K (Na)-promoted Ni, Al layered double hydroxide catalysts for the steam reforming of methanol

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Abstract

Production of hydrogen by methanol steam reforming has been studied over a series of Ni/Al layered double hydroxide catalysts prepared by the co-precipitation method, with the aim to develop a stable catalyst that can be used in a membrane-joint performer at temperatures greater than 300 °C. H_2, CO and CO_2 are generally the major products together with trace amounts of CH_4. The presence of potassium and/or sodium cations was found to improve the activity of methanol conversion. The selectivity for CO_2 rather than CO was better with K ions than Na ions, especially at higher temperatures (e.g. 390–400 °C). Methanol steam reforming over a K-promoted Ni/Al layered double hydroxide catalyst resulted in better activity and similar stability compared to a commercial Cu catalyst.
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1. Introduction

The use of methanol as an on-board hydrogen source is attractive for fuel cell engines based on proton exchange membrane fuel cells (PEMFCs). These fuel cells generate electrical power by the electrochemical oxidation of hydrogen with atmospheric oxygen [1,2]. Catalytic steam reforming of methanol (SRM) is a well-established process for the production of hydrogen ($CH_3OH + H_2O \rightarrow 3H_2 + CO_2$; $\Delta H°_{298} = 49.4$ kJ/mol). The catalysts used in the SRM reaction are mostly Cu-based, particularly, CuZn- or CuZnAl-mixed oxides [3–7]. The raw reformate gas contains approximately 75% H_2, 24% CO_2 and 1% CO by volume. However, even traces of CO (>20 ppm) in the reformed gas have been shown to poison Pt catalysts and dramatically decrease the cell performance [8]. Purification of raw reformate gas is therefore required for the application in PEMFCs. We are interested in the integration of the reformer with a selectively permeable palladium membrane reactor because it has shown considerable potential for high purity H_2 [9,10]. However, the Cu-based catalysts are in general very sensitive to deactivation by thermal sintering, such as at the operating temperatures required for the palladium membrane, i.e. 300–400 °C. Therefore, it is desired to develop a new catalyst that can be used for this purpose.

A number of materials are being developed to replace Cu/Zn/Al catalysts, such as oxides supported precious metal catalysts, including Pd, Pt and Rh [11–17]. Ni/Al layered double hydroxides (LDH) derived catalysts also attracted some attentions [18,19], including our recent work [20–22]. It is well known that Ni–Al co-precipitated materials have been extensively studied in the production of H_2 from methane via reforming or partial oxidation [23–25]. Actually, research into hydrotalcite-like compound and its catalysis can date back to the 1970s [26]. The Ni–Al co-precipitates were first used as precursors for the so-called catalytic rich gas catalysts introduced by British Gas for the steam reforming of hydrocarbons to produce methane-rich gases and they were later studied in great detail for the methanation of CO [27]. These types of compounds consist of positively charged metal hydroxide layers separated from each other by anions and water molecules. As-prepared hydrotalcite-like compounds will decompose to hydroxide or

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oxide mixture with or without maintaining the layered structure, depending on the thermal treatment temperature.

We have found that NiAl-LDH derived catalysts exhibit good reformate composition, i.e. higher selectivity for H_2 and CO_2 and lower selectivity for CO and CH_4, under certain conditions [21,22]. The metallic Cu species were believed as active sites in Cu-based catalyst and the presence of layered structure was also considered necessary in terms of better selectivity for methanol steam reforming [28]. The similar behaviour seems emerged from our previous work for methanol steam reforming over Ni, Al-LDH derived catalyst [22]. However, highly uncertainty in the structure of the catalysts under different experimental procedure and thus in their corresponding catalytic performance make this catalytic system complicated. One purpose in this study is, therefore, further to figure out the structure factors which would determine the activity, selectivity, by directly using the as-prepared NiAl-LDH catalysts. The effect of sodium and potassium ions on the catalytic performance of NiAl-LDH catalysts was investigated and a comparison was made between a Ni, Al catalyst with a commercial Cu catalyst.

2. Experimental

2.1. Catalysts preparation

Three NiAl-LDH compounds with the theoretical Al/(Ni + Al) value of 0.15 were synthesized with the co-precipitation method at pH = 7 and room temperature. An aqueous solution with 0.125 M $Ni(NO_3)_2 \cdot 6H_2O$ and 0.125 M $Al(NO_3)_3 \cdot 6H_2O$ and another aqueous solution with 0.25 M sodium or potassium carbonate were added dropwise into a 2 L beaker with 800 ml distilled water under vigorous stirring. The *first* sample used Na_2CO_3 as the precipitant. The precipitate was aged under stirring for 1 h after addition of the reagents and then completely washed using distilled water before filtration. Subsequently, the resulting solid was re-slurried for another hour and then filtrated. The *second* and *third* sample used Na_2CO_3 and K_2CO_3 as precipitants, respectively. The precipitates were aged for 2 h after addition of the reagents and then directly filtrated without washing to keep more sodium or potassium in the final solids. Finally, the solids of three precursors were dried at 70 °C for about 22 h. These three catalysts were named hereafter as NiAl-1, NiAl-2 and NiAl-3, respectively. Their compositions are presented in Table 1.

