Nickel catalysts for internal reforming in molten carbonate fuel cells

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Abstract

Natural gas may be used instead of hydrogen as fuel for the molten carbonate fuel cell (MCFC) by steam reforming the natural gas inside the MCFC, using a nickel catalyst (internal reforming). The severe conditions inside the MCFC, however, require that the catalyst has a very high stability. In order to find suitable types of nickel catalysts and to obtain more knowledge about the deactivation mechanism(s) occurring during internal reforming, a series of nickel catalysts was prepared and subjected to stability tests at 973 K in an atmosphere containing steam and lithium and potassium hydroxide vapours. All the catalysts prepared showed a significant growth of the nickel crystallites during the test, especially one based on α -Al₂O₃ and a coprecipitated Ni/Al₂O₃ sample having a very high nickel content. However, this growth of nickel crystallites only partially explained the very strong deactivation observed in most cases. Only a coprecipitated nickel/alumina catalyst with high alumina content and a deposition–precipitation catalyst showed satisfactory residual activities. Addition of magnesium or lanthanum oxide to a coprecipitated nickel/alumina catalyst decreased the stability.

Adsorption and retention of the alkali was the most important factor determining the stability of a catalyst in an atmosphere containing alkali hydroxides. This is because the catalyst bed may remain active if a small part of the catalyst bed retains all the alkali.

Keywords: Molten carbonate fuel cell; Nickel; Steam reforming; Lithium; Potassium; Deactivation

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1. Introduction

The molten carbonate fuel cell (MCFC) is likely to be commercialised soon (Hirschenhofer [1]). This cell operates at about 923 K and requires hydrogen as fuel; the hydrogen is usually obtained from natural gas (according to Eq. (1)) or from naphtha by steam reforming in a separate unit (external reforming).

Another possible source of hydrogen is the reforming of natural gas within the fuel cell (internal reforming). The catalyst particles may then be positioned in the anode gas compartment within the corrugations of the plate separating the anode from the cathode of the next cell of the stack, see Fig. 1.

Internal reforming has attracted considerable attention because it offers several extra advantages in comparison with external reforming: (i) the all-over efficiency of the fuel cell increases due to the consumption of the heat evolved in the cell reaction by the endothermic reforming reaction; this heat consumption is about half of the heat production caused by the current flowing through the internal resistances and by the reversible energy losses in the MCFC [2]; (ii) the water required for the steam-reforming reaction is partially provided by the fuel cell reaction; (iii) there is a more evenly distributed supply of hydrogen over the anode compartment; and (iv) the equilibrium conversion in the steam-reforming reaction (Eq. (1)) is further to the right due to the in situ consumption of hydrogen.

Internal reforming, however, requires substantial adaptation of the MCFC construction to allow the catalyst to be incorporated. Of even more importance is that the catalyst is gradually affected by alkali carbonate originating from the electrolyte, a mixture of 62 mol.% Li_2CO_3 and 38 mol.% K_2CO_3 [3,4]. Small amounts of this electrolyte gradually migrate towards the catalyst during operation.

Fig. 1. Cross-sectional view of the repeating unit of a molten carbonate fuel cell stack containing catalyst for internal reforming.

Research on the suppression of deactivation of internal reforming catalysts has mainly been concerned with nickel supported on alkali-resistant supports such as MgO [3–9], γ -LiAlO₂ [3,7] and α -LiAlO₂ [8]. The majority of these publications have shown successful results with these catalysts; however, the times of operation were in many cases rather short and/or the test conditions were less severe than normally encountered under practical conditions.

Because the predominating deactivation mechanism under MCFC conditions is still not clear and mechanisms other than reaction of the support with alkali may be more important, it cannot be concluded that nickel catalysts based on supports not having a high resistance to alkalis do not have better stabilities.

In another paper [10] it is shown that the alkali in the MCFC is predominantly transported from the molten mixture of alkali carbonates towards the catalyst through the vapour phase as LiOH and KOH. All aluminium-containing samples (including α -Al₂O₃) were found to take up alkali hydroxide from the gas phase very rapidly; in contrast, Ni/MgO and Ni/SiO₂ samples hardly took up any alkali hydroxide from the gas phase even though these samples sintered strongly in the presence of the alkali hydroxide vapour.

This paper is concerned with the effect of alkali hydroxide vapour on the steam-reforming activity and other characteristics of different nickel catalysts and with determining the most important causes of deactivation. The deactivation due to deposition of alkali hydroxide vapour may occur in several different ways: (i) pore filling; (ii) pore plugging; (iii) coverage of the surface of the nickel crystallites; (iv) decrease of the specific activity; and (v) enhanced sintering of the nickel crystallites and/or the support. Once the alkali hydroxide is present on the catalyst surface, it can be retransformed to the corresponding alkali carbonate or be converted into other alkali compounds. In order to gain a greater understanding of the deactivation mechanism, a series of stability tests was performed in which alkali hydroxide vapour was slowly added to the catalyst and the steam-reforming activity of the catalyst was measured continuously. The deactivated catalysts were characterised using several techniques.

2. Experimental

2.1. Catalyst preparation

Two catalysts were prepared by impregnation, using the incipient wetness technique with γ -Al₂O₃ and α -Al₂O₃ as supports. The Ni/ γ -Al₂O₃ sample denoted hereafter as I- γ Al was prepared by vacuum impregnation of 10 g of γ -Al₂O₃ extrudates (Akzo alumina 000-1.5E, pore volume = 0.46 cm³ g⁻¹, BET surface area = 188 m² g⁻¹) at 323 K with ca. 4 mol dm⁻³ nickel nitrate. The Ni/ α -Al₂O₃ sample, denoted as I- α Al, was prepared by four-fold impreg-

nation of 10 g of Raschig rings of α -Al₂O₃ (Dycat, 26/RMS E002.B, pore volume = 0.28 cm³ g⁻¹, BET surface area = 0.22 m² g⁻¹) with ca. 3 mol dm⁻³ nickel nitrate and ca. 1 mol dm⁻³ aluminium nitrate; the aluminium nitrate was co-impregnated in order to improve the resistance to sintering [11]. The material was dried at 393 K and calcined at 573 K in air between each of the impregnation steps.

