Studies on the Promotion of Nickel–Alumina Coprecipitated Catalysts

II. Lanthanum Oxide

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(Received 5 April 1988, revised manuscript received 8 August 1988)

ABSTRACT

Two series of lanthanum promoted nickel–alumina catalysts have been prepared by coprecipitation of the metal nitrates, using potassium carbonate. The molar ratio between nickel and the sum of aluminium and lanthanum was kept constant at 2.5 or 9.0 within each series. The calcination and reduction of these samples were studied by thermogravimetry and their structures before and after calcination and reduction were examined by X-ray diffraction. The methanation activities of the final catalysts were determined by differential scanning calorimetry. The results showed clearly that the methanation of carbon monoxide over nickel–alumina catalysts is enhanced by the presence of La_2O_3 . With low percentages of lanthanum, the promoter is built into the precursor structure during the coprecipitation process. This is a meta-stable situation; phase separation occurs during hydrothermal treatment. In both series there was an optimum amount of lanthanum at which the activity per gram of nickel reached a maximum. The optimum specific activity of a lanthanum promoted nickel–alumina catalyst was twice as large as that of the unpromoted material. Above these optimum values, the activity per gram of nickel decreased because of two effects: an increase in the nickel particle sizes and an increase in the amounts of potassium remaining from the precipitation step. Alumina is needed to stabilize the nickel crystallites against sintering. The promoting action of La_2O_3 is slightly higher after reduction at 400°C than after reduction at 600°C . Lanthanum increased the amount of carbon monoxide which was adsorbed slowly; the amount of carbon monoxide which was rapidly adsorbed, however, was not altered. The increase in activity was accompanied by an increase in the apparent activation energy.

INTRODUCTION

Coprecipitated nickel–alumina catalysts have been the subject of a number of articles from our group and also from the group of Van Reijen, in collaboration with whom some of this work was carried out [1–9]. Part of the content of these articles has been reviewed by Ross [7]. The coprecipitated catalysts

can be used in the steam reforming of methane and of higher hydrocarbons as well as for the methanation of carbon monoxide. Most of the experimental work until now has been performed with samples in which the molar ratio of nickel to aluminium was between 2 and 3. Samples with compositions in this range form a hydrotalcite-like (takovite) compound during the precipitation process. The nickel and aluminium ions in this compound are randomly distributed among the octahedral positions in a sandwich of OH-layers which is similar to that found in the brucite structure ($\text{Mg}(\text{OH})_2$). These sandwiches are separated from each other by interlayers which contain water of crystallization and anions, e.g. carbonate or nitrate. Which anion is built in depends on the pH at which the precipitation process was carried out. Puxley et al. [10] described how this compound is transformed into the catalytically active form, metallic nickel on alumina; they also discussed the processes which take place during calcination and reduction and the structures of the final materials. The nickel of the final form of the catalyst is stabilized very well against sintering; this may be caused by the occurrence of paracrystallinity in the nickel phase, this being inherited from the original structure of the precipitate phase [10].

It has also been shown [8,9] that coprecipitated nickel-alumina catalysts with higher nickel-to-aluminium ratios (> 3) can be prepared which have high activities in the methanation reaction. Because these new materials can be reduced relatively easily, the reduction at high temperature which is necessary for materials with $2 \leq \text{Ni}/\text{Al} \leq 3$ can be avoided. It is therefore possible to use these materials in low-temperature hydrogenation reactions with in-situ reduction.

Much research has been carried out over the last few years to examine the promotion of several of the group VIII metals used in $\text{CO} + \text{H}_2$ reactions. A number of combinations have been investigated: for example Pd/SiO_2 promoted with TiO_2 or with one of a number of the lanthanide oxides, for the production of methanol and methane [11,12]. Another example is that of rhodium-based catalysts, promoted with V_2O_5 , MoO_3 or ThO_2 , for the production of higher alcohols [13,14]. In our group, we have investigated TiO_2 -promoted nickel-alumina catalysts for the production of methane [15].

Mok et al. [16] used coprecipitated nickel-alumina catalysts which were promoted with lanthanum for the steam reforming of heptane. They found that addition of lanthanum improved the activity and the stability of the catalyst compared to the unpromoted samples. Gelsthorpe et al. [17] found that both lanthanum and cerium had a beneficial effect on the catalytic activity of precipitated nickel-alumina catalysts in the methanation of carbon monoxide. They used materials with Ni/Al molar ratios between 2 and 3. Inui and co-workers had previously shown that the addition of La_2O_3 to nickel supported on carbon or on SiO_2 had a beneficial effect on the activity of the catalyst for the hydrogenation of both carbon monoxide and carbon [18–20]. The increase in activity was thought to be caused by an increase in the dispersion of the

nickel phase brought about by the La_2O_3 . The overall activation energy for the methanation reaction increased from 93 to 131 kJ/mol. Schaper et al. [21,22] added lanthanum to several types of nickel–alumina catalysts. They found (i) that lanthanum stabilized $\gamma\text{-Al}_2\text{O}_3$ by hindering the phase transition to $\alpha\text{-Al}_2\text{O}_3$ [21] and (ii) that lanthanum had an effect on the methanation reaction itself, because the apparent activation energy increased [22]. Lippens et al. [23,24] investigated the structures of several series of precipitated and calcined materials and they came to the conclusion that lanthanum was built into the takovite compound in some series but not in other series.

The hydrogenation of carbon monoxide has been carried out over a number of lanthanide-containing intermetallics, such as LaCo_5 [25] and LaNi_5 [26,27]. Coon et al. [27] showed that the specific methanation activity of this type of material was an order of magnitude higher than that of a commercial nickel–alumina catalyst. Under the reaction conditions, LaNi_5 was transformed to La_2O_3 and nickel [27].

