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A comparative study of reactions of methanol over catalysts derived from NiAl- and CoAl-layered double hydroxides and their Sn-containing analogues

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Ni- and Co-based catalysts derived from NiAl- and CoAl-layered double hydroxides were tested in four kinds of reactions of methanol, namely decomposition of methanol (DCM), partial oxidation of methanol (POM), steam reforming of methanol (SRM), and oxidative steam reforming of methanol (OSRM), for the purpose of H_2 production for fuel cells. H_2, CO and/or CO_2 were the predominant products with minor amounts of dimethyl ether (DME) and CH_4 depending on the reaction temperature. Among the four kinds of reactions tested, the OSRM reaction was found to be more effective in terms of MeOH conversion and H_2 selectivity over these catalysts. Higher selectivity of H_2 and CO_2 with only traces of CO could be obtained at about 100% methanol conversion around 300 °C in the OSRM reaction over the catalyst derived from CoAl-LDH. Substitution of a part of Al by Sn in the NiAl- and CoAl-LDH systems was found to be inhibiting the methanol conversion. On the other hand, the selectivities to DME and CH_4 were declined with a consequent increase in the selectivity to H_2. In addition, considerable amount of formaldehyde was also noticed, especially over the catalyst derived from CoAlSn-LDH at lower reaction temperatures. The observed difference in the catalytic performance upon Sn incorporation was attributed to an improved redox capability of the Ni- and Co-based oxide catalysts, as determined by temperature-programmed reduction (TPR) experiments.

Keywords: methanol reactions, hydrogen production, partial oxidation of methanol, steam reforming of methanol, Ni-based catalysts, Co-based catalysts, layered double hydroxides

1. Introduction

The use of C_1 sources in applied catalysis research has grown enormously in the past few years. The fact, that methanol can be conveniently synthesized from natural gas, biomass or coal, has promoted research into the reactions involving methanol. The methanol to gasoline conversion, the synthesis of octane-boosting methyl *tert*-butyl ether (MTBE) from methanol and isobutene are a few examples for the effective utilization of methanol in petrochemical production [1,2]. In addition, methanol is considered to be one of the most promising alternative automobile fuels from a non-petroleum source. Methanol has recently been recommended as the best storage medium for hydrogen (H_2) fuel [3], which can be used for fuel cells to drive automobiles. Fuel cell powered vehicles are currently under development word-wide in an effort to mitigate the emissions of green house gas (CO_2) as well as other noxious gases such as NO_x, SO_x, CO and hydrocarbons from the transportation sector.

Hydrogen can be extracted from methanol according to three different processes: decomposition of methanol (DCM, equation (1)), partial oxidation of methanol (POM, equation (2)), and steam reforming of methanol (SRM, equation (3)) [4–6]:

$$CH_3OH \rightleftharpoons 2H_2 + CO \quad \Delta H^0_{298} = 92.0\ \mathrm{kJ\,mol^{-1}}, \tag{1}$$

$$CH_3OH + \tfrac{1}{2}O_2 \rightleftharpoons 2H_2 + CO_2 \quad \Delta H^0_{298} = -192.2\ \mathrm{kJ\,mol^{-1}}, \tag{2}$$

$$CH_3OH + H_2O \rightleftharpoons 3H_2 + CO_2 \quad \Delta H^0_{298} = 49.4\ \mathrm{kJ\,mol^{-1}}, \tag{3}$$

$$CH_3OH + (1-2\delta)H_2O + \delta O_2 \rightleftharpoons (3-2\delta)H_2 + CO_2 \tag{4}$$
$$\text{if } \delta = 0.25, \quad \Delta H^0_{298} = -71.4\ \mathrm{kJ\,mol^{-1}},$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H^0_{298} = -41.1\ \mathrm{kJ\,mol^{-1}}. \tag{5}$$

While DCM and SRM reactions are endothermic, the POM and OSRM reactions are exothermic. The decomposition of methanol to CO and H_2 has been studied extensively by many researchers [4,7,8], because the syngas obtained from methanol is up to 60% more efficient than gasoline and up to 34% better than undecomposed methanol itself. In addition, the endothermicity of the reaction is taken as an advantage as heat recovery system in factories such as power plants and in iron manufacture. On the other hand, for the purpose of fuel cells in mobile applications, the SRM