A series of catalysts containing various combinations of Ni, Al, Mg and La was prepared by coprecipitation using the constant pH method [12,13], yielding about 10 g of catalyst, using the metal nitrates and potassium carbonate as base. Each coprecipitate was filtered off and washed once thoroughly with 1 dm³ of hot deionised water (353 K); it was finally dried in an oven at 353 K overnight. The coprecipitated catalysts are indicated by the prefix C, followed by the ratios of the metal ions used.

The deposition–precipitation was performed according to the method as described by Schaper et al. [14,15]. This catalyst is denoted hereafter by DP.

The catalyst precursors were calcined in a tube furnace in flowing air (200 cm³ min⁻¹), using a heating rate of 2 K min⁻¹ up to a final temperature of 723, 773, 873, or 1073 K, this being maintained for 5 h. Reduction was then carried out in the same tube furnace in 170 cm³ min⁻¹ of 70% H₂ in N₂ using a heating rate of 2 K min⁻¹ to a final temperature of 973 K, this being maintained for 5 h. After cooling to room temperature and flushing with nitrogen, the samples were passivated in 0.75% O₂ in N₂ (200 cm³ min⁻¹) for at least 5 h.

The chemical compositions of the catalysts after calcination and reduction calculated from the atomic absorption spectrometry analyses are shown in Table 1.

The powders prepared by coprecipitation were pressed isostatically at 4000 bar. The resulting lumps and also the extrudates and the Raschig rings were crushed and sieved to give sieve fractions with particle diameters between 0.125 and 0.3 mm for use in the activity and stability measurements.

Table 1
Catalyst composition in wt.% (after reduction)

Catalyst	Ni	Al	La	Mg	K
I- α Al	14.7	n.d.	–	–	–
I- γ Al	13.0	n.d.	–	–	–
C-Ni ₃ Al	78.7	11.2	–	–	0.06
C-NiAl ₃	26.8	38.7	–	–	0.09
C-NiAl _{2.5} La _{0.5}	18.6	24.0	7.9	–	0.03
C-NiAl ₂ Mg	30.8	28.7	–	9.0	0.09
C-NiMg ₃	29.4	–	–	n.d.	n.d.
DP	19.4	40.6	–	–	0.63

n.d.: not determined.

2.2. Stability tests

All the stability tests were performed at 973 K and ca. 1.2 bar. The temperature of 973 K is 50 K higher than the operation temperature of the MCFC and was chosen to allow comparison of the different materials within a relatively short period of time.

The reactor configuration used (Fig. 2) was designed to prevent surface creep of alkali from the impregnated LiAlO_2 towards the catalyst. It consisted of two alumina tubes (each of internal diameter 0.4 cm and length 32.5 cm) fitted inside a quartz tube (length 66 cm, internal diameter 0.9 cm) there being a distance of 1.0 cm between the alumina tubes. A short packed bed containing 200 mg of LiAlO_2 grains (mean pore diameter 0.4 μm , pore volume 0.41 $\text{cm}^3 \text{g}^{-1}$, grain size 0.3–0.6 mm) impregnated with $\text{Li}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ (molar ratio 62:38; 9.8 wt.% of K) between two alumina wool plugs of about 5 mg each (ICI Saffil alumina fibre, calcined at 1473 K for 3 h, $S_{\text{BET}} = 12 \text{ m}^2 \text{g}^{-1}$) was positioned in the lower end of the upper alumina tube. About 80 mg of the catalyst (grain size 0.125–0.3 mm), held between two separate alumina plugs, was positioned in the upper end of the lower alumina tube. The reactor temperature was controlled by a thermocouple which was positioned between the reactor and the oven wall. In all tests, the reactor was heated and cooled in a H_2/He (35/65) mixture.

Initially, several tests were performed to investigate the rate of alkali transport from the impregnated LiAlO_2 grains positioned in the upper alumina tube towards the lower alumina tube. This is necessary for interpretation of the results obtained from the stability tests. $\gamma\text{-Al}_2\text{O}_3$ was used on the position of the catalyst since it adsorbs alkali vapour strongly [10]. The rate was measured by varying the duration of the test and/or by varying the CO_2 content of the gas (and consequently the vapour pressures of the alkali hydroxides [10]), followed

Fig. 2. The reactor used for the stability test in alkali hydroxide vapour (TIC = temperature indicator and controller).

by chemical analysis of the samples. For this, the following three sets of conditions were used.

Set A: 111 cm³(stp) min⁻¹ containing 0.7% CH₄, 3.6% H₂, 50% H₂O, and 45.7% He;

Set B: 111 cm³(stp) min⁻¹ containing 0.7% CH₄, 3.6% H₂, 50% H₂O, 0.3% CO₂ and 45.4% He.

Set C: 50 cm³(stp) min⁻¹ containing 4.0% CH₄, 20% H₂, 20% H₂O, 45% CO₂ and 11% He.

For the stability experiments, the sets of conditions A and C were used. A low concentration of methane was used to prevent a large local temperature drop inside the catalyst bed due to the endothermic steam-reforming reaction. The duration of the tests using Set A was always 161 h. Set C represents better a typical gas composition for internal reforming than does Set A; however, the presence of CO₂ suppresses the evaporation of the alkali to such an extent that very long test durations of 600–880 h were required. During the tests, the alkali hydroxide vapour was gradually transported with the (downward) gas flow towards the catalyst.

The conversions of methane were measured regularly and the samples of 200 µl were analyzed using a gas chromatograph (Varian Type 3300) equipped with Porapak Q columns maintained at 333 K using He as carrier gas. The reaction rates (r , moles CH₄ g_{cat}⁻¹ s⁻¹) were calculated from the conversion of methane (α) assuming plug flow (Dautzenberg [16]) and that the reaction was first order in methane and zero in steam [17–19]:

$$r = k[\text{CH}_4] \text{ where } k = \ln\left(\frac{1}{1 - \alpha}\right) \frac{\phi_{\text{tot}}}{m} \quad (1,2)$$

where k is the reaction rate constant (m³ g_{cat}⁻¹ s⁻¹), [CH₄] is the methane concentration (mol m⁻³), α is the methane conversion, ϕ_{tot} is the total gas flow rate at reactor conditions (m³ s⁻¹), and m is the weight of catalyst (g). Values of the rate coefficients above about $200 \cdot 10^{-6}$ m³ g_{cat}⁻¹ s⁻¹ could not be measured accurately because they were calculated from methane conversions greater than 93% under which conditions there was significant limitation for diffusion and heat transport.

