 350°C</th>
<th>Tc = 450°C</th>
<th>Tc = 525°C</th>
<th>Tc = 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d_{200}</td>
<td>d_{220}</td>
<td>d_{200}</td>
<td>d_{220}</td>
<td>d_{200}</td>
</tr>
<tr>
<td>3</td>
<td>2.071</td>
<td>1.469</td>
<td>2.073</td>
<td>1.468</td>
<td>2.072</td>
</tr>
<tr>
<td>9</td>
<td>2.086</td>
<td>1.477</td>
<td>2.087</td>
<td>1.477</td>
<td>2.084</td>
</tr>
<tr>
<td>20</td>
<td>2.089</td>
<td>1.481</td>
<td>2.084</td>
<td>1.475</td>
<td>2.088</td>
</tr>
</tbody>
</table>

The results for the samples with Ni/Al = 3 are in good agreement with those reported recently by Doesburg et al. [6].

Figure 3 gives the results of particle size calculations from line-broadening measurements for the NiO particles as a function of calcination temperature. It can be seen that the particle size for the sample with Ni/Al = 3.0 is effectively independent of calcination temperature, the crystallites being of the order of 45 Å in diameter. This result is in contrast with results recently reported by Doesburg et al. [6] who obtained particle sizes of 80 and 120 Å for a similar sample calcined at 450°C and 600°C respectively; the difference probably arises from the fact that Doesburg et al. calcined their samples at the uppermost temperature without first raising the temperature slowly to that value. For a Ni/Al ratio of 9.0, the results of Figure 3 show a distinct increase in particle size with increasing calcination temperature. For a calcination temperature of 350°C, the particle size is about the same as that of the sample with the lower Ni content but higher calcination temperatures clearly give rise to a particle growth phenomenon and this is even more obvious from the results for the Ni/Al = 20 sample.

Reduction

Thermogravimetric experiments showed that the reduction of samples of the precipitates calcined at 600°C or below occurs in a single step in each case, there being no evidence for the presence of more than one reducible phase for any of the samples. It is thus convenient to compare the ease of reduction of the various samples by comparing the temperatures of maximum rate of weight loss as is done in Figure 4. It can be seen that the ease of reduction drastically increases with increasing Ni/Al ratio. The ease of reduction also increases with decreasing calcination temperature but in a less marked fashion. With a calcination temperature above 600°C, it was shown previously that a sample with a Ni/Al ratio of 3.0 is reduced in two steps corresponding to the reduction of NiO and NiAl₂O₄ respectively [7,10].
FIGURE 3 Particle sizes of the NiO phase of the calcined samples as a function of calcination temperature $T_c$. $D_{NiO}$ values are calculated from X-ray line broadening.

Reduced phase

Under the conditions described in the experimental section, it is possible to achieve complete reduction for all the samples at a reduction temperature of 600°C. For lower reduction temperatures, the degree of reduction was greater than 80% except for the sample with Ni/Al = 3, for which the degree of reduction was lower.
FIGURE 5a Nickel particle sizes for samples with Ni/Al ratios of 3, 9 and 20 as a function of calcination temperature; \( T_r = 600^\circ C \). \( D_{Ni} \) values are calculated from X-ray line broadening.

FIGURE 5b Nickel particle sizes for samples with Ni/Al ratios of 9 and 20 as a function of reduction temperature; \( T_c = 350^\circ C \). \( D_{Ni} \) values are calculated from X-ray line broadening.

X-ray diffraction showed that reduction of all the samples appears to give rise to phases containing only pure nickel crystallites. The sample with Ni/Al = 3 required temperatures of the order of 600°C to ensure complete reduction; a phase of Ni could not be detected in passivated samples of this material after reduction.
at 300 or 400°C. For the samples with Ni/Al ratios of 9 and 20, Ni phases could be detected without distinguishable NiO phases after reduction at temperatures of 300 or 400°C.

Figures 5a and 5b give the results of particle size measurements based on the Ni (200) diffraction peak. Figure 5a gives the particle size of Ni after reduction at 600°C as a function of the temperature of calcination and Figure 5b gives the particle size as a function of reduction temperature after calcination at 350°C for the samples with Ni/Al = 9 and 20. For the sample with Ni/Al = 9, the particle size after reduction at 600°C is approximately 50 Å, independent of the calcination temperature. This is close to the value obtained for the unreduced sample, in agreement with the conclusion reached earlier [2] that the growth of the nickel phase occurs within the NiO phase and that there is little or no sintering for samples of this composition during the reduction step.

For samples with higher nickel contents, the results are different. For a reduction temperature of 600°C, the Ni/Al = 9 sample gives particle sizes which rise from 91 to 159 Å with increasing calcination temperatures while the sample with Ni/Al = 20 gives particles which increase from 318 to 533 Å.

We must conclude from these results that there is a considerable decrease in the stability of the sample as the amount of aluminium is reduced and that the greatest change in particle size occurs during the reduction stage. However, the calcination stage is also critical, as the growth of the crystallites is not so great for samples calcined at lower temperatures as for those calcined at higher temperatures.

The results given in Figure 5b for the samples with Ni/Al = 9 and 20 reduced at 400 or 300°C show that significant growth of the nickel crystallites for these samples occurs only during reduction at higher temperatures (i.e., about 600°C) as the particle size is relatively low for each of these cases. For the sample with Ni/Al = 9, the particle sizes are not far different from those of the oxide phase (see Figure 3). For the sample with Ni/Al = 20, there is some growth compared with the calcined material (compare Figures 3 and 5), this being greatest for the lower calcination temperatures. For the sample with Ni/Al = 20 reduced at 300°C, the particle size is similar to that of the oxidic material. These results illustrate the lack of stability of the samples containing higher Ni/Al ratios. However, the dispersion of the catalysts is reasonable as long as the calcination and reduction temperatures are kept low.