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reaction is considered to be the most suitable since the reaction produces stoichiometrically more H_2 than is actually available in methanol alone on account of the participation of water in the overall process. Moreover, the by-product is CO_2 rather than CO, which is a poison to the Pt anode of the fuel cells. Fierro and coworkers [5] have recently reported that, because of the exothermicity, the POM reaction is more energy efficient compared with the SRM reaction and could be used for H_2 generation onboard a vehicle. We have recently demonstrated that a combined SRM and POM reaction referred to as "oxidative steam reforming" (OSRM, equation (4)) reaction is the most convenient way for onboard H_2 generation for fuel cells [9]. The catalysts used in the SRM and OSRM reactions are mostly Cu-based, particularly, CuZn- or CuZnAl-mixed oxides. However, because copper has a relatively low melting point (1083 °C), the Cu-based catalysts are in general very sensitive for deactivation by thermal sintering. Furthermore, it is generally difficult to achieve a very low outlet CO level of <20 ppm in the SRM reaction over CuZn-based catalysts because of the involvement of the water–gas shift (WGS) equilibrium (equation (5)) limitation [10]. On the other hand, methanation and CO oxidation reactions are thermodynamically feasible and hence the reformed gas is subsequently refined by CO oxidation and/or methanation reactions before being fed into the fuel cells [11]. If a catalyst possesses reforming and methanation/CO oxidation abilities it may be possible to produce CO-free H_2 from methanol in a single step. The Ni- and Co-based mixed oxides are already known as promising catalysts in methanation, dehydration and oxidation reactions [12,13]. The Co-based oxide catalysts have recently been employed in the CO oxidation reaction [14,15]. Unfortunately, there are no reports available in the literature on the reactions of methanol over Ni- and Co-based catalysts for the production of H_2, although some researchers have investigated the decomposition of methanol over Ni-based catalysts [4,7,13].

In the present investigation we report for the first time the use of Ni- and Co-based catalysts derived from NiAl- and CoAl-layered double hydroxides (LDHs) for four kinds of reactions involving methanol, namely DCM, POM, SRM and OSRM, to produce H_2/syngas. LDHs are represented by the general formula: $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[(A^{n-})_{x/n} \cdot mH_2O]^{x-}$, where M(II) is a divalent cation such as Mg^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}; M(III) is a trivalent cation such as Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mn^{3+}, Ga^{3+}, Rh^{3+}; and A^{n-} is a charge compensating anion such as CO_3^{2-}, NO_3^-, Cl^-, etc. Mixed oxides derived from LDHs have been successfully employed as catalysts in various reactions [12]. We have recently shown the successful incorporation of a tetravalent cation, Sn^{4+} in the M(II)Al-LDH with M(II) being Mg, Ni and Co [16–18]. The incorporation of Sn in the NiAl- and CoAl-LDH systems has been found to greatly modify the structural and redox properties of the resulting oxide materials [18]. Hence, the effect of incorporation of Sn in the layers of NiAl- and CoAl-LDHs on catalytic performance in methanol reactions has also been investigated.

2. Experimental

Experimental details concerning the catalyst preparation, chemical analyses, XRD and TPR methods were presented in [16–18]. The BET surface area, pore volume (V_p) and pore radii (R_p) of the catalysts were determined by the N_2 adsorption–desorption method at liquid-N_2 temperature using a Belsorp-28 SP (Japan) adsorption unit. The values of V_p and R_p were obtained from the desorption branch. The reactions of methanol were performed in a fixed-bed glass flow reactor (4 mm i.d) using a 100 mg of the catalyst (particle size 0.30–0.355 mm) in the temperature range 125–300 °C at atmospheric pressure [19]. The catalyst was first reduced in a stream of H_2 (10–20 $cm^3\,min^{-1}$) from room temperature to 650 °C with a heating rate of 10 $°C\,min^{-1}$ and dwelling at this temperature for 3 h before cooling down to the reaction temperature. Subsequently, pure methanol (for DCM and POM reactions), or a premixed water and methanol with a H_2O/CH_3OH molar ratio $= 1.3$ was fed into the pre-heater by means of a micro-feeder (liquid flow rate $= 1.0$–2.0 $cm^3\,h^{-1}$). Synthetic air (20.2 vol% of O_2 in N_2) at a rate of 10–20 $cm^3\,min^{-1}$ (for POM and OSRM reactions) and Ar (carrier gas, 43 $cm^3\,min^{-1}$) were adjusted by means of a mass flow controller. The reaction products were analyzed on-line using two gas chromatographs (Shimadzu GC-8A and GL Sciences, Japan, GC-320) equipped with thermal conductivity detectors. The GC (GC-8A) equipped with a 2 m long Porapak-Q column was able to detect the liquid products such as water, methanol, formaldehyde, methyl formate and dimethyl ether. On the other hand, the gaseous products such as H_2, air, CO, CO_2 and CH_4 were detected by the GC-320 equipped with an activated carbon column (CO detection limit was about 800 ppm). The catalytic activity was evaluated from the data collected between 3 and 4 h of the on-stream operation.

3. Results and discussion

3.1. Structural and redox properties of the catalysts

The results on the detailed physicochemical properties of the NiAl- and CoAl-LDHs and their Sn-containing analogues as well as their thermally derived materials characterized using XRD, TG/DTA and TPR methods were reported very recently [18] and hence they will be discussed here only briefly. Table 1 summarizes the chemical compositions and lattice parameters of M(II)Al-LDHs, where M(II) $=$ Ni or Co and their Sn-containing analogues, while the structural and textural properties of the these LDHs calcined at 450 °C for 5 h (catalysts) are collected in table 2. XRD patterns of the Ni-based catalysts indicated a rock salt type NiO phase. On the other hand, the Co-based catalysts exhibited a non-stoichiometric Co-spinel phase similar to that of Co_3O_4 in which a part of Co^{3+} is substituted by Al^{3+}/Sn^{4+} or $CoAl_2O_4$ wherein Co^{3+}/Sn^{4+} substitutes a part of Al^{3+} [18]. Figure 1 displays the TPR profiles of

Table 1
Chemical composition and lattice parameters of M(II)Al- and M(II)AlSn-LDHs.