After the test, the reactor was cooled to room temperature. The impregnated LiAlO₂ and the alumina plugs were all weighed to estimate the amount of alkali transported. Several samples were also analyzed chemically for their alkali contents.

2.3. Characterisation techniques

X-ray diffraction patterns were recorded with a Philips PW 1710 diffractometer using Cu K α radiation at room temperature and in air. The crystallite sizes

(*D*) of the nickel, nickel oxide and several other compounds were estimated by X-ray line broadening (XLB), using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where *K* is the Scherrer constant, λ is the wavelength of the radiation and β is the peak width in rad at half the peak maximum. (The peak width was corrected for instrumental line broadening, measured using a sample with nickel crystallites larger than 300 nm, and for broadening caused by $K\alpha_1$ – $K\alpha_2$ division, using the Jones-(b) correction curve [20].) The Scherrer constant (*K*) used was 1.495; this consists of a factor of 0.89 to correct for the fact that the peak width at half maximum instead of the integral peak width is used and another factor of 1.680 [21,22] to take into account the hemispherical rather than the cubic shape of the nickel crystallites.

Nitrogen adsorption/desorption isotherms at 77 K were obtained using a Micromeritics ASAP 2400 system. The values of the specific surface areas (S_{BET}) were calculated using the BET method while the values of the total pore volume (V_p) of the pores with radii smaller than 20 nm (assumed to be cylindrical) were calculated from the adsorption isotherms.

Hydrogen chemisorption for measuring the specific nickel surface areas was carried out using a Micromeritics Pulse Chemisorb 2700 adsorption system. 52.2 μl pulses of mixture of 5.85% hydrogen in argon ($15 \text{ cm}^3(\text{stp}) \text{ min}^{-1}$) were passed through about 50 mg of the sample. The total amount of hydrogen adsorbed was determined by measuring with a TCD the amounts of hydrogen remaining in the gas phase after the passage of each pulse. The nickel surface area was calculated by assuming an adsorption stoichiometry of $\text{H}:\text{Ni} = 1:1$ and a number of $1.54 \cdot 10^{19}$ Ni sites per m^2 (Rostrup-Nielsen [17]). The average nickel crystallite sizes were calculated from the metallic surface areas by assuming a hemispherical crystallite shape.

Transmission electron microscopy was carried out using a JEOL 200CX electron microscope operated at 200 kV. The TEM specimens were prepared by ultrasonically dispersing powdered samples in ethanol and then applying drops of this suspension onto a carbon film supported on a copper grid.

Auger electron spectroscopy (AES) was used to study the outer surface of the catalyst grains. It was carried out using a Perkin Elmer PHI 600 scanning Auger microprobe. Specimens for Auger analysis were prepared by pressing the catalyst particles into an indium foil. The surface concentrations of the elements were determined by measuring the peak-to-peak distances in the differentiated AES spectra after correction for the relative AES peak intensities. Li could not be detected quantitatively. Depth profiles were obtained by etching the surface with an argon ion beam. A surface etching area of $2 \text{ mm} \times 2 \text{ mm}$ was used; using this area, a reference Ta_2O_5 sample was found to be etched at a rate of 12 nm min^{-1} .

3. Results and discussion

3.1. Rate of alkali transport

The results of the tests to investigate the rate of alkali transport in the test reactor using $\gamma\text{-Al}_2\text{O}_3$ on the position of the catalyst are shown in Table 2. The K contents of the impregnated LiAlO_2 and the $\gamma\text{-Al}_2\text{O}_3$ grains are shown as a function of time in Fig. 3. The results show that the vaporisation of alkali from the bed of impregnated LiAlO_2 grains occurred rapidly; both the K and the Li (not shown) vaporised totally within about 40 h of operation when the standard gas flow was used. The figure also shows that the rate at which the K arrived at the $\gamma\text{-Al}_2\text{O}_3$ was lower than that at which it was transported away from the LiAlO_2 ; it took roughly 100 h before the rate of increase of alkali concentration in the $\gamma\text{-Al}_2\text{O}_3$ approached zero. About 50% of the total amount of K and only about 5% of the Li was finally transported from the LiAlO_2 towards the $\gamma\text{-Al}_2\text{O}_3$; this resulted in a Li content of about 0.35 wt.% and a K content of about 12.3 wt.%. The loss of alkali on the way from the impregnated LiAlO_2 to the $\gamma\text{-Al}_2\text{O}_3$ and the slow transport of the alkali mentioned above were probably caused by adsorption and reaction with the surrounding quartz tube and the alumina wool plugs used to support the grains of impregnated LiAlO_2 and the adsorbent bed. Table 2 also shows that the addition of CO_2 to the gas substantially retarded the rate of alkali transport as a consequence of lowering the partial pressures of the alkali hydroxides [10].

3.2. Catalyst behaviour during the stability tests

The steam-reforming activities of the catalysts were measured continuously during the stability tests and the results of the tests in which the gas flow of Set A was used are shown for a number of catalysts in Figs. 4–6. For reasons of

Table 2

Measured alkali contents in the $\gamma\text{-Al}_2\text{O}_3$ bed after different times of operation using different gas compositions

Time on stream (h)	Amounts of alkali (metal) present in the $\gamma\text{-Al}_2\text{O}_3$ grains (mg)					
	Lithium			Potassium		
	0% CO_2 ^a	0.5% CO_2 ^a	45% CO_2 ^a	0% CO_2 ^a	0.5% CO_2 ^a	45% CO_2 ^a
0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
10	0.01	n.d.	n.d.	0.42	n.d.	n.d.
35	0.02	< 0.01	n.d.	1.49	0.28	n.d.
88	0.35	< 0.01	< 0.01	7.35	0.25	0.14
100	0.21	n.d.	n.d.	9.47	n.d.	n.d.
161	0.29	n.d.	n.d.	10.6	n.d.	n.d.

n.d.: not determined.