Hicks, Bell and co-workers have investigated palladium catalysts supported on SiO_2 and La_2O_3 [11,28–32]. They found by X-ray photoelectron spectroscopy (XPS) measurements that La_2O_3 lowered the binding energy of the $\text{Pd}_{3d5/2}$ electrons by donating electrons to the palladium crystallites [28]. Another effect of lanthanum was that the strength of adsorption of carbon monoxide was decreased compared to that of Pd/SiO_2 . The authors suggested that this was a consequence of the charge transfer to the palladium crystallites. They suggested that the palladium surface was partially covered by LaO_x -patches, similar to the situation in SMSI catalysts (e.g. Ni/TiO_2). The stoichiometry of the hydrogen chemisorption remained unchanged, the ratio being $\text{H}_a/\text{Pd}_s = 1$, a value found also on SiO_2 -supported palladium. However, the catalytic behaviour changed strongly. The specific rates for the formation of methanol and methane increased up to a factor of five when palladium was supported on La_2O_3 [30]; the reaction-orders in carbon monoxide and hydrogen differed strongly from those found for Pd/SiO_2 and the activation energy also changed [31]. When Pd/SiO_2 was promoted with La_2O_3 , the resulting material behaved similarly to $\text{Pd}/\text{La}_2\text{O}_3$: the distribution of adsorbed hydrogen species was not altered significantly (although the total amount adsorbed was decreased) but the distribution of adsorbed carbon monoxide species was altered so that adsorption in strongly bound states was reduced. The LaO_x species facilitated the dissociation of adsorbed carbon monoxide to produce adsorbed carbon while the presence of adsorbed hydrogen also facilitated the dissociation of carbon monoxide [32]. Similar effects were found when Pd/SiO_2 was promoted with other lanthanide oxides such as CeO_2 , Pr_6O_{11} , Nd_2O_3 or Sm_2O_3 . In all cases, increased activities and increased activation energies were found [11].

We shall describe in this article the preparation, characterization and catalytic behaviour of two series of lanthanum-promoted nickel–alumina coprecipitates. One series had a molar composition given by $\text{Ni}/(\text{Al} + \text{La}) = 2.5$ and one

by 9.0. The latter series is an extension of the work on unpromoted nickel-alumina catalysts with high nickel contents [8,9], whereas the series with the lower nickel content was made partly for comparison purposes with the work of Lippens et al. [23,24]; in this series new results will also be presented. The temperature of reduction was varied and the effect of this on the catalytic activity was studied. The effect of thermal ageing is also reported.

EXPERIMENTAL

Catalyst preparation

The catalysts were made by the coprecipitation method described for the nickel-alumina system by Kruissink et al. [1]. The precipitation was carried out at 80°C and at a constant pH of 7.0 by the simultaneous addition, with vigorous stirring, of a solution containing the nitrates of Ni^{2+} , Al^{3+} and La^{3+} in known proportions in water (total metal concentration 0.5 mol per dm^3) and another of potassium carbonate (1 mol per dm^3) to deionised water (starting volume 100 cm^3) maintained in a Pyrex vessel. Two series of coprecipitates with increasing lanthanum contents were made with different ratios of Ni^{2+} to Al^{3+} plus La^{3+} : for *series A*, the molar ratio $\text{Ni}/(\text{Al} + \text{La})$ was 2.5; and for *series B*, the molar ratio $\text{Ni}/(\text{Al} + \text{La})$ was 9.0.

The samples from the A-series are denoted by A-X, while those of the B-series are denoted by B-X where X is in both cases the mol% lanthanum defined by:

$$X = (\text{mol La} / (\text{mol La} + \text{Al} + \text{Ni})) \cdot 100\%$$

The precipitation process took 30 min and no thermal ageing was applied at this stage. The freshly precipitated samples were washed thoroughly with 1 dm^3 deionised water (80°C) and were then dried overnight in air at 110°C. Because all alkali metals have a detrimental effect on catalytic activity [16,33], the drying step was followed by a second washing and drying cycle in order to lower the potassium content as much as possible. Some samples, to which a few drops of water were added, were thermally aged in an autoclave at 120°C for a period which varied between 16 h and 5 days.

Calcination of the samples was carried out in a stream of nitrogen in a Stanton Redcroft tube-furnace which was maintained at a temperature of 350°C for 13 h, after an initial rate of temperature increase of 2°C/min. Some samples were calcined in air following exactly the same procedure. Each sample was then reduced in a stream of 50% hydrogen in nitrogen, the final temperature being 600°C (for 4 h) or 400°C (for 14 h); the temperature was initially raised at a rate of 2°C/min. After reduction, the samples were passivated in a stream of 1% oxygen in nitrogen at 20°C (20 h) and were stored in air at room temperature.

All the chemicals used were pro analysis quality and the gases were 99.999% pure.

Characterization

Chemical analysis was performed by atomic absorption spectroscopy (AAS) and X-ray fluorescence (XRF) to determine the contents of potassium, nickel and lanthanum. The processes of calcination and reduction were followed by thermogravimetric analysis (TGA-DTG, DuPont 951 TG-system), using the same gases as those used with the tube furnace. The sample weight was approximately 7–9 mg and the heating rate was circa 20°C/min. The degrees of reduction of the reduced and passivated samples were calculated from the weight increase during reoxidation at 400°C after re-reduction at this temperature.

Carbon monoxide chemisorption was performed in the TGA apparatus after initial re-reduction in a 50% hydrogen in nitrogen gas stream at a temperature of 500°C. The temperature at which the chemisorption was carried out was 200°C and the carbon monoxide partial pressure was 100 Torr (1 Torr = 133 Pa).