LDH	M(II) : Al : Sn[a] atomic ratio	M(II)/ Al	M(II)/ (Al + Sn)	Lattice parameters (Å) a	c	FWHM[b] (2θ)	t[c] (Å)
NiAl-LDH	3 : 1.00 : 0.00	2.88	2.88	3.046	23.280	1.45	55
NiAlSn-LDH	3 : 0.95 : 0.40	3.16	2.22	3.064	22.754	1.97	41
CoAl-LDH	3 : 0.86 : 0.00	3.49	3.49	3.074	23.047	1.05	76
CoAlSn-LDH	3 : 0.93 : 0.36	3.23	2.33	3.103	22.750	1.18	68

[a] Determined by X-ray fluorescence spectroscopy.
[b] Full width at half maximum (FWHM) of (003) plane.
[c] Crystallite size (t) calculated from (003) plane using the Debye–Scherrer equation.

Table 2
Structural and textural properties of NiAl- and CoAl-LDHs, and their Sn-containing analogues calcined at 450 °C for 5 h.

LDH	XRD data		N_2 adsorption–desorption measurements		
	Phase obtained	Lattice parameter (Å)	A_{BET} ($m^2\,g^{-1}$)	R_p (Å)	V_p ($cm^3\,g^{-1}$)
NiAl-LDH	NiO	4.166	140	24	0.46
NiAlSn-LDH	NiO	4.182	152	26	0.48
CoAl-LDH	Co-spinel	8.076	103	29	0.39
CoAlSn-LDH	Co-spinel	8.096	156	35	0.60

all these catalysts. The Ni-based catalysts exhibit a broad TPR profile in the range 300–700 °C due to the reduction of Ni^{2+} to Ni^0. The temperature required for maximum rate of H_2 consumption decreases upon Sn incorporation, indicating that the reducibility of Ni is enhanced when Sn is present. Pure SnO_2 exhibited a single TPR peak centering at around 650 °C corresponding to the reduction of Sn^{4+} to Sn^0 [18]. However, no TPR peak could be observed above 600 °C in the catalyst derived from NiAlSn-LDH, demonstrating that the reduction peak of Sn^{4+} is overlapped with that of Ni^{2+}. The reducibilities of both Ni^{2+} and Sn^{4+} are improved if they were present together. In the case of the catalyst derived from CoAl-LDH, the TPR displays at least two reduction regions, one between 200 and 400 °C and the other above 450 °C. On the basis of comparison of TPR results of standard samples of CoO, Co_3O_4 and $CoAl_2O_4$, the reduction in region I has been attributed to the reduction of Co^{2+}–Co^{3+}-like species in the non-stoichiometric spinel having chemical environments similar to that of the Co_3O_4 spinel. On the other hand, the reduction in region II has been assigned to the reduction of Co^{2+}–Al^{3+}-like species, which behave chemically like $CoAl_2O_4$ spinel. Furthermore, the TPR profile has not recovered the base line indicating that the reduction of $CoAl_2O_4$-like species has not been completed even up to 700 °C. The temperature for maximum rate of H_2 consumption in the reduction region I increased while that in region II decreased upon Sn incorporation. These results reveal that the reducibility of Co_3O_4-like species in the non-stoichiometric spinel are declined while that of $CoAl_2O_4$-like species are improved when Sn is present in the Co-based catalyst. The significant influences observed in the redicibilities of Ni- and Co-containing species upon Sn incorporation in the present system implies that some sorts of interaction or

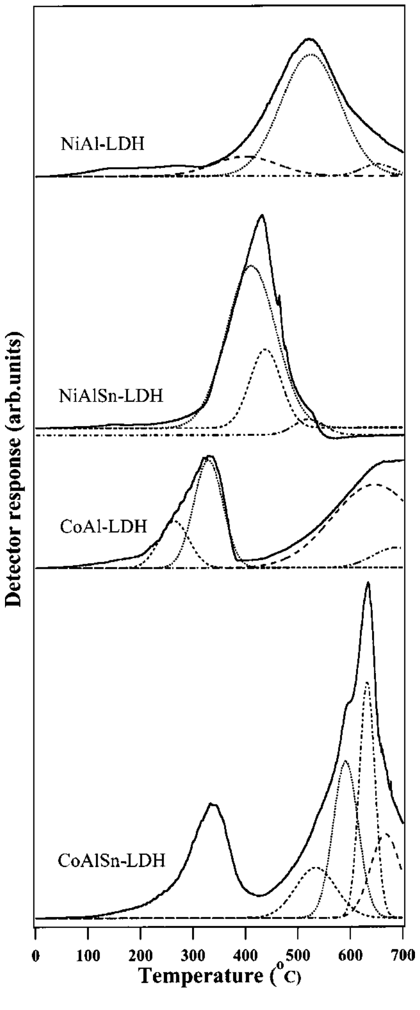

Figure 1. TPR profiles of catalysts derived from NiAl- and CoAl-LDHs, and their Sn-containing analogues. Solid lines are experimental curves and dotted lines are deconvoluted curves.