^a Concentration of CO_2 in the gas flow (for further details, see Section 2).

Fig. 3. Amount of K in the bed of impregnated LiAlO_2 grains and that in the bed of $\gamma\text{-Al}_2\text{O}_3$ at the position of the catalyst during the stability test when the gas flow of Set A, containing 0% CO_2 , was used.

clarity and to make a clear distinction between the different curves presented in the figures, only a limited number of the measured points are shown for each catalyst. The numerical values of the initial and final activities of all the catalysts tested, as well as the observed weights before and after the tests, the

Fig. 4. Reaction rate coefficients of the impregnated catalysts as a function of time during the stability test using the gas flow of Set A: (Δ) I- α Al, 80 mg, ($\blacktriangle$) I- α Al, 160 mg, ($\bullet$) I- γ Al.

Fig. 5. Reaction rate coefficients of several coprecipitated catalysts as a function of time during the stability test using the gas flow of Set A: (▲) C-Ni₃Al, (●) C-NiAl₃, (△) C-NiAl₂Mg, (○) C-NiAl_{2.5}La_{0.5}.

estimated alkali contents after the test and the physical condition of the samples after the test are shown in Table 3.

Fig. 4 gives the performances obtained for the catalysts I- α Al and I- γ Al prepared by impregnation of α -Al₂O₃ and γ -Al₂O₃ respectively; both showed a

Fig. 6. Reaction rate coefficients of several other catalysts as a function of time during the stability test using the gas flow of Set A: (▲) C-NiMg₃, (●) DP, (○) NiO/ γ -Al₂O₃ (see Note 6, Table 3), (△) Ni (see Note 7, Table 3).

Table 3
Characteristics of the catalysts after the stability test

Catalyst	Ni wt. %	T_{cat} (K)	Gas flow ^a	Reaction rate coefficients ($\text{m}^3 \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$)		Weight change (%)	Estimated ^d alkali content (wt. %)		Physical condition after the test
				Start ^b	End ^c		Li	K	
I- α Al	14.7	873	Set A	$9.1 \cdot 10^{-6}$	$2.0 \cdot 10^{-6}$	+14.8	0.24	8.6	Top 30% sticky
I- α Al, 160 mg	14.7	873	Set A	$9.1 \cdot 10^{-6}$	$6.1 \cdot 10^{-6}$	+5.3	0.10	3.4	Top 25% sticky
I- γ Al	13.0	873	Set A	$2.2 \cdot 10^{-5}$	$6.7 \cdot 10^{-6}$	+12.8	0.28	10.1	Top 30% sticky
C-Ni ₃ Al	78.7	723	Set A	$9.2 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	-7.6	^e	^e	Very sticky
C-NiAl ₃	26.8	873	Set A	$8.7 \cdot 10^{-5}$	$2.4 \cdot 10^{-4}$	+0.2	0.07	2.6	Upper part slightly sticky
C-NiAl _{2.5} La _{0.5}	18.6	873	Set A	$3.1 \cdot 10^{-5}$	$1.1 \cdot 10^{-5}$	+14.3	0.30	10.8	Slightly sticky
C-NiAl ₂ Mg	30.8	1073	Set A	$4.6 \cdot 10^{-5}$	$2.1 \cdot 10^{-5}$	+7.7	0.21	7.5	Top 20% stuck together
C-NiMg ₃	29.4	773	Set A	$6.9 \cdot 10^{-6}$	$3.1 \cdot 10^{-5}$	-8.0	^e	^e	Unchanged
DP	19.4	873	Set A	$4.6 \cdot 10^{-5}$	$3.6 \cdot 10^{-4}$	+10.5	0.25	8.7	Top 25% sticky
NiO/ γ -Al ₂ O ₃ ^f	21.0	—	Set A	$5.1 \cdot 10^{-6}$	$2.0 \cdot 10^{-6}$	+6.4	0.19	6.8	Top 20% sticky
Ni ^g	100	773	Set A	$2.3 \cdot 10^{-4}$	$0.9 \cdot 10^{-6}$	-1.0	^e	^e	Single lump, not sticky
C-NiAl ₂ Mg	30.8	1073	Set C	$4.6 \cdot 10^{-5}$	$1.1 \cdot 10^{-5}$	-0.7	0.08	2.9	Slightly sticky
DP	19.4	873	Set C	$4.6 \cdot 10^{-5}$	$3.5 \cdot 10^{-5}$	-6.4	^e	^e	Unchanged

^a See Section 2.

^b Reaction rate coefficients measured at 673 K, taken from Ref. [24]; the values given for the samples NiO/ γ -Al₂O₃ and Ni, however, were measured at 973 K.

^c Reaction rate coefficients measured at the end of the deactivation test.

^d Due to the small amounts of material per sample, only the Li and K contents of some samples not included in this paper were determined by chemical analysis. From these results followed that the alkali contents of the samples shown in the table could be estimated reasonably from the weight changes observed by using four assumptions: (a) Li is present in the samples as LiAlO₂ or Li₂O; (b) K is present as KOH; (c) the Li/K ratios are equal to those of the γ -Al₂O₃ samples used to determine the rate of alkali transport (Table 2); and (d) the samples with large surface areas ($S_{\text{BET}} > 50 \text{ m}^2 \text{g}^{-1}$) lose 5% of their weight upon heating (due to loss of adsorbed water).

^e These values are not shown because the estimation resulted in small negative alkali contents.

^f Physical mixture of NiO powder (BDH) and γ -Al₂O₃ powder, isostatically pressed at 4000 bar and crushed and sieved to yield a particle size between 0.15 and 0.30 mm.