The hydrogen chemisorption capacity was determined using a TPD apparatus. The maximum take-up of hydrogen was reached by cooling the sample in a stream of 10% hydrogen in argon after initial re-reduction at 430°C. The gas stream was then switched to argon and the amount of strongly-adsorbed hydrogen was detected by subsequent temperature-programmed desorption (starting after flushing after 10 min of argon) to a temperature of 600°C, using a calibrated thermal conductivity detector for analysis of the gas. The nickel surface area was calculated assuming the H_a/Ni_s ratio to be 1.0. The area of one nickel surface atom was assumed to be 0.065 nm² [34].

Phase analysis and particle size measurements

Phase analysis measurements were carried out using a X-ray powder diffractometer (Philips PW 1370, using Ni-filtered Cu $K\alpha$ radiation). The samples were characterized at different stages of the activation process: as a coprecipitate (both before and after thermal ageing), as a calcined phase, and as a passivated phase after reduction. The particle sizes of the passivated samples were calculated from X-ray line broadening (XLB) measurements of the (111) and (200) reflections of nickel, using the Scherrer equation:

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (1)$$

The measured line broadening B (at half maximum) was corrected for instrumental broadening (b) using:

$$\beta = (B^2 - b^2)^{0.5} \quad (2)$$

In eqn. (1), D is the cube root of the volume of the crystal. In order to get the diameter d_v , the value of D has to be multiplied by a constant value which is determined by the crystal shape. In the case of spheres, $K = 1.0747 \cdot 0.89$ and the constant is equal to $(6/\pi)^{0.333}$ [35]; in the case of hemi-spheres, the constant is equal to $(12/\pi)^{0.333}$ [36]. The nickel nucleus is surrounded by a passivation layer of NiO which does not contribute to the nickel reflections. However, after re-reduction, the nickel present in this layer will form part of the nickel crystal. Thus, the diameter which is calculated from XLB has to be increased by a number which is twice the thickness of the passivation layer. The thickness was estimated from the weight loss during re-reduction to be three atom layers. Coenen and Linsen [37] found for Ni/SiO₂ a value of two atom layers (using quantitative X-ray analysis) while Dell et al. [38] found three atom layers from oxygen chemisorption and Montes et al. [39], using XPS, found three to four monolayers. These values agree very well with that which we have found.

Activity measurements

Activity measurements were carried out using differential scanning calorimetry (DSC, DuPont 910 unit) following the same procedure as that described earlier [8,40]. Thus 1–1.5 mg of a passivated sample was put in an aluminium DSC pan and the DSC cell was flushed with hydrogen [gas flow = 30 ml(STP)/min] for at least 30 min. The temperature was then increased to 400°C at a rate of 10°C/min in order to re-reduce (or de-passivate) the sample. After cooling to 150°C in hydrogen, carbon monoxide was admixed [10 ml(STP)/min] and the cell was again heated at a rate of 10°C/min. The heat evolved in the exothermic methanation reaction was used to calculate the activity of the catalysts, assuming that the only reaction which takes place was:

The activities will be given below at a temperature of 300°C; the activation energies were determined from measurements in the range 260–310°C. It will also be shown that only carbon dioxide is produced in addition to methane at 300°C, possibly by the reaction between the water produced and carbon monoxide:

Since the amount of carbon dioxide formed was relatively small compared to the amount of methane, the error introduced by assuming that only the first reaction occurs is also small.

Selectivity and stability measurements

Selectivity measurements were carried out in a fixed-bed reactor with on-line gas analysis. Catalyst powder was pressed into granules and the fraction between 0.3 and 0.6 mm was used. The reactor, which was made of quartz (internal diameter 5 mm), was operated at atmospheric pressure. The catalyst (20 mg) was first re-reduced in a stream of 13.3% hydrogen in helium [total flow 60.0 ml(STP)/min], heating to 500°C being carried out at a rate of 10°C/min. After 30 min, the catalyst was cooled to the desired reaction temperature and carbon monoxide was admixed [2.6 ml(STP)/min]; the H₂/CO ratio was 3.0–3.1. Gas analysis was performed on-line with a Varian 3300 gas chromatograph with Carbosieve-S columns and a thermal conductivity detector. Helium was used as carrier gas. Reactants and possible products which could be detected were: CO, H₂O, CH₄, CH₃OH and C₂H_x (x = 2, 4 or 6). Hydrogen could not be detected quantitatively because helium was used as carrier gas. In a few experiments, the gas mixture coming out of the reactor was collected in a gas burette and was then analyzed in another gas chromatograph with Porapak-Q columns; this was done to check for the presence of higher hydrocarbons. The carbon balance at a the reaction temperature of 300°C was at all times within 5%; however, especially at lower temperatures (e.g. 190°C), significant amounts of C₃₊ products, which could not be detected on-line, were found.

Stability measurements were performed in the same apparatus under identical reaction conditions at a temperature of 250°C or 300°C. Experiments were performed for up to 100 h.

RESULTS AND DISCUSSION

The precipitate phase

XRD patterns of some of the precipitates from the A-series (molar ratio Ni/(Al+La)=2.5) are shown in Figs. 1 and 2. The sample with 0 mol-% lanthanum which had not been aged (A-0 in Fig. 1) shows the most characteristic reflections of the takovite phase described earlier by Allmann [41] and by Puxley et al. [10]. The chemical composition of this phase is approximately Ni₅Al₂(OH)₁₄CO₃·4H₂O. It consists of two sorts of layers: (i) a brucite-type layer in which the Ni²⁺ and Al³⁺ ions are randomly distributed among octahedral sites; and (ii) an interlayer which contains the water of crystallization and the carbonate groups. In the samples prepared without ageing, up to 4 mol-% lanthanum could be added without formation of a separate phase; the samples with 5, 10 and 15 mol-% lanthanum contained large crystals of La₂O(CO₃)₂·xH₂O (x = 1–2) in addition to the takovite phase. The intensities of the takovite reflections decreased with increasing amount of lanthanum. This was caused by the fact that the amount of aluminium relative to nickel

Fig. 1. XRD patterns for non-aged samples, A-series $[\text{Ni}/(\text{Al}+\text{La})=2.5]$.

decreased: the amount of takovite which could be formed was thereby also lowered. The samples A-20 and A-28.6 were amorphous.