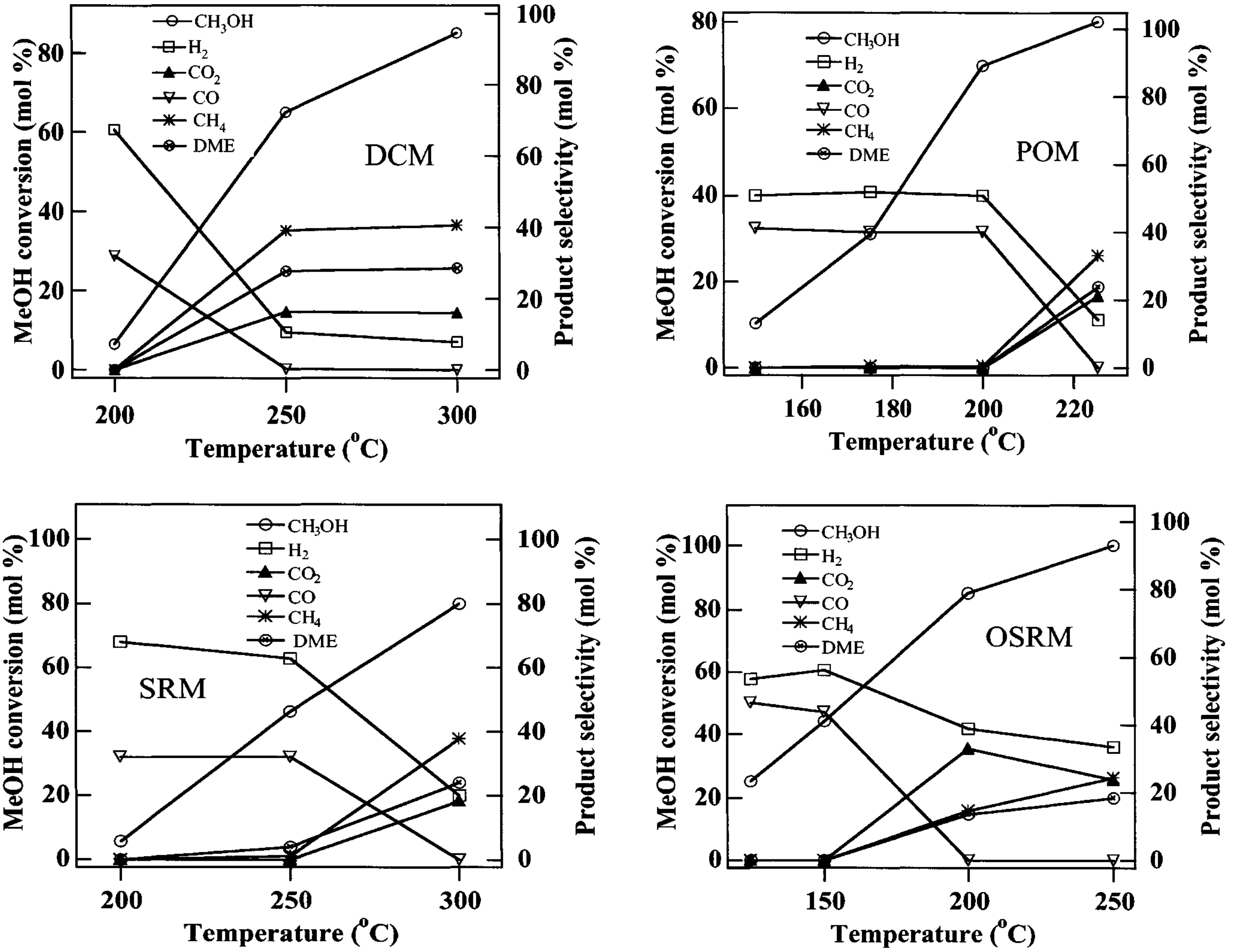

Figure 2. Effect of temperature on catalytic performance in the reactions of methanol over catalyst derived from NiAl-LDH.

synergism would exist between Ni/Co and Sn. Such an interaction or synergism is expected to bring about substantial changes in the catalytic activity and product distribution in the reactions of methanol.