^g Nickel obtained from nickel nitrate hexahydrate by calcination at 773 K and reduction at 673 K, followed by sieving to yield a particle size between 0.15 and 0.30 mm.

rather rapid decrease of the activity during the test. The catalyst I- γ Al deactivated less rapidly than the catalyst I- α Al, but its activity approached that of the latter after 80 h. The influence of doubling the amount of catalyst was examined for the catalyst I- α Al. The period for which the activity was higher than $100 \cdot 10^{-6} \text{ m}^3 \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$ was increased but there was only a slight increase in the final activity.

Fig. 5 shows that better results were obtained for the aluminium-containing coprecipitated catalysts. The catalyst C-NiAl₃ was more stable than the other coprecipitated catalysts, including C-NiMg₃ (Fig. 6). An increase of the nickel content or the addition of La or Mg thus apparently decreased the stability. A

stability even better than that of C-NiAl₃ was found for the deposition–precipitation catalyst DP (see Fig. 6, after about 140 h of operation the activity dropped slowly below a value of $400 \cdot 10^{-6} \text{ m}^3 \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1}$).

The Ni/MgO catalyst showed an unusual behaviour during the stability test (see Fig. 6); after a very rapid deactivation over the first 10–20 h, the catalyst regained activity significantly over the following 20 h (to give a value of about $40 \cdot 10^{-6} \text{ m}^3 \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1}$) and then gradually deactivated again. Fig. 6 also shows the results obtained for pure nickel and for a physical mixture of NiO and γ -Al₂O₃; both materials had a very low activity from the beginning of the test.

The final activities of most of the catalysts, given in Table 3, appear to be insufficient to allow them to be used in the IR-MCFC: a conservative value of the minimum steam-reforming activity required at 973 K was estimated to be $5.4 \cdot 10^{-5} \text{ m}^3 \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1}$ under typical IR-MCFC operation conditions [23]. Only for the catalysts C-NiAl₃ and DP were the final reaction rate coefficients higher than the value minimum required for application in IR-MCFC.

Table 3 also shows some other characteristics of the catalysts after the tests. Due to the amounts of alkali taken up, the weight of the samples had usually increased. These weight increases are used to estimate the total alkali uptake of the catalyst, see Table 3. The physical condition of the catalysts at the end of the tests is described briefly in the last column the table. In many cases, the upper part of the catalyst bed was sticky; this probably being caused by the adsorption of water vapour from the atmosphere on the K and/or Li species (presumably KOH); such species are hygroscopic and were probably present on the outer surface of the catalyst grains. It is likely that the sticky parts of the catalyst samples contained the main part of the alkali taken up; it thus appears that the majority of the alkali did not migrate through the whole catalyst bed in these cases. This was confirmed by the results of chemical analysis of the sticky upper part and the non-sticky lower part of the γ -Al₂O₃ sample removed from the reactor after 88 h on stream in the gas flow of set A; the upper part contained 1.0 wt.% Li and 20.2 wt.% K while the lower part only contained 0.03 wt.% Li and 1.1 wt.% K.

The relatively high residual activities for the catalysts C-NiAl₃ and DP suggest that these samples retained the alkali very strongly in the upper part of the bed, thus preventing poisoning of the lower part of these samples. The difference in stability found for these catalysts and that found for the impregnated Ni/ γ -Al₂O₃ catalyst can be explained by the higher resistance to sintering of the nickel crystallites in the catalysts C-NiAl₃ and DP due to the stronger nickel–support interaction arising from the preparation technique based on precipitation. The presence of magnesium and lanthanum oxide in the coprecipitated catalysts may have decreased the stability as a result of the interaction of these species with the alumina which results in turn in a weaker interaction with the alkali. Although the geometry of the reactor does not resemble the real MCFC configuration, it seems likely that a strong retention of the alkali on a

small part of the catalyst will also enhance the stability of the catalyst under practical conditions.

The alkali content of the catalyst C-Ni₃Al after the test (see Table 3) was estimated to be negligible; however, the observation that the sample was very sticky after the test indicates that it must at least contain a small amount of alkali. A considerable proportion of the alkali thus migrated through the whole catalyst bed, thereby causing almost total deactivation. This also explains the weight increase of the alumina wool plug below this catalyst observed after the test and the fact that this plug was rather sticky after the test.

The unusual deactivation behaviour found for the C-NiMg₃ catalyst (Fig. 6) was probably caused by a very weak interaction of alkali with the Ni and MgO, as indicated by the absence of any increase of weight of the catalyst during the deactivation test. The alkali probably migrated rapidly through the catalyst bed in the beginning of the test, thereby causing almost immediate deactivation of the catalyst and sintering of the MgO; as the test progressed and the partial pressure of the alkali in the feed decreased, the rate of alkali transport out of the catalyst bed probably increased to such an extent that the alkali content of the catalyst bed started to decrease and the activity increased once more.

The two catalysts C-NiAl₂Mg and DP were also tested using a gas flow containing 45% CO₂. The activities of these two catalysts as a function of time are shown in Fig. 7; note that the scale of the time axis is larger than that in Figs. 4–6. Reaction rate coefficients higher than $115 \cdot 10^{-6} \text{ m}^3 \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1}$ could not be measured because of approaching the steam-reforming equilibrium composition. The presence of CO₂ clearly retarded the deactivation but it did

Fig. 7. Reaction rate coefficients of two catalysts as a function of time during the stability test using the gas flow of Set C, containing 45% CO₂: (▲) C-NiAl₂Mg, (●) DP.