A detailed examination of the patterns for A-0 to A-5 showed that these did not remain unchanged with increasing amount of lanthanum. The lattice parameter calculated from the third reflection (occurring at $2\theta \approx 35^\circ$) is given in Fig. 3 as a function of the lanthanum content. This reflection is caused by the (012) planes and it can be seen that d_{012} increases with increasing mol-% lanthanum up to 4 mol-%. For sample A-5, in which phase separation had occurred, d_{012} was lowered again. We will return to this point later.

Fig. 2 shows the effect of ageing on the XRD patterns. The aged sample without lanthanum (A-0) showed very sharp takovite reflections, indicating that large crystals were formed. During the ageing process of the sample with 3 mol-% lanthanum (A-3), phase separation occurred and a $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ phase was formed. This phase was present also in non-aged samples with ≥ 5 mol-% lanthanum (Fig. 1). During the ageing procedure, the value of d_{012} of sample A-3 also decreased to nearly the same value as found in A-0. The value of d_{012} and the presence or absence of a separate $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ phase are thus somehow connected to one another; it can be hypothesized that lanthanum was built into the takovite structure for non-aged samples (up to 4 mol-%), thereby increasing d_{012} , which as a consequence of phase separation

Fig. 2. XRD patterns of some aged and non-aged samples, A-series $[\text{Ni}/(\text{Al} + \text{La}) = 2.5]$; the time of ageing is given in hours, e.g. A-3/16 is sample A-3 after ageing for 16 h.

Fig. 3. d_{012} (Å) as a function of mol-% lanthanum, A-series $[\text{Ni}/(\text{Al} + \text{La}) = 2.5]$.

is lowered to the value which was found in lanthanum-free takovite. Since the separate lanthanum-containing phase was not present in A-3 without the ageing procedure, the non-aged sample represents a meta-stable structure.

Compared to the A-series, the B-series were rather amorphous and showed neither any separate crystalline lanthanum-containing phase nor very clear reflections of a nickel-aluminium-hydroxy carbonate compound. No ageing experiments were carried out with this series.

The potassium content, as measured with AAS, was very low for the sample without lanthanum (0.003 wt.-% potassium), but increased with increasing lanthanum content (A-series: A-5, 0.04 wt.-%; A-20, 0.25 wt.-%; and A-28.6, 0.48 wt.-%; and B-series: B-6, 0.02 wt.-%; and B-10, 0.07 wt.-%). A similar result to those obtained for the A-series was obtained by Lippens et al. [23] for the sodium content in a series of materials which were made by using Na_2CO_3 as the precipitating agent. However, their suggestion that the Na^+ is associated with $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ does not seem to be confirmed by our results, since the amorphous samples A-20 and A-28.6 contain the largest amounts of alkali ions.

Calcination

The DTG profiles of the calcination process of samples from the A-series are shown in Fig. 4. The samples with lanthanum contents below 5 mol.-% showed peaks identical to those found earlier: one peak below 100°C which is caused by the removal of adsorbed water; one at about 200°C caused by the loss of water of crystallization; and the largest peak at about 350°C , which is caused by the transformation of the hydroxycarbonates into the oxides [1]. Small temperature shifts occurring in the DTG peaks can be caused by variation of the sample weight and of the heating rate and do not need to stem from the sample itself. For the samples A-10 and A-15, a peak was observed at $460\text{--}470^\circ\text{C}$; at this temperature a clear shoulder could be observed in the sample A-5. For the samples A-20 and A-28.6, this peak was no longer present, although in the latter sample a very broad shoulder was present. In parallel with this, it was shown above that the samples A-5, A-10 and A-15 contained a separate $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ phase and it seems likely that the new DTG peak was caused by the decomposition of this compound. Because the temperature of the last DTG peak is much higher than the temperature used in the tube-furnace during normal calcination (350°C), this compound will probably not decompose during calcination but will remain intact.

The samples from the B-series showed DTG curves similar to those from the A-series. However, the peak at about 200°C (water of crystallization) was missing. This is in agreement with earlier results [8]. In the B-series, no extra peaks were found, indicating that no separate phases were formed.

The calcined material

For the calcined materials of the A-series which had not been aged before calcination, XRD showed the presence of poorly crystalline NiO for all samples

Fig. 4. DTG patterns of the calcination process, A-series $[\text{Ni}/(\text{Al} + \text{La}) = 2.5]$.

up to 15 mol-% lanthanum. In addition, the samples A-5, A-10 and A-15 again showed the separate phase of $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ ($x=1-2$) which was also present in the uncalcined samples with identical composition. As discussed above, the results of Fig. 4 showed that this compound does not decompose at or below the calcination temperature of 350°C . Two diffraction peaks of unknown origin were observed in addition to this compound (at $d=3.72$ and $d=2.03 \text{ \AA}$). These are not caused by LaNiO_3 , $\text{LaNi}_{2.7}$, $\text{La}_2\text{Ni}_2\text{O}_5$ or LaNiO_2 , all of which have different lattice parameters [42-44].

Samples A-20 and A-28.6 remained amorphous after calcination.

Reduction

The DTG-reduction profiles for the samples of the A and B-series are given in Fig. 5 and 6. In both series, the ease of reduction increases with increasing

Fig. 5. DTG profiles of the reduction process, A-series $[\text{Ni}/(\text{Al} + \text{La}) = 2.5]$.