3.2. Reactions of methanol over Ni-based catalysts

The effect of temperature on catalytic performance in the DCM, POM, SRM and OSRM reactions over catalysts derived from NiAl-LDH is illustrated in figure 2. MeOH conversion increases with increasing reaction temperature in all four reactions. The temperature required for above 80% methanol conversion depends on the kind of reaction and is around 300 °C for DCM and SRM reactions while for POM and OSRM reactions it is around 230 and 250 °C, respectively. H_2, CO and/or CO_2 are the predominant products in all the four reactions. The selectivity to H_2 and CO decreases with consequent increase in the selectivity of dimethyl ether (DME), CH_4 and CO_2 with increasing reaction temperature. These results infer that the dehydration of methanol to DME (equation (6)) and hydrogenation of CO/CO_2 to methane (equation (7)) are also taking place in a significant extent, particularly in the DCM reaction wherein relatively large amounts of CH_4 and DME are observed. The presence of Al in the catalyst is likely to introduce acidity which is responsible for the formation of DME as similar results have also been observed in an earlier report on the decomposition of methanol over Al_2O_3 and $NiAl_2O_3$ catalysts [13]. In contrast to this, the formation of DME has not been observed in the DCM reaction over Ni supported on silica catalyst [7]. Both CH_4 and DME are undesirable by-products in the reactions of methanol for the purpose of producing H_2, because the formation of these products reduces the selectivity of H_2 considerably. The formation of CO_2 even in the DCM reaction indicates the involvement of the steam reforming reaction of H_2O formed in dehydration and methanation reactions (equations (6) and (7), respectively) with methanol (equation (3)) as proposed already in the decomposition of methanol over Cu-based catalysts [20]. Interestingly, the selectivities to DME and CH_4 are reduced considerably in the POM and OSRM reactions involving O_2. Most importantly, the CO selectivity in the later reactions is greatly suppressed (almost to 0 mol%, within TCD detection limit of ca. 800 ppm) at higher methanol conversions. Among the four reactions tested, the OSRM reaction offered a high methanol conversion and H_2 selectivity at relatively lower temperatures. Moreover, the undesirable by-products, DME and CH_4 remain considerably lower. In addition, the CO selectivity is suppressed to almost 0% above 200 °C.

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \quad \Delta H^0_{298} = -24.8\ \mathrm{kJ\,mol^{-1}}, \qquad (6)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad \Delta H^0_{298} = -206.4\ \mathrm{kJ\,mol^{-1}}. \qquad (7)$$

The effect of temperature on the catalytic performance in the reactions of methanol over the catalyst derived from NiAlSn-LDH is shown in figure 3. Incorporation of Sn in the NiAl-LDH system inhibits the catalytic activity for methanol conversion. In fact, the catalyst was found to be almost inactive in the DCM reaction under our present experimental conditions. H_2 and CO are the major products in all the other three reactions, namely POM, SRM and OSRM, and the selectivity to these products remains almost unaffected with increasing reaction temperature. The selectivities to DME, CH_4 and CO_2 are also suppressed. These results reveal that the rates of dehydration, methanation and reforming reactions are poor over the Sn-containing catalyst. Interestingly, traces of formaldehyde are also observed above 250 °C only in the POM reaction, indicating that the added Sn favors the oxidative dehydrogenation of methanol to formaldehyde (equation (8)) to some extent. In the oxidation of methanol over oxide catalysts, it is generally accepted that surface acid sites produce the dehydration product, DME, while the redox sites produce formaldehyde, methyl formate, etc. [21,22]. It is therefore likely that substitution of a part of Al by Sn alters the acidity and improves the redox capability of the catalyst. Although, acidity of catalysts has not been evaluated at this moment, the enhanced reducibility of Ni upon Sn incorporation as evidenced from the TPR results corroborates our assumption.

$$CH_3OH + \tfrac{1}{2}O_2 \rightleftharpoons HCHO + H_2O \quad \Delta H^0_{298} = -156.5\ \mathrm{kJ\,mol^{-1}}. \qquad (8)$$

3.3. Reactions of methanol over Co-based catalysts

Figure 4 depicts the effect of temperature on catalytic performance in the DCM, POM, SRM and OSRM reactions over the catalyst derived from CoAl-LDH. Similar to that observed in the Ni-based catalysts, the methanol conversion increases with increasing reaction temperature in all the four reactions of methanol. Interestingly, the selectivity to H_2 remained relatively higher and the selectivities to the undesirable by-products, CH_4 and DME, are lower in all the reactions of methanol.

The effect of Sn incorporation in the layers of CoAl-LDH on the catalytic performance in the reactions of methanol has also been investigated. The catalyst derived from CoAlSn-LDH was found to be almost inactive in the DCM as well as SRM reactions. The catalyst offered about 60% methanol conversion at around 300 °C in the reactions involving oxygen, namely the POM and OSRM reactions (see figure 5). Similar to that observed in the catalyst derived from NiAlSn-LDH, the formation of formaldehyde, in addition to the usual products, H_2, CO_2 and CO, has been observed. Traces of formaldehyde appeared only in the POM reaction above 250 °C in the Ni-containing ana-