Table 4
Results of pre-test and post-test XRD analyses

Catalyst	Ni wt. %	Gas flow	D_{Ni} (nm)		Other phases
			Pre-test	Post-test ^a	
I- α Al	14.7	Set A	47	U: n.d., L: > 100	L: α -Al ₂ O ₃ , γ -LiAlO ₂ , X ^b
I- α Al, 160 mg	14.7	Set A	47	U, L: > 100	U and L: α -Al ₂ O ₃ , X ^b
I- γ Al	13.0	Set A	14	U: n.d., L: 78	L: γ -Al ₂ O ₃
C-Ni ₃ Al	78.7	Set A	12	> 100	X ^b
C-NiAl ₃	26.8	Set A	21	~ 100	γ -Al ₂ O ₃ , X ^b
C-NiAl _{2.5} La _{0.5}	18.6	Set A	7.8	~ 100	LaAlO ₃ , X ^b , (K ₂ CO ₃ ?)
C-NiAl ₂ Mg	30.8	Set A	16	U: n.d., L: 57	L: MgAl ₂ O ₄ , MgO, X ^b
C-NiMg ₃	29.4	Set A	12	76	MgO
DP	19.4	Set A	18	U: n.d., L: ~ 90	L: γ -Al ₂ O ₃ , α -Al ₂ O ₃ (traces)
NiO/ γ -Al ₂ O ₃	21.0	Set A	> 100	U: n.d., L: > 100	L: γ -Al ₂ O ₃ , X ^b
Ni	100	Set A	76	> 100	—
C-NiAl ₂ Mg	30.8	Set C	16	~ 90	MgAl ₂ O ₄
DP	19.4	Set C	18	70	γ -Al ₂ O ₃

n.d.: not detected.

^a U = upper part, L = lower part.

^b Phase(s) with reflections at about 18.7°, 20.3° and 40.5° (see text).

not decrease the extent of deactivation (see also Table 3). It thus appears that an atmosphere with only a low partial pressure of alkali can also deactivate the catalyst significantly, although it needs a longer period of time.

It should be noted that the water–gas shift equilibrium was always attained when the rates of the steam-reforming reaction were higher than $1 \cdot 10^{-5} \text{ m}^3 \text{ g}_{\text{cat}}^{-1} \text{ s}^{-1}$.

3.3. Further characterisation of the deactivated catalysts

The nature of the crystalline phases and the nickel crystallite sizes of the deactivated catalysts were determined by X-ray diffraction (XRD) and X-ray line broadening and the results are shown in Table 4.

The XRD patterns generally showed narrow nickel peaks due to large size of the nickel crystallites. The nickel crystallites of the nickel/alumina catalysts which did not contain a large amount of high-surface-area alumina (i.e. I- α Al, C-Ni₃Al) sintered extensively. The catalysts containing magnesia (C-NiAl₂Mg and C-NiMg₃) had smaller nickel crystallites after the test than had the other catalysts; however, these catalysts did not have the highest final activities. All the nickel crystallite sizes found after the test were significantly larger than those obtained after sintering in a steam-containing atmosphere without the addition of alkali vapour at 1073 K [24]; this indicates that alkali enhances sintering of the nickel crystallites much more strongly than does steam. Enhanced sintering of metal crystallites by the presence of alkali metal ions has

been reported before. A well-known example is that of the K-promoted iron catalyst used for ammonia synthesis [25]. Enhanced sintering of the metal crystallites due to Li^+ and K^+ has also been observed for nickel catalysts supported on SiO_2 [26] and MgO [27].

The deactivation test had little effect on the nature of the crystalline phases present in the catalysts in most of the samples. However, part of the alumina present in the $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ catalyst had reacted to form $\gamma\text{-LiAlO}_2$; the perovskite compound LaAlO_3 had formed in the catalyst $\text{C-NiAl}_{2.5}\text{La}_{0.5}$; and a small part of the MgAl_2O_4 of the $\text{C-NiAl}_2\text{Mg}$ catalyst was dealuminised to give MgO . The MgO of the catalyst C-NiMg_3 did not react with alkali; however, the alkali caused extensive sintering of the MgO crystallites, the average size had increasing from 12 nm to more than 200 nm. Several samples also showed reflections which could not be assigned to known phases. The reflections at about 18.7° , 20.3° and 40.5° appeared most frequently and were therefore assumed to arise from an unknown phase X. The absence of K-containing crystalline phases indicates the presence of one or more amorphous alkali-containing compound(s). It seems likely that alkali-containing phases had dissolved in water originating from the atmosphere prior to and during the XRD analysis.

Finally, the results of Table 4 also show that the milder but much longer stability test carried out using the gas flow containing 45% CO_2 caused about the same extent of sintering of the nickel crystallites but did not visibly affect the crystalline structure of the support.

The specific surface areas (S_{BET}) and pore volumes (V_p) of some of the catalysts were measured by nitrogen physisorption before and after the deactivation test and the results are shown in Table 5. In those cases that the gas flow of Set A was used, both the surface area and the pore volume with pore radii smaller than 20 nm had decreased significantly. Comparable results were obtained for other catalysts not included in this paper [24]. Perrichon and Durupt [28] have also reported that the presence of alkali compounds enhances the sintering of catalyst support materials, such as MgO and, to a lesser extent $\gamma\text{-Al}_2\text{O}_3$, as well SiO_2 and Cr_2O_3 .

When aged with 45% CO_2 (Set C), the sintering of the $\gamma\text{-Al}_2\text{O}_3$ structure of

Table 5
BET surface areas and pore volumes of several catalysts before and after the stability test

Catalyst	Ni wt. %	Gas flow	Pre-test		Post-test ^a	
			S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$) ^b	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$) ^b
$\text{C-NiAl}_{2.5}\text{La}_{0.5}$	18.6	Set A	166	0.36	7	0.02
DP	19.4	Set A	150	0.36	U: n.d., L: 41	U: n.d., L: 0.12
DP	19.4	Set C	150	0.36	105	0.32

n.d. Not detected.

^a U = upper part, L = lower part.

^b Pore volume with pore radii smaller than 20 nm.

the DP catalyst was much less significant in spite of the fact that the final activity of this sample was much lower than when it was tested in the gas without CO₂ (Set A). This indicates that the presence of CO₂ prevents the formation of high concentrations of alkali compounds on the catalyst surface, thereby suppressing the affection of the γ -Al₂O₃ structure. However, the CO₂ cannot prevent penetration through the whole catalyst bed by alkali compounds during several hundred hours.

TEM examinations of some samples of deactivated catalysts showed a rather wide distribution of nickel crystallite sizes; as well as relatively small crystallites, varying from ca. 10 nm (DP catalyst) to ca. 50 nm (C-Ni₃Al), there were in most samples a small number of large nickel crystallites, varying from ca. 80 nm (DP catalyst) to more than 300 nm (C-Ni₃Al) [24]. The crystallite sizes obtained from TEM were in reasonable agreement with those from X-ray line broadening given in Table 4; the differences probably arise from the fact that the results of X-ray line broadening give volume-averaged crystallite sizes in which large crystallites contribute strongly to the average size obtained.