Fig. 6. DTG-profiles of the reduction process, B-series $[\text{Ni}/(\text{Al} + \text{La}) = 9.0]$.

amount of lanthanum (and hence decreasing amount of aluminium). We have shown before for samples without lanthanum which contain different amounts of aluminium that the ease of reduction is largely determined by the Ni/Al ratio [8,9].

Since the sum of aluminium and lanthanum is constant in all samples of a series and the reduction becomes easier with increasing amounts of lanthanum, it is clear that lanthanum does not interact with nickel in the same way as does aluminium, and that it does not stabilize nickel oxide to the same extent against reduction.

The calcination of a part of sample A-3 was carried out in nitrogen (as with the rest of the samples) and that of another part was carried out in air. The maximum of the DTG peak in subsequent reduction experiments occurred at 462°C in the first case and at 575°C in the second. Calcination in air clearly makes reduction more difficult.

The reduced material

In the XRD patterns of the reduced and passivated materials A-0 and A-4 only nickel reflections were present; above 4 mol-% lanthanum, $\text{La}(\text{OH})_3$ and La_2O_3 were present in addition to nickel. It is clear that the $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ phase was decomposed during the reduction process, possibly to La_2O_3 ; this could take up water at room temperature to form the $\text{La}(\text{OH})_3$ phase [45,46]. The sample of A-3 which was thermally aged for 5 days also contained $\text{La}(\text{OH})_3$ after reduction at 600°C and subsequent passivation. In the B-series, only B-

10 reduced at 600°C contained La_2O_3 and $\text{La}(\text{OH})_3$; all other samples in this series showed only nickel reflections.

The structures of the samples from the A-series during the different stages of the activation process are summarized in Table 1.

The nickel particle sizes were estimated from X-ray line broadening (XLB) as described in the Experimental section. Since there was good agreement between the particle sizes calculated from the (111) and (200) reflections, only those calculated from the (200) reflection are given in Tables 2 and 3.

The particle sizes were lowered somewhat by the addition of small amounts of lanthanum. Above a certain mol percentage the particle diameters increased again; this is presumably because the amount of aluminium in the sample has

TABLE 1

Phases observed by XRD for the samples of the A-series which had not been aged

	Phases			
State	Lanthanum content (mol-% La)			
	0 5 10 15 20 25			
Copr.*	T.V.**	T.V.+La ₂ O(CO ₃) ₂ ·xH ₂ O	amorphous	
Calc.	NiO	NiO+La ₂ O(CO ₃) ₂ ·xH ₂ O	amorphous	
R/P***	Ni	Ni+La(OH) ₃ +La ₂ O ₃		

*Copr. = coprecipitate.

**T.V. = takovite.

***R/P = reduced (at 600°C) and passivated.

TABLE 2

Nickel particle sizes calculated from XLB of the Ni(200) reflection, assuming spheres or hemi-spheres; A-series reduced at 600°C

Mol-% La	Crystal diameter (nm)	
	Spheres	Hemi-spheres
0	7.8	9.5
1	8.2	10.0
1.5	6.9	8.4
2	7.2	8.8
3	6.8	8.3
5	8.0	9.7
10	9.2	11.3
15	9.8	12.0
20	~ 10	~ 12

TABLE 3

Nickel particle sizes calculated from XLB of the Ni(200) reflection assuming spheres or hemi-spheres; B-series, reduced at 400°C or 600 °C

Mol-% La	Crystal diameter (nm)			
	Tr=400°C		Tr=600°C	
	Spheres	Hemi-spheres	Spheres	Hemi-spheres
0	8.9	10.9	11.4	14.1
1	8.2	10.0	10.2	12.5
2	~ 8.3	10.2	9.8	12.0
4	~ 7	~ 9	9.0	11.0
6	~ 7	~ 8	12.2	10.6
10	~ 10	12.5	> 100	> 100

become too low to stabilize the nickel against crystallite growth. This is in agreement with the results obtained earlier for samples without lanthanum with different Ni/Al ratios [8,9]. The samples without aluminium (A-28.6 and B-10) contained very large nickel crystallites after reduction at 600°C and did not show any discernable line broadening in addition to the instrumental broadening. However, sample B-10 reduced at 400°C consisted of relatively small crystals. This indicates that La_2O_3 does stabilize the nickel crystallites to a certain extent but very much less efficiently than does alumina.

The minimum degree of reduction of all the samples mentioned in Tables 2 and 3, as determined from the weight increase during re-oxidation, was 94%. There was no measurable influence of the amount of lanthanum on the degree of reduction. It has been suggested by Fleisch et al. [28] that La_2O_3 can be reduced to a certain extent. Because the weight loss associated with such a reduction would only be a very small part of the total weight loss in our catalyst system, this idea cannot be confirmed for our samples using TGA.

Since the influence of the lanthanum content on the crystal diameters is at most 20% at low mol percentages, we would not expect the nickel surface area to differ greatly in these samples. In contrast, the nickel surface areas of A-28.6 and of B-10 (reduced at 600°C) will be very low because of the large crystal diameters.

Carbon monoxide chemisorption

The adsorption of carbon monoxide was initially (for 1–2 min) very rapid but a constant weight was still not reached after 30 min, even though the rate

TABLE 4

Weight increase due to the adsorption of carbon monoxide (mg per g of nickel) for samples of the A-series

Mol-% La	$\Delta W(\text{rapid})$ (mg/gNi)	$\Delta W(\text{slow})$ (mg/gNi)	$\Delta W(\text{total})$ (mg/gNi)
0	25	15	40
3	28	26	54
4	33	36	69
10	27	22	49

of weight increase had become small. The values of the rapid, slow and total weight increases occurring in 30 min processes are given in Table 4 for some samples of the A-series.