Post-addition of three potassium compounds (K_2CO_3, KCl and KOH, 3 wt.% K) into the parent catalyst, NiAl-3 was accomplished by the incipient wetness method, followed by drying in air at 70 °C for 22 h.

A commercial methanol steam reforming Cu-based catalyst, MDC-3, was provided by Sud-Chemie Catalyst Japan, Inc. It is composed of 42 wt.% CuO, 47% ZnO and 10% Al_2O_3.

2.2. Catalyst characterization

The physico-chemical properties of the catalysts were studied using a variety of techniques. Neutron activation analysis (NAA) was employed to analyze the chemical composition of three basic studied catalysts by using a SLOWPOKE-2 reactor at half power, which produces a flux of 5×10^{11} neutrons $cm^{-2} s^{-1}$. After the sample was made radioactive, it was counted on a Perkin-Elmer Ortec high purity germanium detector. The X-ray detector in the system of energy dispersive analysis of X-rays (EDAX) which is connected with the scanning electron microscope (SEM, EDAX International Inc., USA), was employed to estimate the relative surface atomic content of elements in some fresh and spent catalysts. A flat surface of the sample stacked on the holder was made and the average value of three measurements at different spots was used in order to minimize the analysis error, especially for C measurement because the substrate is carbon based material. Powder X-ray diffractions (XRD) were recorded by using SCINTAG X_1 diffractometer (USA) with λ = 1.5406 for angle 2θ = 2–70° and step 0.01° with Cu Kα radiation operated at 40 kV and 45 mA. Thermogravimetric analysis (TGA) was performed on a 2050 thermogravimetric analyser (Texas Instruments, USA), in which the heating rate was 10 °C/min from room temperature to 700 °C under a N_2 atmosphere). The composition of the gases evolving from the TG experiments was detected continuously on-line with a quadrupole residual gas analyser (RGA) by using mass analyser technology (MKS Instruments, Inc., USA).

2.3. Activity measurements

The catalytic activity tests were carried out in an isothermal fixed-bed tubular reactor at atmospheric pressure as previously described [5]. 0.150 g of the catalyst was used and purged in He gas at 200 °C overnight before pre-treatment. Unless otherwise indicated, a feed with nominal 1:1 mol ratio water to methanol was delivered into the catalytic reactor using a Gilson model

Table 1
Chemical composition of three NiAl-LDH catalysts

Catalyst	Metal composition (wt.%)[a]				X[b]	Chemical formula[c]
	Ni	Al	Na	K		
NiAl-1	41.9	4.48	0.012	–	0.19	$Ni_{0.81}Al_{0.19}(OH)_2(CO_3)_{0.07} \cdot 0.34H_2O$
NiAl-2	42.0	3.98	1.16	–	0.17	$Ni_{0.78}Al_{0.16}(OH)_2(CO_3)_{0.11} \cdot 0.41H_2O$
NiAl-3	41.5	3.92	–	2.14	0.17	$Ni_{0.78}Al_{0.16}(OH)_2(CO_3)_{0.15} \cdot 0.66H_2O$

[a] Determined by neutron activation analysis (NAA).

[b] X: atomic ratio of Al/(Al + Ni).

[c] Chemical formulas derived from NAA and TGA results.

302 pump at a total flowrate of about $3\,ml\,h^{-1}$. After flowing through the reactor, the product was passed through a condenser (chilled to around $-4\,°C$) to trap any unreacted CH_3OH and H_2O. The mixture of dry gases was analysed by a GOW-MAC 550P gas chromatograph (GC) using a 3.2 mm Carbosieve-S column at intervals of 2 h. The compositions of H_2, CO_2, CO and CH_4 were calculated based on calibration standards. Dry gas composition was defined as the ratio of each product formation to the sum of all four products. The amount of methanol consumed was calculated from the CO, CO_2 and CH_4 flowrates in the reactor effluent. Other products were negligible and not counted in calculation based on a reasonable material balance.