TEM photographs of the sticky upper parts of several catalyst beds showed that these consisted mainly of particles totally covered with a glue-like layer, probably an alkali-containing compound. On the contrary, the alumina structure of the non-sticky lower parts of the catalysts C-NiAl₃ and DP consisted of crystallites smaller than 10 nm, as with the unused catalysts.

AES was applied to examine the outer surfaces several of the deactivated catalysts. For the catalyst C-Ni₃Al, the outer surface contained mainly K, Al and O; the nickel content was very small and varied from place to place on the surface between 0 and 4%. The composition of surfaces which had been formed by crushing this sample did not differ significantly from that of the outer surface, thus indicating that the K had penetrated throughout the grains. With the deactivated catalyst C-NiAl₃, which has a much higher alumina content than C-Ni₃Al, the outer layer did not contain Ni since only K, Al and O were observed. The nickel content was still unmeasurably small after etching for 6 min. When this sample was broken up, however, the surfaces exposed did not have such a nickel-free layer. This indicates that the K had probably not penetrated throughout the grains of this sample.

Hydrogen chemisorption was applied to several of the deactivated catalysts; however, the sensitivity of the measurement was too low to measure any adsorption of hydrogen which was probably a consequence of coverage of much of the surface of the nickel crystallites by a protective layer of alkali-containing compounds. Only the catalysts which had high steam-reforming activities after the deactivation test showed measurable hydrogen chemisorption; however, the average nickel crystallite sizes calculated from the amounts of hydrogen chemisorbed were still generally of one order of magnitude or more larger than those determined by X-ray line broadening.

The steam-reforming reaction rates of several of the deactivated catalysts

Fig. 8. Arrhenius plots of several catalysts (I): (●) C-NiAl₂Mg, fresh; (○) C-NiAl₂Mg, post-test (Set A); (+) C-NiAl₃, post-test (Set A); (△) C-NiMg₃, post-test (Set A).

were measured as a function of temperature. Arrhenius plots of some of the data obtained are shown in Figs. 8 and 9. For comparison, these figures also contain the results for two fresh samples, taken from Ref. [24].

The Arrhenius curves obtained for the post-test samples were very differently from those for the fresh samples, showing an apparent activation energy of ca. 140 kJ mol^{-1} with a slight decrease at higher temperatures which is probably due to the onset of diffusion limitation. Very low gradients (corresponding to apparent activation energies as low as 10 kJ mol^{-1}), particularly at lower temperatures, were generally obtained, especially for those catalysts which had

Fig. 9. Arrhenius plots of several catalysts (II): (●) freshly reduced nickel sample prepared from nickel nitrate (see Table 3, Note 7); (▲) DP, fresh; (△) DP, post-test (Set A); (+) DP after the test with 45% CO₂ in the gas flow (Set C).

deactivated most strongly (C-NiAl₂Mg and C-NiMg₃). However, the gradients were higher at higher temperature. As the data were reproducible on decreasing the temperature, it is unlikely that gradual removal of alkali species was responsible for the observed behaviour. Despite the fact that the samples had been stored in air for some time before the measurements, the activities at 973 K were close to those measured in the deactivation tests; this indicates that the behaviours shown in Figs. 8 and 9 were also not due to cooling to room temperature, exposure to air and reheating.

The relatively high gradients in the Arrhenius plots for the C-NiAl₃ and DP catalyst after the stability test using the gas flow of Set A suggests that at least a part of these catalyst beds had not been poisoned by alkali to any appreciable degree; this probably being the lower parts of the beds. This result suggests that the upper parts of the beds of these catalysts had been able to retain virtually all the alkali. More alkali probably moved further down in the DP catalyst bed during the 600 h test in the gas flow containing 45% CO₂, thus causing a more perceptible deactivation.

4. General discussion

The results obtained show clearly that the presence of alkali metal compounds caused significant deactivation of all the catalysts tested. Although the exact deactivation mechanism has not become clear, some tentative explanations can be given for several of the results found.

No satisfactory explanation has yet been given in literature for the sintering of alumina and magnesia in the presence of alkali compounds. Two processes might play a role.

(i) It is possible that alkali hydroxide (or alkali carbonate) adsorbs on the surface of the support (e.g. on the alumina) and has an effect similar to that of adsorbed H₂O [24,29,30]; both the alkali-hydroxide (or alkali-carbonate) species and the H₂O molecule have a dipole moment and contain negatively charged oxygen. Because the alkali species are much more strongly adsorbed than is H₂O, the effect of alkali on the sintering may be much stronger.

(ii) When the surface of the catalyst is almost completely covered by adsorbed alkali, liquid phases may be formed. Such liquid phases would enhance sintering of the catalyst support by facilitating the transport of the ions from the support (e.g. Al³⁺ and O²⁻) by dissolution and re-precipitation.

It is not clear to what extent the nickel surface was covered by alkali species during the deactivation process. While there is strong deactivation of the catalysts and a large decrease of the amount of hydrogen that can be chemisorbed on the catalysts compared, there is relatively little growth of the nickel crystallites; this suggests that the surface of the nickel had become covered by other species. Although alkali compounds are more strongly adsorbed on metal oxide

surfaces than on metal surfaces, several authors have reported that alkali ions also reside on metal surfaces. Significant amounts of monodispersed alkali (mostly K) species have been found on a nickel surface by Praliaud et al. [31,32] and by Bailey et al. [33]. Martin and Praliaud [34] have also concluded that a potassium silicate layer is present on the nickel surface of K-promoted Ni/SiO₂ catalysts. The presence of alkali species on the metal itself has also been found for several other supported metal catalysts, such as Rh [35], Ru [36,37] and Fe [38–40]. In the present work, the AES results also indicate that a potassium (and lithium) aluminate-like layer on the nickel surface is well possible.

