

Alkali Metal-doped Transition Metal Oxides Active for Oxidative Coupling of Methane

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Abstract

Addition of alkali metals to the oxides of transition elements endowed the oxides with the ability for converting methane into C₂ compounds (C₂H₆ + C₂H₄). Among the combinations of alkali metals and transition metal oxides tested, the lithium added nickel oxide was the most active catalyst for the reaction. X-ray diffraction (XRD) analysis showed that the catalyst was a solid solution of lithium in NiO. The reaction of methane with the lattice oxygen atoms of the stoichiometric solid solution, LiNiO₂, produced C₂ compounds very selectively. The XRD analysis of the sample showed that the reaction proceeded as $2\text{LiNiO}_2 + 2\text{CH}_4 \rightarrow \text{Li}_2\text{O} + 2\text{NiO} + \text{C}_2\text{H}_6 + \text{H}_2\text{O}$. Oxidation of the reduced catalyst by oxygen regenerated LiNiO₂ as $\text{Li}_2\text{O} + 2\text{NiO} + 1/2\text{O}_2 \rightarrow 2\text{LiNiO}_2$. Thus, it is concluded that the oxidative coupling of methane proceeds via the redox mechanism of LiNiO₂. The stability of the solid solution of alkali metals with transition metal oxides under steady state reaction conditions is essential for the alkali-doped oxides to be effective in the oxidative coupling of methane.

Introduction

Methane is the major component of natural gas and is primarily used as a fuel. The abundance of methane makes it a raw material of great synthetic importance. However, because of the high stability of methane it must first be processed through a steam reforming step in any route to the desired chemicals. However, the steam reforming process suffers from the requirement of a lot of energy and complicated engineering steps. Obviously, direct conversion of methane to useful chemicals by partial oxidation would be a very desirable process.

Direct conversion of CH₄ into higher hydrocarbons by partial oxidation is one of the most challenging problems in heterogeneous catalysis. Since Keller and Bhasin [1] reported the possibility of synthesis of C₂ compounds (C₂H₆ + C₂H₄) by

oxidative coupling of CH₄ over metal oxides, many groups [2–11] are beginning to work in this area and there is increasing industrial activity [12]. The active and selective catalysts reported so far were alkali metal-doped alkaline earth oxides [3, 5, 6], rare earth oxides [4a, 4d, 4e] and the oxides of non-transition metals such as Bi₂O₃, PbO, ZnO with or without alkali metals added [1, 2, 6, 8, 9]. In addition to these catalysts, we have demonstrated that the Li-added first series transition metal oxides produced C₂ compounds with high selectivity and yield at 1023 K [4b, 4c]. Alkali-promoted Mn/SiO₂ is another example of the transition metal oxides used for the oxidative coupling of methane [11]. It is well known that the transition metal oxides in the absence of alkali metals are very active for catalyzing deep oxidation of CH₄ into CO and CO₂ at high temperatures (>873 K). The favorable effect of alkali metals has also been demonstrated for many non-transition metal oxides [2, 3, 5, 6, 9]. However, only a small amount of fundamental work has been reported concerning the effect of alkali metals in the host transition metal oxides for improving the partial oxidation of CH₄ into higher hydrocarbons. Thus, the first purpose of this work is to examine the best combination of transition metal oxides with alkali metals which give active catalysts for oxidative coupling of methane. The second aim is to describe the role of alkali metals for the best catalyst. Finally, the reaction mechanism and the role of lattice oxygen atoms for the best catalyst will be discussed.

Experimental

Powder metal oxides of the first transition elements in the periodic table were used as catalysts. The initial composition of the oxides used were Cr₂O₃, MnO₂, Fe₂O₃, Co₂O₃, NiO, and CuO. The transition metal oxides were impregnated with various alkali salts by immersing the oxides in aqueous solutions of the salts. The content of the alkali metals was adjusted to 20 mol% for each catalyst. The alkali salt-impregnated oxides were calcined in air at 673 K for 2 h and at 1023 K for 2 h before

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the experiments. The tests of the catalytic activities of the catalysts were carried out using a fixed-bed reactor with a conventional gas-flow system at atmospheric pressure using helium as a carrier gas. The reaction conditions for the test of catalytic activity were as follows: $T = 1023$ K, $P(\text{CH}_4) = 10.1$ kPa, $P(\text{O}_2) = 5.1$ kPa, weight of catalyst = 1.00 g, and $W/F = 0.167$ g h $^{-1}$. The gas–solid reaction of methane with catalysts was carried out by using a closed gas-circulation apparatus of 360 ml dead volume. The conversion of CH_4 , the selectivity to C_2 compounds, and the yield of C_2 compounds were calculated on the basis of carbon number of methane reacted.