3. Results and discussion

3.1. Characterization of the catalysts

The thermal stability of the three NiAl-LDH precursors was examined by the thermogravimetry performed in a N_2 atmosphere. Their TG weight loss and differential curves are shown in Fig. 1. There are two major endothermic weight loss processes identified for all three samples. As previously described for NiAl-1 [22], the first weight loss process at temperatures lower than $200\,°C$ has been attributed to the loss of the physisorbed and interlayer water with respect to the peaks centred at $49\,°C$ and the range of $80–100\,°C$, respectively. The second weight loss process in the temperature range $200–380\,°C$ has been ascribed to the loss of structural water and CO_2 from the interlayer because of the destruction of layered structure. Compared to the NiAl-1, the endothermic peaks shifted towards a lower temperature in NiAl-2 and NiAl-3, indicating that they are thermally less stable. The total weight loss was about 33 wt.% for all three samples. In addition, NO species were not detected by on-line monitor-
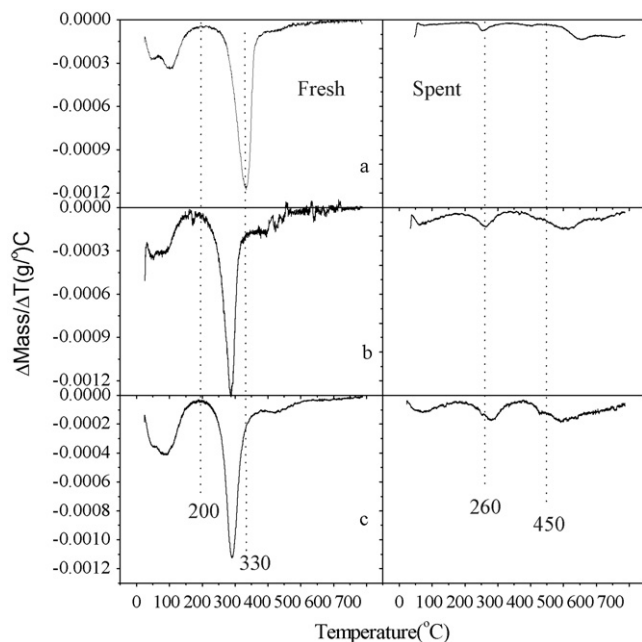

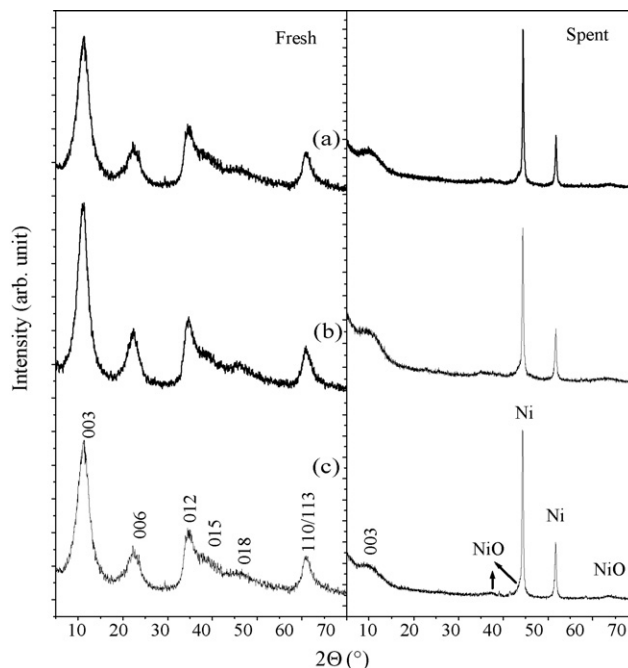Fig. 1. DTA curves for fresh and spent catalysts of NiAl-LDHs: (a) NiAl-1, (b) NiAl-2, and (c) NiAl-3.

Fig. 2. XRD patterns for fresh and spent catalysts of NiAl-LDHs: (a) NiAl-1, (b) NiAl-2, and (c) NiAl-3.

ing the exhausted gases during TGA analysis. This suggests that nitrate species do not insert into the structure in our case.

The XRD patterns of three as-prepared NiAl-LDH catalysts are shown in Fig. 2. It can be clearly seen that all three samples exhibit a single-phase corresponding to the layered double hydroxide (JCPDS file no. 15-0087) with the peaks at 2θ of 11.2, 23.6, 35.1, 39.7 47.3, 61.2, 62, respectively. The interlayer distances for three samples, calculated from the position of the $(0\,0\,3)$ reflection in the XRD patterns [29,30], are around 7.54 Å. On the other hand, the intensity and sharpness of all diffraction peaks for NiAl-2 and NiAl-3 slightly decrease, probably because of more sodium and potassium ions introduced, respectively, evidenced by NAA analysis (Table 1). Na/K cations should not insert into the hydrotalcite framework because of their large ionic radius.

3.2. Evaluation of catalytic performance

3.2.1. Catalytic performance of the three as-synthesized catalysts

The initial investigation on reactivity of the catalysts was performed as follows. The catalyst was kept at $200\,°C$ overnight in a He atmosphere before the nominal molar 1:1 feed of methanol and steam was delivered. The reaction temperature was then raised by steps of $20\,°C$ and maintained at each temperature for 1 injection of sample until a detectable dry gases flowrate was observed. The temperature was then maintained at each of 340, 360, 380 and $400\,°C$ for 1 day. The corresponding catalytic performances of the three catalysts are summarized in Table 2.