The weight increase caused by the rapid part of the adsorption process is relatively constant and increases when the particle sizes (Table 2) decrease and vice versa. The changes in the slow uptake of carbon monoxide cannot be explained by the changes in the particle sizes alone and they must therefore be influenced by the lanthanum content as well.

Hydrogen chemisorption

The nickel surface area, S_{Ni} , calculated from the amount of hydrogen desorbed in the TPD apparatus (using the procedure described in the Experimental section) was calculated for samples of A-0 and A-3. For the sample of A-0, the specific nickel surface area was calculated to be 82 m² per gram of nickel. If we assume the nickel particles to be hemi-spheres which are attached to the support with their equatorial plane, then their surface-averaged diameter d_s can be calculated by using:

$$d_s = \frac{6}{\rho_{\text{Ni}} \cdot S_{\text{Ni}}} \quad (3)$$

For A-0, we find for d_s a value of 8.2 nm. The volume-averaged diameter (determined by XLB), also assuming hemi-spheres, is given in Table 2 as 9.5 nm. Since a particle size distribution is always present in these materials, it is expected that d_s will be somewhat smaller than d_v . Hence, we can conclude that hydrogen chemisorption and XLB analysis are in good agreement with each other for this sample.

The nickel surface area of sample A-3 was calculated from the amount of hydrogen desorbed to be 74 m²/g nickel. This is lower than the value found for A-0. Since the volume-averaged nickel particle size of A-3 is lower than that of A-0, we would have expected the nickel surface area to be larger. From the volume-averaged diameters given in Table 2, the estimated nickel surface area for sample A-3 was calculated to be 94 m²/g nickel, the measured value of 74 m²/g nickel is circa 80% of the expected value. Similar observations made by

Rieck and Bell [11] in a study of hydrogen chemisorption on La_2O_3 -promoted Pd/SiO_2 were ascribed to suppressed chemisorption capacities. In the case of the Pd/SiO_2 samples, the saturation coverage of the palladium was 1.03, whereas it was only 0.45 on a 4.4% $\text{La}/2\% \text{Pd}/\text{SiO}_2$ sample. In our case the saturation coverage has decreased to 0.8, so the chemisorption of hydrogen was less affected than in the case studied by Rieck and Bell.

Catalytic behaviour

Selectivity measurements were performed in a fixed-bed reactor with on-line gas analysis. No products other than methane and carbon dioxide were observed at 250 or 300°C; the carbon balance at these temperatures was within 5%. The selectivity towards methane was not influenced by the presence of lanthanum under the conditions used. The selectivity was 84–86% at 300°C and 92–93% at 250°C. However, substantial quantities of higher hydrocarbons were formed at 190°C; the selectivity towards the C_2+ fraction was circa 62% and compounds up to C_6 were found.

Since the selectivities at temperatures in the range 260–320°C were not influenced strongly by the presence of lanthanum or by the temperature, it is acceptable to use the overall rate of heat production measured with DSC in order to calculate the rate of reaction. The error introduced by assuming that only the methanation reaction occurs (and no other reactions) is at most 15%. However, when comparing different samples, this error will be much smaller, since the selectivity patterns are nearly identical.

The *activities* at 300°C (expressed as $\text{mol CO}/\text{gNi}\cdot\text{h}$) are given for the A and B-series in Figs. 7 and 8 respectively as a function of the mol-% of lanthanum. The activities increased by factors of 2.5 and 3.3 respectively at the maximum compared with the unpromoted samples. These increases are much higher than those to be expected on the basis of the particle diameters measured by XLB. It must therefore be concluded that lanthanum has a promoting effect on the methanation reaction itself and that the increase in rate is not merely due to a geometric effect.

This can also be concluded from the results of Figs. 9 and 10, in which the overall (apparent) activation energies are plotted as a function of the mol percentage lanthanum for the A and B-series respectively. The activation energy increases significantly in the presence of lanthanum.

The effect of lanthanum is almost equal in series A and B and seems to be influenced by the reduction temperature (400 or 600°C). The fact that the series of samples of the B-series reduced at 600°C have a lower activity than the series reduced at 400°C can be explained partly by the larger crystal diameters (and hence lower nickel surface areas) of the former.

The samples with the highest amounts of lanthanum had a very low activity. For the samples A-28.6 and B-10 (both reduced at 600°C), this was to be ex-

Fig. 7. Activity in the methanation reaction at 300°C (mol carbon monoxide per g nickel per hour) as a function of the mol-% lanthanum; A-series, reduced at 600°C.

Fig. 8. Activity in the methanation reaction at 300°C (mol carbon monoxide per nickel per hour) as a function of the mol-% lanthanum; B-series, reduced at 400°C (●) or 600°C (○).

Fig. 9. The overall activation energy in the methanation reaction for the A-series reduced at 600°C.

Fig. 10. The overall activation energy in the methanation reaction for the B-series reduced at 400°C (●) and 600°C (○).

pected because of the large crystal diameters (Tables 2 and 3); however, the low activity for A-20 and for B-10 reduced at 400°C must have another cause since the crystal diameters were fairly small (10–12.5 nm). It is probable that

the loss of activity was caused by the higher amount of potassium present in these samples.