Besides covering the nickel surface to a large extent, the alkali may also influence the properties of the nickel, thus influencing the specific activity, the shape of the Arrhenius plots and/or the adsorption stoichiometry of hydrogen on the nickel. A decrease of the specific steam-reforming activity brought about by the presence of alkali has been observed by Rostrup-Nielsen [41,42] and by Andrew [43]. Rostrup-Nielsen found that deactivation was more pronounced with catalysts based on the more alkali-resistant supports MgO and MgAl₂O₄, when compared with γ -Al₂O₃. In contrast, Parmaliana et al. [27,44] did not find a decrease of the specific steam-reforming activity of a Ni/MgO catalyst on addition of Li and K.

A significant decrease of the specific activity of the methanation of CO, i.e. the reverse of the steam-reforming reaction, due to the addition of alkali metal ions has been reported frequently [45–48]. The decrease of specific activity has been ascribed to electron donation from the alkali metal species to the nickel, thereby influencing the rates of the surface processes and/or the adsorption equilibria and/or the adsorption kinetics [29,31,32,49,50].

Furthermore, the presence of alkali species has been found to decrease the adsorption enthalpy of electron-donating molecules such as hydrogen and methane and to increase the adsorption enthalpy of electron-withdrawing molecules such as CO by an electron enrichment of the metal [51–56]. This effect may be partially responsible for the decrease in the amounts of hydrogen which can be chemisorbed on the deactivated catalysts. Electron enrichment of the nickel may also cause stabilisation of adsorbed carbon [57,58]. Finally, in addition to influencing the adsorption characteristics of the nickel by electron enrichment, the alkali may also interact directly with adsorbed molecules and/or reaction intermediates [59].

A decrease of the steam-reforming activity as a consequence of a decrease of the rate of methane adsorption is plausible since several authors have reported that the (dissociative) adsorption of methane is the rate determining step (RDS) for the reaction (see e.g. the review by Ross [60]).

The non-linear form of the Arrhenius plots obtained for the deactivated catalysts could be caused by:

1. Change of the RDS as a function of temperature in the presence of alkali species. For example, if dissociative methane adsorption would become the

RDS at lower temperature, it may explain the values of the apparent activation energies much lower than 140 kJ mol^{-1} which were found because the apparent activation energy for dissociative adsorption of CH_4 on Ni(111), Ni(110) and Ni(100) single crystal planes have been reported to be $40\text{--}50 \text{ kJ mol}^{-1}$ [61–63]. Another step may become rate determining at higher temperature.

2. Change of the distribution of alkali on the catalyst as a function of temperature. If the distribution of alkali species over the surface improves upon heating, diffusion limitation due to pore plugging may decrease. Another effect may be that if the alkali abandons a (small) proportion of the nickel surface upon heating, this surface would become available for steam reforming. Coverage of the external surface of the catalyst grains by a layer containing K, Al and O and possibly also Li was found for the catalyst C-NiAl₃.
3. Preferential coverage of the most active sites of the nickel surface by alkali species, as found by Hoost and Goodwin, Jr. [64] for K added to a Ru/SiO₂ catalyst. This explanation is based on two observations: (i) the extensive and rapid deactivation during alkali ageing of a sample consisting of a physical mixture of NiO and $\gamma\text{-Al}_2\text{O}_3$ and of a sample of pure nickel (see Fig. 6), and (ii) the Arrhenius plot obtained for this pure nickel sample *prior* to the stability test (see Fig. 9), which also shows an increasing slope when going to higher temperatures. Because compounds such as metal oxides other than NiO were absent during the final stages of the production of the nickel oxide used for the physical mixture as well as in the preparation of the sample consisting of pure nickel, these samples probably only contained nickel crystallites larger than about 100 nm. Such large nickel crystallites probably contain significantly fewer sites active for the various steps required for the steam-reforming reaction (e.g. the dissociative adsorption of the CH_4 molecule) than do small nickel crystallites. Such active sites might occur on low coordination planes (other than Ni(111), Ni(110) and Ni(100)), steps and other irregularities on the surface (e.g. sites in the direct vicinity of species such as alumina). The small number of active sites of the samples only containing large nickel crystallites would thus have been poisoned rapidly by alkali and/or other adsorbed compounds and/or reaction intermediates. The less active sites which are not poisoned and which have higher activation energies for the various steps of the steam-reforming reaction will start to dominate the total reaction rate when the temperature is increased.

5. Conclusions

The following conclusions can be drawn from the stability tests and from the characterisation of the deactivated samples.

1. The highest stabilities in an alkali-containing atmosphere were obtained for the coprecipitated nickel/alumina catalyst with high alumina content, C-NiAl₃, and for the deposition–precipitation catalyst, DP. The residual activities of these catalysts were sufficient for application in internal reforming in the MCFC. The high stability of these catalysts was probably caused by their ability to adsorb and retain the alkali very strongly.
2. Addition of Mg and La to the coprecipitated nickel/alumina catalyst decreased the stability; this was probably due to interaction of these compounds with the alumina, decreasing the interaction of the latter with the alkali.
3. Catalysts having a relatively weak interaction with the alkali (Ni/ α -Al₂O₃, Ni/MgO, and nickel/alumina samples with very high nickel contents) deactivated rapidly in an alkali-containing atmosphere; this was probably due to a rapid migration of the alkali through the whole catalyst bed.
4. Retardation of the supply of alkali to the catalyst by addition of CO₂ to the gas also retarded the catalyst deactivation; however, the added CO₂ only decreased slightly the extent of deactivation after a longer time of operation when approximately the same total amounts of alkali had been supplied to the catalyst as in the test without addition of CO₂ to the gas.
5. The deactivation of the catalysts by alkali is likely to have been caused by the following phenomena:
 - enhanced Ni-crystallite growth to sizes of about 50–100 nm and larger;
 - deactivation of the most active Ni sites by adsorption of alkali;
 - chemical interaction of alkali with nickel and/or adsorbed species;
 - sintering of the support materials, especially MgO;
 - chemical reaction with Al-containing support materials;
 - coverage of a large part of the internal surface of the catalyst, followed by plugging of the pores by alkali compounds.

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