Under these conditions the activity of methanol conversion increases with reaction temperature for all three catalysts. The catalyst of NiAl-1 shows deactivation with time on line at each

Table 2
Methanol steam reforming over three catalysts

Catalyst	Reaction temperature (°C)	Run time (h)	CH$_3$OH conversion		H$_2$ production rate (mmol kg^{-1}(cat.) s^{-1})	H$_2$ production rate/ CH$_3$OH conversion rate	Φ_w	Dry reformate composition (mol%)			
			mol%	Rate (mmol kg^{-1} (cat.) s^{-1})				H$_2$	CO$_2$	CO	CH$_4$
NiAl-1	340	2	22.5	22.8	45.3	2.0	0.01	68.2	9.8	22.0	0
		10	18.5	18.7	36.0	1.9	0.01	68.4	11.0	20.3	0.3
	360	2	27.1	27.4	58.2	2.1	0.03	68.8	12.1	18.6	0.6
		10	26.2	26.5	57.6	2.2	0.02	68.9	12.2	18.6	0.4
	380	2	40.3	40.8	92.4	2.2	0.06	69.5	13.0	17.3	0.3
		10	41.3	41.8	91.1	2.2	0.05	68.5	12.0	18.9	0.6
	400	2	61.5	62.2	119.8	1.9	0.06	67.5	9.8	21.9	0.8
		10	50.1	50.7	97.3	1.9	0.02	65.1	5.0	28.8	1.1
NiAl-2	340	2	24.4	24.7	57.3	2.3	0.05	70.6	16.6	12.3	0
		10	27.6	27.9	62.2	2.2	0.03	69.4	13.7	16.7	0.2
	360	2	56.2	56.8	116.2	2.0	0.01	65.7	4.4	29.3	0.6
		10	48.2	48.7	98.2	2.0	0.01	65.7	4.3	29.5	0.5
	380	2	50.7	51.2	118.0	2.3	0.02	66.3	5.7	27.4	0.6
		10	48.1	48.6	113.9	2.3	0.02	66.4	6.1	27.1	0.5
	400	2	70.0	70.8	149.3	2.1	0.06	67.0	7.6	24.8	0.6
		10	70.6	71.3	149.1	2.1	0.06	66.8	7.4	25.2	0.6
NiAl-3	340	2	39.1	39.5	86.2	2.2	0.02	67.5	8.5	24.0	0
		10	41.4	41.7	89.6	2.1	0.02	67.1	8.4	24.1	0.4
	360	2	52.2	52.7	115.0	2.2	0.03	67.1	8.2	24.4	0.4
		10	50.4	50.8	109.3	2.1	0.02	66.9	8.0	24.5	0.6
	380	2	66.9	67.4	146.3	2.2	0.06	67.4	9.6	22.2	0.8
		10	68.5	69.1	150.2	2.2	0.06	67.4	9.8	22.2	0.7
	400	2	84.2	84.9	188.4	2.2	**0.31**	69.5	15.5	14.0	1.1
		10	84.8	85.5	186.7	2.2	**0.43**	69.6	17.5	11.9	1.0

SRM = 1.0. $\Phi_w = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O} K_w$, $\log K_w = 2096/T - 2.042$, ref. [5].

tested temperature, while NiAl-2 and NiAl-3 present much better stability in addition to their higher activities in methanol conversion and H_2 production than that of NiAl-1. It can be seen that H_2, CO and CO_2 are generally the major products together with trace amounts of CH_4. The selectivity for hydrogen is almost constant over the range 340–400 °C for all three catalysts. In general, methanol is predominantly converted to CO rather than CO_2. It is interesting to note from Table 2 that CO_2 production decreased at higher temperatures for NiAl-1 and NiAl-2, which were prepared by using Na_2CO_3 as precipitant. For the catalyst NiAl-3 with K_2CO_3 as precipitant, higher temperatures are more favorable for CO_2 production so that selectivity for CO_2 is greater than that for CO at 400 °C.

The average gas composition in the reactor, relative to the WGS equilibrium, can be represented by the parameter where: $\Phi_w = P_{CO_2} P_{H_2} / P_{CO} P_{H_2O} K_w$, in which P is the partial pressure of the components, K_w is the equilibrium constant at given temperature [5]. Here it should mentioned that P_{H_2O} was calculated using the mass-balance of the reaction. This data could be smaller than the right value because additional water is gradually produced due to the decomposition of the catalyst itself during reaction. However, the contribution of the decomposed water of the catalyst during reaction can be negligible because the amount of decomposed water is smaller than the amount of water in feed by two order of magnitude, if we assume half of weight loss in the second endothermic peak in Fig. 1 is the contribution from the structured H_2O and this part of water gradually release into the reactor in the temperature range of 340–380 °C in above applied reaction procedure. The value of Φ_w will be equal to 1.0 when the gas composition is at WGS equilibrium. As we can see from Table 2, Φ_w value is quite small in most cases, except in the case of NiAl-3 at 400 °C. This suggests that the rate of WGS reaction was negligible and there are parallel reaction paths from methanol to CO through the decomposition reaction and to CO_2 through the steam reforming reaction for three catalysts. However, WGS reaction probably makes some contribution in the CO_2 production for NiAl-3 at 400 °C.