In the A-series, the maximum in activity was very sharp and occurred at exactly the same composition at which the formation of crystalline $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ was observed in the uncalcined and in the calcined material; this species decomposed to La_2O_3 during reduction (see Table 1). If the diameters d_v calculated from XLB are used as a measure of the nickel surface areas (assuming an inverse relationship between d_v and S_{Ni}), the activities per m^2 nickel (in arbitrary units) can be calculated according to:

$$r(/ \text{m}^2 \text{Ni}) \simeq r(/ \text{gNi}) \cdot d_v$$

It was shown previously for samples without lanthanum that this approach gives a fairly good correlation [8]. The activity per m^2 of nickel is plotted against the mol percentage of lanthanum in Figs. 11a and b for the A and B-series respectively. It can be seen that the drop in activity (per gram of nickel) in the A-series between 4 and 5 mol-% lanthanum (Fig. 7) must be caused by crystallite growth of the nickel phase and not primarily by the formation of crystalline La_2O_3 , since the activity per m^2 of nickel remains almost constant in this region. However, it is possible that even higher specific activities would have been reached if no phase separation had occurred. The samples A-10 and A-15 have activities per m^2 of nickel which are lower than the maxima but this is probably caused by the higher potassium content of these samples. It can be seen that although (part of) the lanthanum in samples A-5, 10 and 15 is present as crystalline La_2O_3 , these materials still show a promoting effect (relative to the unpromoted sample A-0) which was observed in samples A-1 to A-4.

The activities per m^2 of nickel in the B-series after reduction at 600°C were almost the same as those of the A-series. This indicates that the nickel to aluminium ratio has no influence on the promoting action of lanthanum. The temperature of reduction does seem to influence the specific activity. The sam-

Fig. 11. Activities per m^2 nickel at 300°C (a.u.) as a function of the lanthanum content. (a) A-series $[\text{Ni}/(\text{Al} + \text{La}) = 2.5]$, reduced at 600°C ; (b) B-series $[\text{Ni}/(\text{Al} + \text{La}) = 9.0]$, reduced at 400° (●) and 600° (○).

ples of the B-series which were reduced at 400°C were slightly more active (per m² nickel) than those reduced at 600°C. However, the estimated error in the activity per m² of nickel is 10–15%. Hence, the differences for the series B reduced at 400° and 600°C do not need to be significant.

Stability tests were performed in the fixed-bed reactor using sample A-5. Only slight deactivation was observed during a test of 100 h at a temperature of 300°C; the conversion after 1.5 h on stream was 92% and after 97 h it was 70%. However, a much faster deactivation process took place under identical circumstances at 250°C; the conversion of carbon monoxide decreased from 38% after 1 h on stream to 7% after 24 h on stream. A comparable sample without lanthanum tested at the same temperature showed a decrease from 28% after 1 h to 20% after 24 h on stream; even after 120 h on stream the conversion was still 10%. This difference in behaviour must be caused by the presence of lanthanum. Either the promoter is converted into a form in which it actually deactivates the catalyst, or the presence of the promoter causes the formation of a small amount of some product or intermediate which then deactivates the catalyst.

The effect of hydrothermal ageing

A sample of A-3 which had been hydrothermally aged for 5 days showed the presence of crystalline $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ before reduction (Fig. 2); this phase was transformed into crystalline La_2O_3 during the reduction process. The nickel particle size of the aged sample was increased somewhat compared to the non-aged sample: 7.4 nm for the aged A-3 sample and 6.8 nm for the non-aged sample (both values being based on the assumption of spherical particles). However, the aged sample was much less active than the non-aged sample: $r_{300} = 1.9$ mol CO/gNi·h for the aged sample as opposed to $r_{300} = 4.4$ mol CO/gNi·h for the non-aged sample. The activity for A-0 at 300°C was 1.8 mol CO/gNi·h. The specific activities (arbitrary units, see above) were: 16.0 for the aged A-3 sample, 29.7 for the non-aged A-3 sample and 14.3 for the sample without lanthanum (A-0).

These results show that, once the lanthanum has been removed thoroughly from the uncalcined nickel–alumina phase by hydrothermal ageing, the nickel of the resultant catalyst is no longer promoted.

As was shown in Fig. 1a, the nickel phase in the samples A-5, 10 and 15 was promoted by lanthanum (both the activity and the activation energy were increased compared with the unpromoted sample). In all these samples a crystalline separated La_2O_3 phase was present. Hence, although both these samples and the hydrothermally treated sample A-3 contain separated La_2O_3 , there is some difference between them.

A promoter normally can influence the active material in a catalyst only when there is contact between them. Hence, it might seem strange that the

lanthanum in samples A-5, A-10 and A-15 still shows a promoting effect. There are two possible explanations for this phenomenon: (i) that only a small part of the lanthanum interacts with the nickel phase, the rest forming crystalline non-interacting La_2O_3 ; or (ii) that the crystalline La_2O_3 phase becomes mobile after reduction and then interacts with the nickel. The latter explanation is similar to the decoration model in SMSI catalysts [47,48]. If explanation (i) is the case, that part of the lanthanum which interacts must be restricted to some form which cannot be observed with powder-XRD (e.g. surface layers or very small crystallites).

The fact that in the hydrothermally treated sample A-3 lanthanum did not promote the nickel phase any more, indicates that the possibility of LaO_x migration to the nickel surface during the reduction process is rather unlikely. Thus, it seems that only explanation (i) is correct and that at least a part of the lanthanum of all the non-aged samples of the A-series must be interacting with the nickel throughout the whole preparation process (including calcination and reduction/passivation).

The whereabouts of lanthanum in the coprecipitates

It has been suggested by Lippens et al. [23] that lanthanum ions can be built into the takovite structure by substitution on a site normally occupied by Al^{3+} . This suggestion was based mainly on the fact that no separate lanthanum-containing phases were found in certain series. It was shown in Fig. 3 that the lattice parameter of the (012) planes of the samples of the A-series increased with increasing percentage of lanthanum, up to 4 mol-%. The value of d_{012} for the sample which contained 5 mol-% lanthanum was nearly equal to the value which was found for the unpromoted sample. Both these values were clearly lower than the values found for A-3 and A-4. The lattice spacings of the (012) planes of the hydrothermally aged sample of A-3 was significantly lowered compared with the non-aged sample of A-3. In addition to this, phase separation of $\text{La}_2\text{O}(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ occurred during the ageing process.