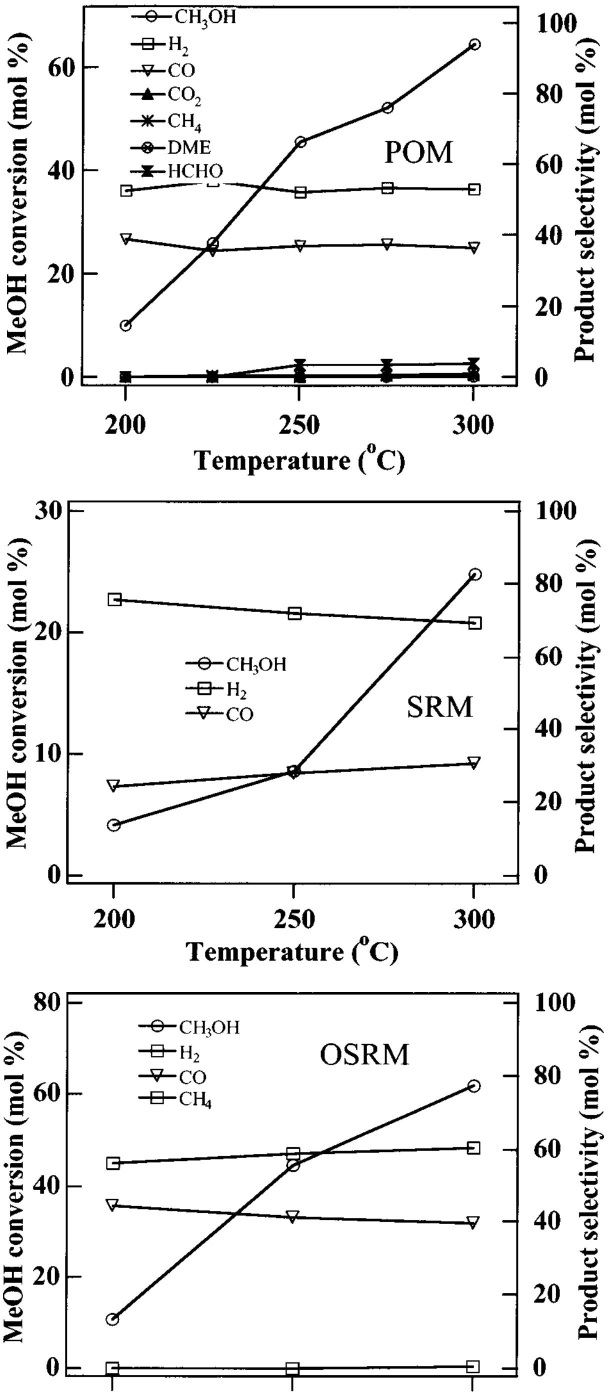

Figure 3. Effect of temperature on catalytic performance in the reactions of methanol over catalyst derived from NiAlSn-LDH.