All three spent catalysts were then characterized by TGA and XRD. The results are shown in right hand side in Figs. 1 and 2, respectively, and compared with the catalyst before reaction. It is clear that the initial Ni/Al LDH material undergoes significant changes in structure and composition during reaction. The sharp reduction of two endothermic peaks for three spent samples, shown in the right-hand side in Fig. 1, account for a major destruction of the LDH structure during reaction. fourfold larger TGA traces of NiAl-1, as shown in Fig. 3, and corresponding residual gases analysis indicate that the layered structure maintains at certain extent even after 400 °C reaction. Moreover, carbon deposition occurred and most of carbon species could be carbonate from RGA data. The decomposition of the precipitates to form the corresponding oxides and thereafter the reduction of the oxides to give Ni-rich catalysts during reaction has also been observed, indicated by peaks of the well-crystallized metallic Ni shown in Fig. 2. From the results of TGA analysis shown in Fig. 1, the interlay distance of these three LDH catalysts may change after the catalysts were heated in He stream at 200 °C overnight because of loss of interlay water. The collapse of lay-
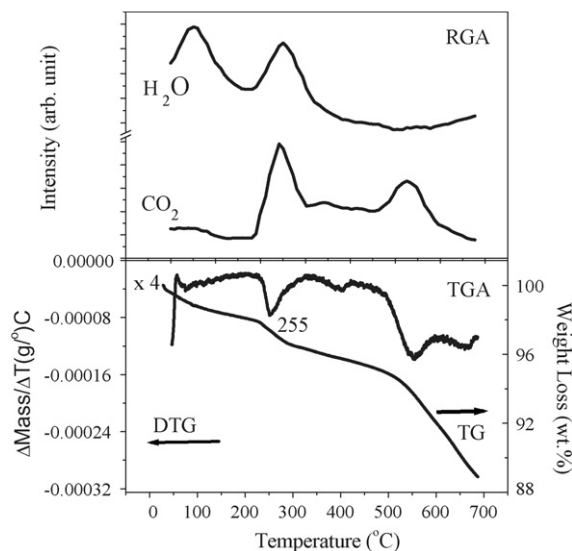

Fig. 3. TGA and RGA results of spent catalyst NiAl-1.

ered structure starts from approximately 250 °C for NiAl-1 and 210 °C for NiAl-2 and NiAl-3 and finally the mixture of oxides were formed after completely decomposition of LDH materials at temperatures 130–140 °C higher. Since the contact of reactants with the catalysts starts from 200 °C and small amount of product flowrate was observed at approximately 300 °C, reduction of oxidic Ni in the Ni-LDH compound could be thus initiated when H_2 was produced, simultaneously with structure collapse of LDH catalysts. With an increase in reaction temperature, formation of more metallic Ni may be expected, probably somehow reflected by a slight increase in CH_4 production; however, not all of NiO was reduced to metallic Ni after reaction proceeded at 400 °C from XRD results of the spent catalysts shown in the right hand side in Fig. 2. Partial maintenance of LDH structure is also identified by the (0 0 3) reflection, in agreement with TGA analysis. In combination of the catalytic data in Table 2, the above change in catalyst structure during reaction seems not to affect product selectivity very much. If there is any influence, an intermediate phase at the stage of initial collapse of LDH structure, which corresponded to 360 °C for NiAl-1 and 340 °C for NiAl-2, may be favorable for CO_2 production. This, however, is not applicable for the catalyst of NiAl-3 with potassium ions.