On substituting La^{3+} for Al^{3+} , some increase in d_{012} is expected because the radius of La^{3+} is nearly twice as large as that of Al^{3+} . According to Shannon [49], the radii are 1.032 Å and 0.535 Å respectively for octahedrally surrounded ions. In principle, all the lattice parameters should increase somewhat, some more than others. Using the law of Vegard, this increase can be theoretically calculated. However, several problems can arise. For instance, the lattice parameters measured have relatively large possible errors because the diffraction peaks are broad. Hydrothermal ageing would have solved this problem; unfortunately, however, phase separation occurs during this process. Furthermore, as was pointed out by Lippens et al. [24], the overall chemical composition of the samples can also change; they found increasing amounts of carbonate with increasing amounts of lanthanum.

We have made a theoretical calculation of the increase in d_{012} which is to be expected in a sample which contains 4 mol-% lanthanum, using the law of Vegard. It was assumed (i) that the La^{3+} substitutes for the Al^{3+} , and (ii) that the overall chemical composition remains unchanged (except for the amounts of aluminium and of lanthanum). This calculation shows that the expected increase in the value of d_{012} is 1.29%. The experimentally determined increase is $0.98 \pm 0.39\%$, the relatively large error being caused by the uncertainty in the exact position of the peak maximum.

The agreement between theoretical and experimental value is satisfactory. It can be concluded that at least 4 mol-% of lanthanum can be built into the takovite compound. This is a meta-stable situation because phase separation occurs in hydrothermally treated samples with lanthanum contents below 4 mol-% (Fig. 2). Above 4 mol-% lanthanum, phase separation occurred without hydrothermal treatment.

The role of lanthanum in the methanation reaction

As was mentioned in the Introduction, all investigations on lanthanum promotion have led to the conclusion that lanthanum enhances the activity of various catalysts for the methanation reaction. Furthermore it has been shown by most of the authors that the apparent activation energy increases. Several possible causes for these effects have been given. For instance, Inui et al. [18–20] suggested that the increase in activity was caused by a better dispersion of their nickel phase. Schaper et al. [22] performed kinetic measurements on their nickel–alumina materials; from an analysis of their data, they concluded that lanthanum lowered the heats of adsorption of both hydrogen and carbon monoxide, the value for the adsorption of carbon monoxide being lowered more than that for hydrogen. Hicks, Bell and co-workers [11] claimed that the increased activity of lanthanum-promoted Pd/SiO_2 stems from an increased rate of the dissociation of carbon monoxide, together with a suppression of the amount of strongly bound carbon monoxide.

The interpretation of Inui et al. [18–20] cannot explain the effects of lanthanum in our case, since we have shown above that the activity per m^2 of nickel surface is altered. We also feel, along with the other authors mentioned, that the adsorption of the reactants plays an important role in determining the catalytic activity in the methanation reaction. As was shown in Table 4, the amount of carbon monoxide which adsorbs rapidly at 200°C (thought to be strong adsorption) remains almost constant; the amount of slowly adsorbed carbon monoxide increased and decreased in parallel with the catalytic activity. It could thus well be that the catalytic activity is associated with the slowly adsorbed carbon monoxide. However, further experiments are necessary to investigate the role of each type of carbon monoxide in the formation of meth-

ane. Our results do not show any suppression of carbon monoxide adsorption as observed by Rieck and Bell [11] with their La_2O_3 -promoted Pd/ SiO_2 system.

We also have investigated TiO_2 -promoted nickel-alumina catalysts [15]. These materials showed typical SMSI properties: suppression of both hydrogen and carbon monoxide adsorption and increased activity. The apparent activation energy in the methanation reaction over these materials was lowered compared to that for the unpromoted nickel-alumina material. This could be explained in terms of lower heats of adsorption of both carbon monoxide and hydrogen, this giving rise to a more favourable ratio between the amounts of adsorbed carbon monoxide and hydrogen. The results presented above for La_2O_3 -promoted nickel-alumina showed that the apparent activation energy for the methanation reaction is increased by the addition of the promoter. Furthermore it was shown that no suppression of rapid carbon monoxide adsorption occurred. Both results indicate that La_2O_3 and TiO_2 behave differently as promoters.

CONCLUSIONS

The methanation of carbon monoxide over nickel-alumina catalysts is enhanced by the addition of La_2O_3 . At low percentages of lanthanum, the promoter is built into the precursor structure during the coprecipitation process. This is a meta-stable situation and care must be taken to avoid a thorough thermal ageing as this irreversibly separates the promoter and the active material and inhibits the promoting action. The increase in activity with increasing lanthanum content is accompanied by an increase in apparent activation energy. The specific activity of lanthanum promoted nickel-alumina at its maximum is twice as high as that of the unpromoted material. In a series with molar ratios of nickel to (La + Al) of 2.5, the optimum activity is reached at 4 mol-% lanthanum; in the other series with a ratio of 9 the optimum is found at 6 mol-%. Above these optimum values, the activity per gram of nickel decreases because of both increasing particle sizes and increasing amounts of potassium, a poison for the reaction. Alumina is required to stabilize the nickel crystallites against sintering. The promoting action of La_2O_3 is slightly stronger after reduction at 400°C than after reduction at 600°C. Lanthanum increases the amount of carbon monoxide which is adsorbed slowly but does not alter the amount of rapidly adsorbed carbon monoxide; it also suppresses somewhat the amount of adsorbed hydrogen.

ACKNOWLEDGEMENTS

We should like to thank Hans Weber for performing the chemical analyses, Jaap Boeijma for his help in XRD measurements, and George van de Velde for helpful discussions.

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