Activity measurements

For the sample with Ni/Al = 3 reduced at 600°C, the activity as a function of Tc is approximately constant, rising slightly with increasing Tc, in agreement with the relatively constant particle sizes shown in Figure 5. The results of activity measurements for samples calcined at a temperature of 350°C are shown graphically in Figure 6. For the samples with Ni/Al = 9, the activities after
FIGURE 6 Activities for methanation of CO at 300°C as a function of $x_{Ni}$ for different reduction temperatures; $T_c = 350°C$; $x_{Ni} = Ni/(Ni+Al)$.

reduction at 600°C are somewhat lower than those for the sample with Ni/Al = 3 and those of the sample with Ni/Al = 20 are very much lower, again in agreement with the particle size measurements. For the sample with Ni/Al = 3 reduced at 300 and 400°C, the activities are relatively high despite the relatively low degrees of reduction. We must conclude that this reduction is restricted to the surface layers and that the active metallic areas of these samples are close to those of the fully reduced samples.

The lower reduction temperatures give rise to improved activities in the samples with higher nickel contents compared with the activities after reduction at higher temperatures. This is particularly marked for reduction at 300°C, the activities approaching those of the most active samples with Ni/Al = 3.

One of the most reliable ways to measure the nickel surface area which is accessible to reactants, is hydrogen chemisorption. Another method used here, is to calculate the area from XRD line broadening measurements. We have to bear in mind that the XRD method gives only a rough estimate of surface area. Because the values can be too high (due for example, to polycrystalline particles or embedding of the nickel crystallites in alumina) or too low (the smallest particles are not seen by XRD). We therefore give the surface areas determined in arbitrary units. Preliminary measurements have shown that a fair correlation exists between chemisorption and XRD-data.

Figure 7 shows the activity data plotted against the nickel areas of the samples, the latter having been calculated from the particle size data of Figure 5,
FIGURE 7 Plot of methanation activities as a function of Ni areas (a.u.) calculated from particle size measurements; ●: Ni/Al = 3; ○: Ni/Al = 9; ⊕: Ni/Al = 20.

it being assumed that the particles were hemispherical; this implies that a fixed proportion of the surface of each nickel particle is active for methanation, regardless of the Al content. (It should be noted that this conclusion does not depend on the model chosen for the shape of the crystallites). We thus conclude that the alumina of the samples has no apparent effect on the specific activities of the samples and that its predominant effect is that of a structural promoter; the more alumina the catalyst contains, the more stable is the nickel phase in that material.

A model for the catalysts

Puxley et al. have suggested [7] that reduced catalysts with Ni/Al = 3 contain paracrystalline nickel phases, the paracrystallinity arising from the inclusion within the nickel crystallites of the aluminium ions of the materials; they have given a detailed description of the nature of the oxidic phases which give rise on reduction to the paracrystalline nickel phases. The model of Puxley et al. does not exclude the possibility that there exists a separate alumina phase but the alumina-rich phase of the reduced catalyst arises from the mixed phase during
reduction and does not exist as a discrete phase before this. Doesburg et al. [6] have recently combined this model with a model originally put forward by Alzamora et al. [2], suggesting that a reduced catalyst with Ni/Al = 3 comprises of two phases, one of paracrystalline Ni particles and the other, consisting of alumina with a proportion of dissolved nickel ions (i.e., an aluminate-type phase), acting as a support for the paracrystalline particles. The important difference between this model and that of Puxley et al. is that the alumina-rich skeleton of the catalyst existed before reduction. The physical appearance of the catalyst is the same at all stages, as precipitate, calcined material, reduced catalyst and even after the removal of the nickel from the lattice as the carbonyl [5] and thus it is concluded that the alumina-rich phase provides the physical skeleton of both the oxidic and reduced forms of the catalyst. The essential difference in the two models arises from the presence of the alumina-rich phase in the oxidic form in the latter model.

Accepting the model of Doesburg et al. [6] as the more reasonable, we must now see if it can be applied to the catalysts with higher Ni contents studied here. With materials with Ni/Al higher than 3, there is not so much aluminium available to provide the physical skeleton of the lattice. One can imagine two situations: in the first, a lowering of the aluminium content of the catalyst results only in a decrease of the amount of aluminium in the alumina-rich phase, the ratio of Ni and Al in the nickel crystallites remaining constant; the second possible situation is one in which the amount of aluminium in each phase is reduced in proportion to the Ni/Al ratio of the sample. In the first case, the properties of the catalyst are unlikely to be changed with increasing Ni/Al ratio; the only result would be a decrease in the total area as the amount of the alumina-rich phase which largely determines the total area would be reduced. The second case seems more likely. The degree of paracrystallinity of the nickel-rich phase is decreased and this gives rise to a greater ease of reduction and a lower stability than found for samples with lower Ni/Al ratios.

A third possible model can be suggested: that there exists a separate amorphous phase of Ni(OH)$_2$ or Ni(OH)$_x$(CO$_3$)$_y$ in the precipitate which gives rise to NiO in the calcined material and then to Ni on reduction; this phase would then sinter more readily than the paracrystalline Ni-Al phases and this could give rise to the behaviour observed. Although we cannot exclude this possibility, it is not so likely as we cannot observe any evidence for additional phases; for example, the decomposition and reduction of all the samples seem to indicate that there is present a material with only a single type of nickel.

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REFERENCES

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