The procedure of the temperature programmed desorption (TPD) measurement of oxygen was as follows. Before the experiments, the sample catalyst in a quartz reactor was calcined in air for 2 h using a closed gas circulation system and degassed in a vacuum for 1 h at 1023 K. The sample was then allowed to stand for 30 min in oxygen (13.3 kPa) at 1023 K. The sample was quickly cooled to room temperature by removing the electric furnace. After degassing gaseous oxygen at room temperature the TPD spectra were measured by increasing temperature at the rate of 20 K min^{-1} under vacuum and the relative pressure of oxygen desorbed was measured by a quadrupole mass spectrometer.

Results and Discussion

The Best Combination of Transition Metal Oxides and Alkali Metals

Table I shows the conversion of CH_4 , C_2 selectivity ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$) and C_2 yield measured for various alkali metal-added transition metal oxides. The combinations of the starting alkali salts with transition metal oxides for preparing the catalysts are indicated in the first column of Table I. The catalytic activities for some catalysts decreased with time on stream of the reactants in 60 min. However, the decrease was not so appreciable after 60 min. Therefore, the data at time on stream 60 min are shown in Table I. The host transition metal oxides in Table I did not produce any C_2 compounds but catalyzed only deep oxidation of CH_4 when the alkali metals had not been added to the oxides. Addition of alkali metals endowed the oxides with the ability for converting CH_4 into C_2 compounds as can be seen in Table I. The alkali metal-added cobalt oxides and the lithium added nickel oxide are active catalysts on the basis of observed C_2 yield. The lithium added nickel oxide showed the highest catalytic activity in the formation of C_2 compounds. Therefore, the catalytic behavior of the lithium-added nickel oxide will be investigated further.

TABLE I. Effect of Alkali Salts (20 mol%) on the Conversion of CH_4 , C_2 Selectivity, and C_2 Yield^a

Starting materials	CH_4 conversion (%)	C_2 selectivity (%)	C_2 yield (%)
$\text{LiNO}_3/\text{Cr}_2\text{O}_3$	18.9	0.00	0.00
$\text{NaNO}_3/\text{Cr}_2\text{O}_3$	7.19	1.16	0.08
$\text{KNO}_3/\text{Cr}_2\text{O}_3$	3.55	2.98	0.11
$\text{LiNO}_3/\text{MnO}_2$	19.8	0.36	0.07
$\text{NaNO}_3/\text{MnO}_2$	25.8	1.80	0.47
$\text{KNO}_3/\text{MnO}_2$	25.4	2.74	0.70
$\text{LiNO}_3/\text{Fe}_2\text{O}_3$	22.2	2.25	0.50
$\text{NaNO}_3/\text{Fe}_2\text{O}_3$	24.8	2.41	0.60
$\text{KNO}_3/\text{Fe}_2\text{O}_3$	24.3	3.00	0.73
$\text{LiNO}_3/\text{Co}_2\text{O}_3$	19.9	2.52	0.50
$\text{NaNO}_3/\text{Co}_2\text{O}_3$	17.6	9.86	1.73
$\text{KNO}_3/\text{Co}_2\text{O}_3$	11.7	21.2	2.49
$\text{RbOH}/\text{Co}_2\text{O}_3$	25.3	16.6	4.20
$\text{CsOH}/\text{Co}_2\text{O}_3$	25.3	10.0	2.57
LiNO_3/NiO	20.7	46.9	9.71
NaNO_3/NiO	8.24	5.04	0.41
KNO_3/NiO	14.6	11.0	1.61
LiNO_3/CuO	15.1	4.15	0.63
NaNO_3/CuO	12.8	5.93	0.76
KNO_3/CuO	16.7	5.11	0.86

^aReaction conditions are described in 'Experimental'.

Li-doped NiO

XRD analysis for the nickel oxide with lithium of 20 mol% calcined at 1023 K showed the diffraction patterns of Fig. 1a. The patterns indicate the presence of NiO and solid solutions of lithium in NiO represented by the formula $\text{Li}_x(\text{Ni}^{2+})_{1-2x}(\text{Ni}^{3+})_x\text{O}$ [14]. Calcination of the mixture of NiO and LiNO_3 (20 mol%) at 1073 K in air for 20 h gave only the solid solution of Li and NiO without any NiO phase. This observation suggests that the diffusion of Li cations into NiO lattice is incomplete when the mixture is calcined at the temperatures lower than 1023 K for only 2 h.