3.3. Long-term performance of the catalyst NiAl-3 at 390 °C in the feed with a higher steam to methanol ratio of 1.2:1

A selective, active and stable methanol steam reforming catalyst at higher temperatures is preferred to be used in membrane-joint performer. NiAl-3 was, therefore, drawn more attention and a different experimental procedure was applied to make things simple. All samples were kept at 200 °C overnight in a He atmosphere and then preheated at 240 °C in the feed with a higher steam to methanol ratio, 1.2:1, for 6 h before the temperature of the reactor was enhanced to 390 °C. Finally the catalyst was continuously run at 390 °C for 108 h. Since the rates of the reforming reaction ($CH_3OH + H_2O \rightarrow CO_2 + 3H_2$) and the for-
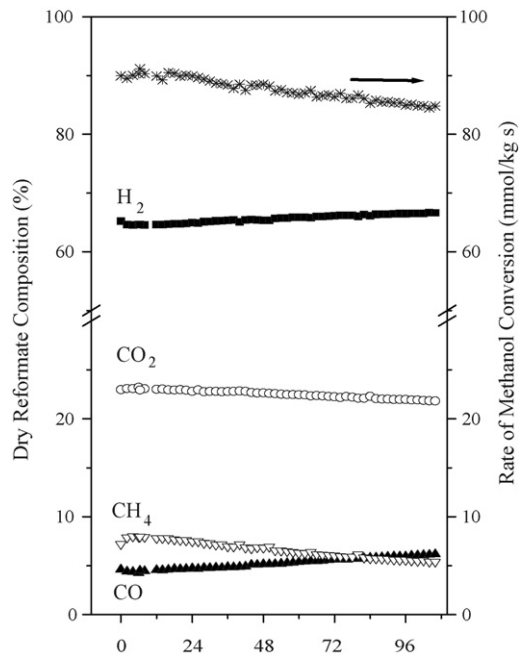
Fig. 4. Steam reforming of methanol at 390 °C over NiAl-3 with the H_2O/CH_3OH ratio of 1.2. The catalysts were pre-heated at 240 °C for 6 h in situ on reactive stream prior to reaction.
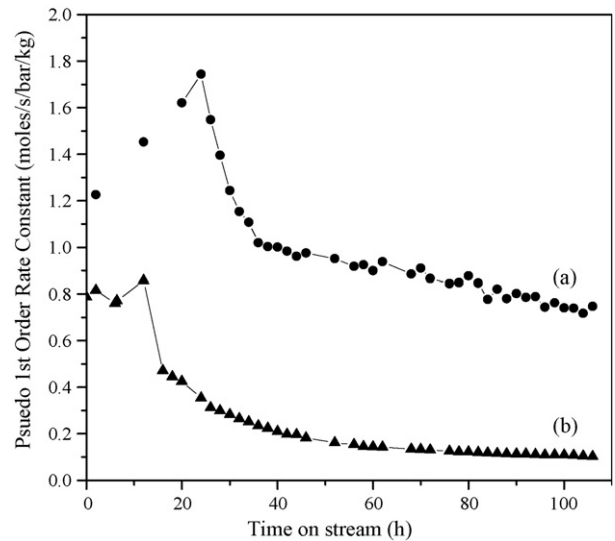

Fig. 5. Pseudo 1st reaction rate constant of methanol steam reforming at 390 °C over (a), NiAl-3 and (b), MDC-3. The catalysts were pre-heated at 240 °C for 6 h in situ on reactive stream prior to reaction. The H_2O/CH_3OH ratio is 1.2.

ward WGS reaction ($CO + H_2O \rightarrow CO_2 + H_2$) are favoured by addition of steam in the feed, one would expect the initial CO levels to drop and production of CO_2 to increase. The corresponding data shown in Fig. 4 confirms this and these results are in consistent with the results of NiAl-3 at 400 °C in Table 2. Though, a certain amount of methane was also formed, leading to a reduction in H_2 production. In this case WGS reaction is close to equilibrium. We can see that the conversion of methanol drops gradually with time on line, showing an acceptable stability at such high temperature. An evaluation was made of the time on stream in comparison with a commercial Cu-based catalyst, MDC-3, as shown in Fig. 5. Pseudo 1st reaction rate constant [20] was used to express the activity of methanol conversion by using the following function:

$$k = \left(\frac{F_{methanol}}{W_{cat} p_{methanol}} \right) [-(1 + \varepsilon) \ln(1 - x_{methanol}) - \varepsilon x_{methanol}]$$

where $F_{methanol}$ is the flowrate of methanol, W_{cat} the mass of the catalyst, $P_{methanol}$ the partial pressure of methanol, $x_{methanol}$ the conversion of methanol, ε is the molar fraction of methanol in feed. There is an induction period for both catalysts. The catalyst of NiAl-3 is, therefore, supposed to be stable in its chemical composition and textural structure after induction period (about 40 h). Obviously, it is more active than the commercial Cu catalyst but with similar deactivation trend with time on stream.