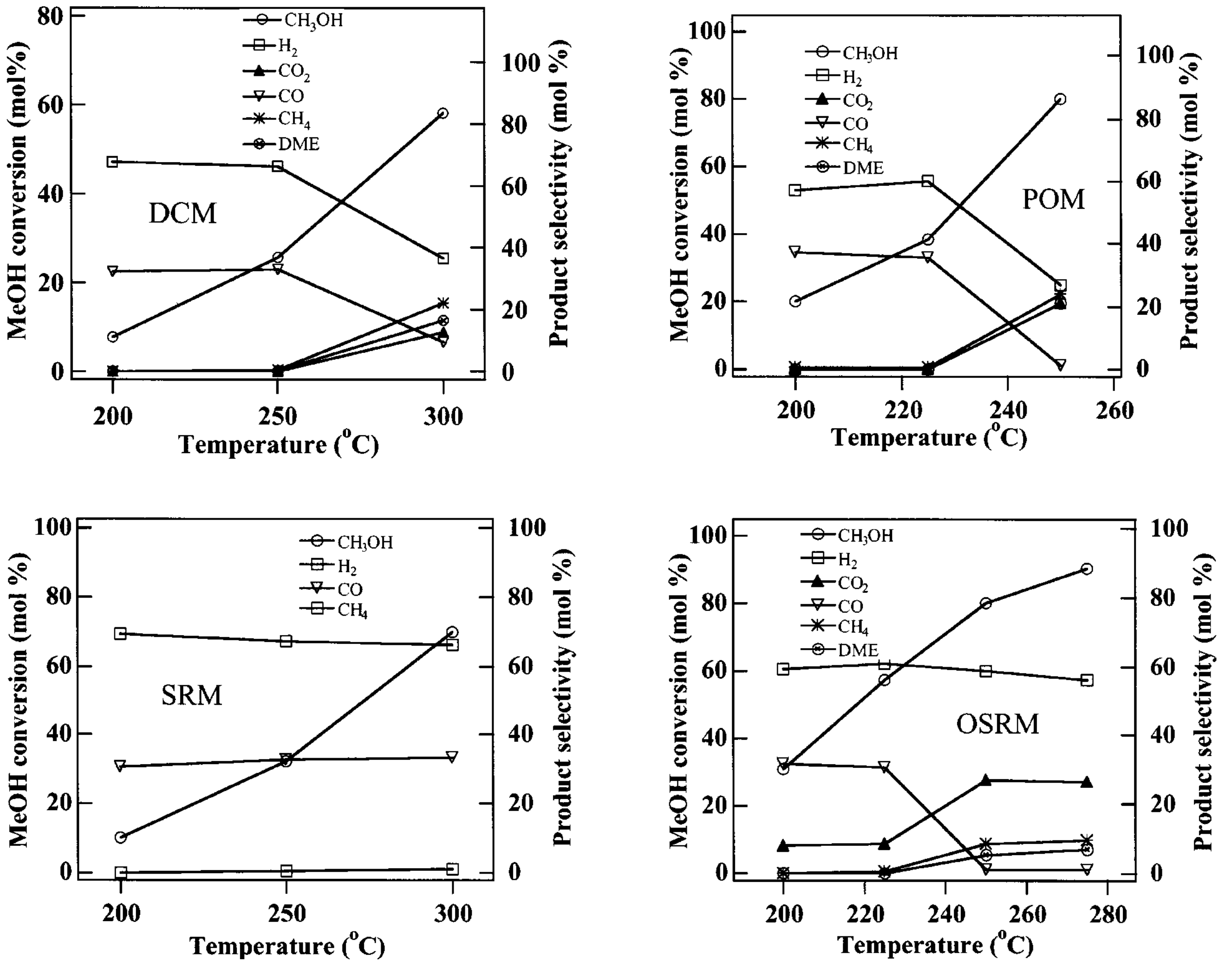

Figure 4. Effect of temperature on catalytic performance in the reactions of methanol over catalyst derived from CoAl-LDH.

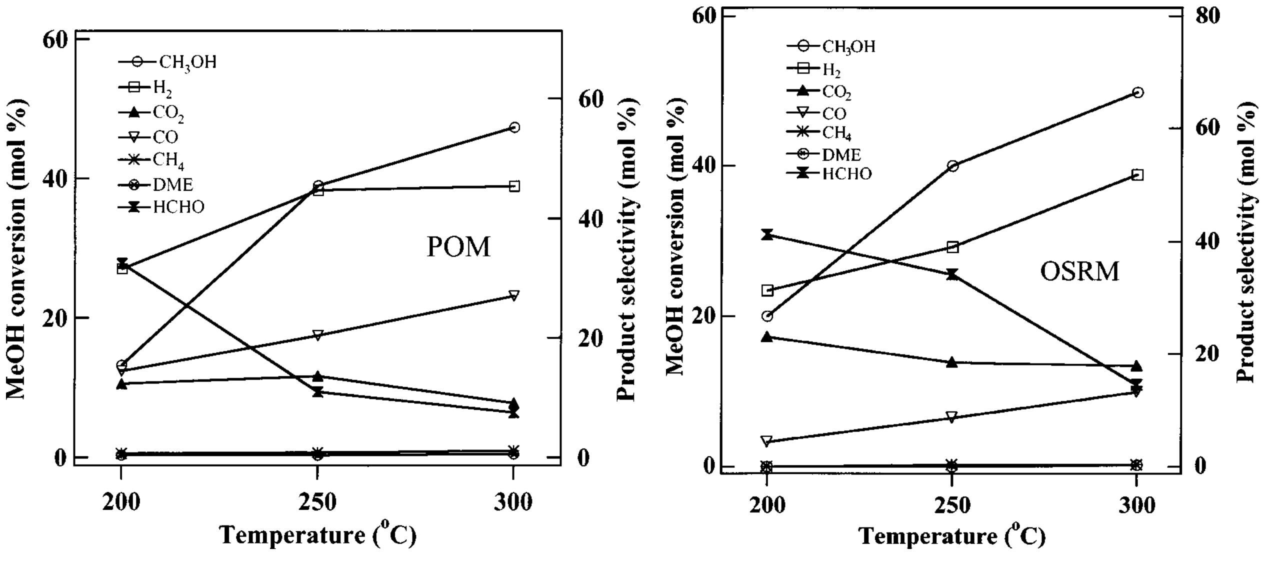

Figure 5. Effect of temperature on catalytic performance in the reactions of methanol over catalyst derived from CoAlSn-LDH.

logue. On the other hand, significantly large amounts of formaldehyde production (up to about 40% selectivity) are noticed in both POM and OSRM reactions around 200 °C and its selectivity decreases with increasing reaction temperature. The incorporation of Sn in the CoAl-LDH system improves the reducibility of Co^{2+}–Al^{3+}-like species