The structure characters of NiAl-3 at each above step were investigated by XRD technique and the corresponding patterns are displayed in Fig. 6. An intermediate LDH phase was observed after the catalyst precursor was heated at 200 °C overnight in He atmosphere. The transformation is accompanied by a shift to higher degree in the position of the (0 0 3) refection as well as by loss of intensity for (0 0 6) [31]. It is related to

the lost of interlayer H_2O. This intermediate phase was almost re-built followed by treatment on reactive mixture at 240 °C, i.e. hydrothermal condition, due to so-called memory effect of LDH compounds [32]. It is interesting to notice that most of LDH planes were kept even after 108 h reaction at temperature up to 390 °C, simultaneously with formation of metallic Ni. Only few NiO is probably existed in the spent catalyst and impurity of Al_2O_3 that was used for diluting the catalyst was observed. Unlike the spent NiAl-3 tested at different temperatures by stepwise, in this case, the LDH structure was not seriously collapsed and most metallic Ni atoms are still sitting in the brucite
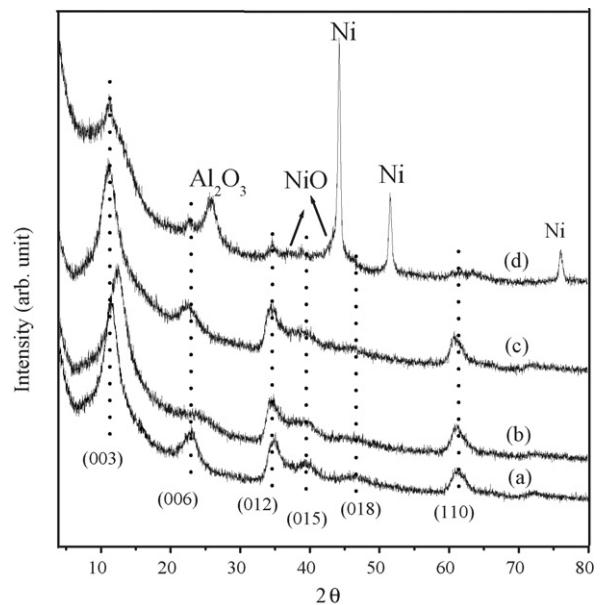

Fig. 6. XRD patterns of NiAl-3 catalyst at following conditions: (a) as-prepared precursor, (b, a) purged by He at 200 °C overnight, (c, b) in situ pre-heated at 240 °C for 6 h on reactive stream ($H_2O/CH_3OH = 1.2$), (d, c) after 108 h reaction at 390 °C ($H_2O/CH_3OH = 1.2$).

Table 3
Methanol steam reforming over the catalyst of NiAl-3 plus post-added K salts, SRM = 1.2

Catalyst	Time on stream (h)	CH$_3$OH conversion		H$_2$ production rate (mmol kg^{-1}(cat.) s^{-1})	H$_2$ production rate/ CH$_3$OH conversion rate	Φ_w	Dry reformate composition (mol%)			
		mol%	Rate (mmol kg^{-1} (cat.) s^{-1})				H$_2$	CO$_2$	CO	CH$_4$
NiAl-3	10	93.3	93.3	173.8	1.9	0.98	64.5	23.1	4.4	7.9
	20	93.3	90.4	175.5	1.9	0.95	64.7	22.9	4.7	7.7
	40	90.7	87.8	175.9	2.0	0.93	65.4	22.8	4.8	6.9
	60	89.9	87.1	178.0	2.0	0.86	65.8	22.5	5.3	6.4
	108	87.6	84.8	179.7	2.1	0.73	66.6	21.8	6.2	5.4
NiAl-3 + KOH	10	31.0	28.7	61.2	2.1	0.04	70.2	12.2	17.6	0.0
	20	74.4	68.9	158.1	2.3	0.13	69.8	11.2	18.8	0.2
	40	74.7	69.1	162.2	2.3	0.14	70.3	12.8	16.5	0.4
	60	86.9	80.4	202.7	2.5	0.39	72.4	15.4	11.9	0.3
	108	77.5	71.7	183.2	2.6	0.47	73.0	16.9	9.6	0.5
NiAl-3 + K$_2$CO$_3$	10	78.5	72.9	158.9	2.2	0.10	68.9	12.2	18.8	0.1
	20	77.3	71.7	156.1	2.2	0.11	68.8	12.5	18.5	0.2
	40	91.4	84.9	196.1	2.3	0.23	69.6	14.7	15.3	0.4
	60	91.0	84.5	201.1	2.4	0.35	70.3	16.5	12.7	0.5
NiAl-3 + KCl	10	70.3	69.6	164.0	2.4	0.27	70.7	16.7	12.4	0.2
	20	73.1	72.4	170.8	2.4	0.27	70.6	16.4	12.8	0.2
	40	78.9	78.1	182. 3	2.3	0.25	70.1	15.5	14.2	0.2
	60	82.0	81.2	193.2	2.4	0.33	70.4	16.4	12.8	0.3
	102	83.5	82.7	193.7	2.3	0.29	70.1	15.7	13.8	0.4

layer, probably due to rapid decomposition of hydroxide and thereafter simultaneously reduction of oxidic nickel at 390 °C during initial contact hours. The catalyst is likely hydrothermal stable under steam reforming conditions after the induction period.