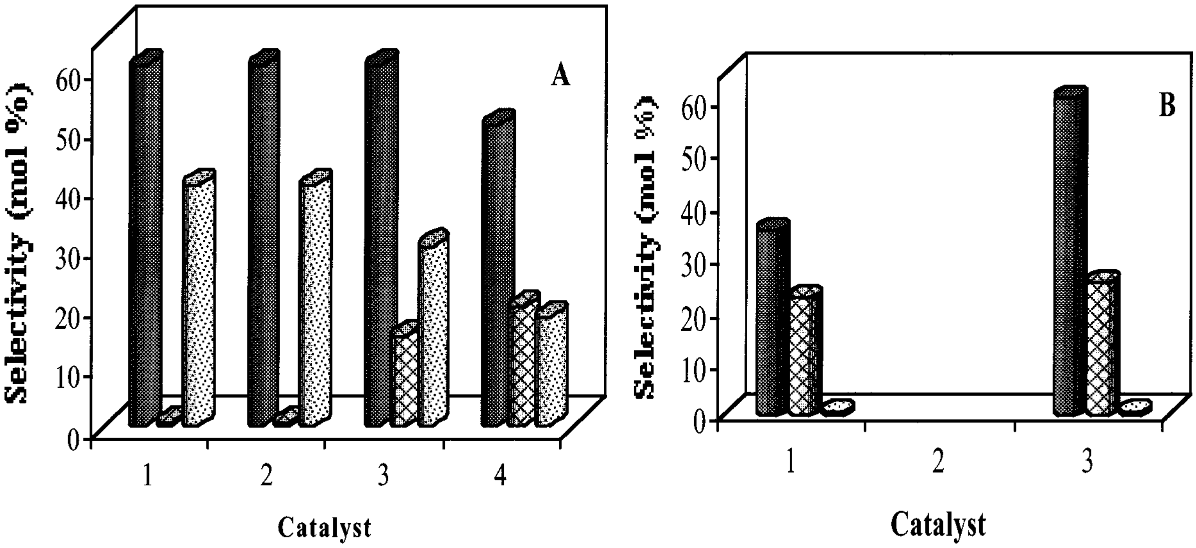

Figure 6. Comparison of product selectivity at constant methanol conversion levels in the OSRM reaction over various catalysts: (A) 50% conversion level and (B) 90% conversion level. Catalysts 1, 2, 3 and 4 are those derived from NiAl-, NiAlSn-, CoAl- and CoAlSn-LDHs, respectively. (▩) Hydrogen, (☒) carbon dioxide and (⊡) carbon monoxide.

in the reduction region II (see figure 1) indicating that incorporation of Sn in the CoAl system introduces a strong interaction or synergism with Co. Such an interaction or synergism would favor the oxidative dehydrogenation of methanol to formaldehyde activity.

Our experiments clearly demonstrate that among the four kinds of reactions of methanol studied, the OSRM reaction exhibits a better methanol conversion and H_2 selectivity over all the catalysts tested. The product selectivity in the OSRM reaction over various catalysts at a constant methanol conversion of about 50% (figure 6(A)) and 90% (figure 6(B)) is compared. The temperature required for 50% methanol conversion is around 160, 265, 220 and 300 °C for catalysts derived from NiAl-, NiAlSn-, CoAl- and CoAlSn-LDH, respectively. H_2 selectivity is about 60% in all the catalysts together with considerable amount of CO as a by-product. The CO selectivity is greatly suppressed at high methanol conversion of about 90% over catalysts derived from NiAl- and CoAl-LDHs. The H_2 selectivity reduced to about 40% in the case of the NiAl catalyst because of the subsequent hydrogenation of CO to CH_4 at higher conversions. On the other hand, the H_2 selectivity remains around 60% over the CoAl catalyst with lower selectivities to DME and CH_4. Furthermore, the selectivity to CO attained around 0% at about 250 °C with a consequent increase in the selectivity to CO_2 indicating that oxidation of CO to CO_2 (equation (9)) is preferentially taking place over Co-based catalyst. From these results it can be concluded that the Co-based catalyst is very attractive as a promising catalyst in the OSRM reaction for the selective production of H_2 for fuel cells.

$$\mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \rightleftharpoons \mathrm{CO_2} \qquad \Delta H^0_{298} = -283\ \mathrm{kJ\,mol^{-1}}. \qquad (9)$$

4. Conclusions

The Ni- and Co-based catalysts derived from corresponding LDH precursors are active in four kinds of reactions of methanol, namely DCM, POM, SRM and OSRM reactions, to produce H_2. Among them, the OSRM reaction offered a better catalytic performance in terms of methanol conversion and hydrogen selectivity. The selectivity of CO has been greatly suppressed at higher methanol conversions with a consequent increase in the selectivity to CO_2. The catalyst derived from CoAl-LDH was found to be more promising in the OSRM reaction for the selective production of H_2 for fuel cells. The formation of undesirable by-products, DME (dimethyl ether) and CH_4, decreased the selectivity to H_2. However, further modifications of catalyst formulation would be expected to improve the selectivity to H_2 by minimizing the formation of DME and CH_4.

Partial substitution of Al by Sn exhibited an inhibiting effect of methanol conversion with two beneficial consequences: (i) The selectivities to DME and CH_4 were suppressed and the selectivity to H_2 improved. (ii) The catalyst, especially the Co-based one, produced formaldehyde, one of the value-added products, with a reasonably good selectivity at lower reaction temperatures. The presence of Sn in the Ni- and Co-based catalysts improves the reducibility of Ni- or Co-containing species, and the catalysts exhibit more redox capability.

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