3.3.1. Effect of potassium ions on the performance of NiAl-3 for methanol steam reforming at 390 °C

K ions have been reported to be poison for the methanation reaction and favourable for preventing coke formation [33]. An attempt was made to reduce or depress methane production by adding three types of potassium salts into the parent catalyst, NiAl-3. Table 3 summarizes their corresponding catalytic performance of methanol steam reforming at 390 °C together with that over NiAl-3 for comparison. Indeed, post-addition of potassium salts greatly reduced the formation of methane. However, production of CO was appreciably enhanced no matter which kind of K compound was used. This strongly suggests that the reaction of CO + 3H$_2$ → CH$_4$ + H$_2$O was the source of CH$_4$ with respect to the results over the parent catalyst. This indicates that addition of potassium ions does not block the active sites for this reversible reaction. On the other hand, post-addition of potassium salts resulted in an initial decrease in methanol conversion, which finally reached the same level with that over NiAl-3. Thermal decomposition of K salts and hence possible redox reaction could account for the gradual increase in the conversion with time on line for the respective catalysts. The anions of chloride might not seriously influence the reformate composition in comparison with the catalysts having post-added KOH and K$_2$CO$_3$.

Atomic concentrations of elements in fresh and spent NiAl-3 catalyst and its analogues with post-added K compounds were analyzed by EDAX technique and summarized in Table 4. The molar ratio of Al/(Al + Ni) of the NiAl-3 is higher than that in Table 1 analyzed by NAA method. However, similar Al/Ni ratios for all analyzed samples demonstrate that the comparison among the data is reliable. It can be seen that partial potassium in the catalysts was lost for all samples. Since the amount of methane formation did not change much with time on stream, one would assume that potassium ions could be washed off before reaction at 390 °C, probably when the LDH structure reconstituted after

Table 4
Relative atomic concentrations of elements in the catalysts of NiAl-3 and its analogues with post-added K compounds before and after 390 °C reaction

Catalyst	SRM[a]	Element/Ni[b]					
		C/Ni	O/Ni	Al/Ni	K/Ni	Al/Ni + Al	Cl/Ni
NiAl-3							
Fresh		0.12	2.72	0.27	0.08	0.21	–
Spent	1.2	0.41	0.72	0.29	0.01	0.22	–
+KOH[c]							
Fresh		0.35	1.89	0.27	0.20	0.21	–
Spent	1.2	3.75	0.76	0.28	0.10	0.22	–
+K$_2$CO$_3$[d]							
Fresh		0.62	2.46	0.28	0.40	0.22	–
Spent	1.2	1.39	0.71	0.26	0.13	0.21	–
+KCl[e]							
Fresh		0.42	2.04	0.27	0.34	0.21	0.17
Spent	1.2	1.42	0.67	0.26	0.05	0.21	0.03

[a] SRM: steam/methanol ratio.
[b] Average atom% is an average data of three measurements for one sample.
[c] +KOH: NiAl-3 + KOH.
[d] +K$_2$CO$_3$: NiAl-3 + K$_2$CO$_3$.
[e] +KCl: NiAl-3 + KCl.

introducing the feed into the collapsed catalyst at 240 °C. One would expected that, from the results in Table 4, an optimal potassium content of between 0.01 and 0.05 of K/Ni and steam to methanol ratio (a little higher than 1.2:1) could give the best performance in terms of better selectivity for H_2 and CO_2.

Carbon deposition took place over the spent catalysts from the results of atomic concentration analysis listed in Table 4. Probably there are two kinds of carbonaceous species; one is carbonate anions, adsorbed on the surface during reaction, which was supported by the combination of thermogravimetric and residual gas analysis, as previously described. Another may be carbon root, probably leading to the occurrence of the reactions of $C + H_2O \rightarrow CO + H_2O$ and $C + CO_2 \rightarrow 2CO$. Small amount of carbon deposition may partially cause the gradual deactivation of NiAl-LDH catalysts with time on stream.

4. Conclusions

The reduction of CO and methane content in the reformate mixture of methanol steam reforming has been reported in this paper over as-synthesized NiAl-LDH catalysts. This was accomplished by means of adding more alkaline cations (K, Na) to the catalysts and adjusting the H_2O/CH_3OH ratio. The following conclusions can be drawn:

(i) H_2, CO, CO_2 and CH_4 are produced over the NiAl-LDH catalysts. Their composition varies with the steam-to-methanol ratio, promoter (K, Na) and the reaction temperature.

(ii) Addition of Na and K cations promotes the methanol conversion activity and stability. K^+ is a better promoter for enhancing CO_2 production.

(iii) The LDH structure of the catalyst was partly destroyed and reduction of oxidic Ni occurred during reaction. At least three kinds of chemical structures of Ni exist in the spent catalysts. The ratio among different Ni species strongly depends on pre-activation and reaction procedure. After pre-activation at lower temperature, direct reaction of as-synthesised catalyst precursor at certain high temperature (like 390 °C) may give a relative stable catalyst.

Acknowledgements

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