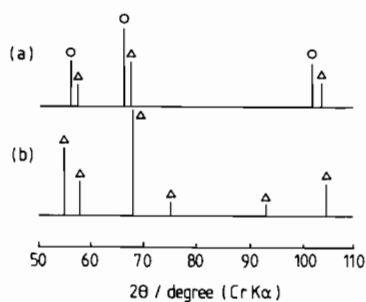


Fig. 1. X-ray diffraction spectra for Li-doped NiO: (a) Li(20%)–NiO prepared at 1023 K for 2 h in air; (b) Li(50%)–NiO prepared at 1073 K for 20 h. \circ , NiO; \triangle , Li–NiO solid solution.

TABLE II. Results of Oxidative Coupling of Methane Observed for the Li–NiO Solid Solutions with Different Contents of Li^a

Li content (%)	Surface area (m ² /g)	Lattice parameters (Å) (rhombohedral)	CH ₄ conversion (%)	O ₂ conversion (%)	C ₂ selectivity (%)	C ₂ yield (%)
10	0.29	<i>a</i> = 2.944 <i>c</i> = 14.41	29.4	97.3	23.8	7.0
20	0.31	<i>a</i> = 2.930 <i>c</i> = 14.33	27.6	81.7	30.7	8.5
50	0.33	<i>a</i> = 2.900 <i>c</i> = 14.25	22.2	43.6	59.0	13.1

^aExperimental conditions were the same as those for Table I.

Table II shows the results of the reaction for the solid solutions of Li and NiO with different contents of Li prepared by calcination of the LiNO₃ and NiO mixtures at 1073 K for 20 h in air. Li(50%)–NiO, for example, indicated in Table II means the NiO contained 50 mol% of Li (Li:Ni = 1:1). The XRD spectrum of Li(50%)–NiO is shown in Fig. 1b. Lattice parameters of the samples assuming rhombohedral structure [13,14] are shown in the third column in Table II. The parameters decrease with increasing the content of Li as expected. The kinetic results in Table II show that, although the conversions of methane and oxygen decrease, the C₂ selectivity and C₂ yield increase with a rise in the content of Li in NiO. These observations suggest that the compound lithium nickelate(III), LiNiO₂ would be the active species in the Li-added NiO for oxidative coupling of methane. Moreover the results in Table II suggest that the catalytic activity of the host oxide for deep oxidation is reduced by the addition of alkali metals. The XRD spectrum and the lattice parameters observed for Li(50%)–NiO (Fig. 1b and Table II) show that this sample can be assumed to be a pure lithium nickelate(III) [13,14]. Therefore, this sample will be denoted as LiNiO₂ hereafter.

Figure 2 shows the TPD spectra of oxygen for the samples of LiNiO₂, Li(20%)–NiO, Li(10%)–NiO and NiO. The quantities of the samples used were 10 mg for the former three catalysts but 1.0 g for NiO. As can be seen in Fig. 2, the quantity of oxygen desorbed increases as the content of Li in NiO increases. The desorption begins at lower temperatures for the sample containing a larger quantity of Li. The XRD analysis for LiNiO₂ and Li(20%)–NiO after the TPD measurement of Fig. 2 showed a decrease in the intensity of the diffraction peaks of Li–NiO solid solution, but the spectra showed the sharp peaks due to NiO crystals. These observations strongly suggest that the Li-doped NiO is readily decomposed or reduced in a vacuum with

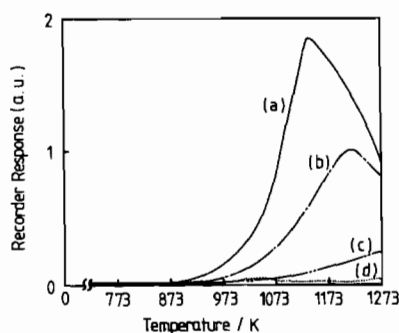


Fig. 2. TPD spectra of oxygen for Li–NiO solid solutions: (a) LiNiO₂; (b) Li(20%)–NiO; (c) Li(10%)–NiO; (d) NiO.

a rise in temperature above 873 K probably according to eqn. (1).



Reaction of Methane with Lattice Oxygen Atoms

The gas–solid reaction between methane and LiNiO₂ has been examined to get information about the oxygen species responsible for oxidative coupling of CH₄. Figure 3 shows the kinetic curves of oxidation of CH₄ by LiNiO₂ in the absence of gaseous oxygen. Here, the quantities of the C₂ compounds indicated are on the basis of carbon atoms, *i.e.* twice of the mole of C₂ compounds produced. The reaction was carried out at 973 K and 5.3 kPa of initial pressure of CH₄ using closed gas-circulation apparatus. The pretreatment of the catalyst was the same as that for the TPD experiment. The weight of LiNiO₂ used in the experiment for Fig. 3 was 1.00 g. Prior to the experiment, the temperature of the catalyst bed was quickly raised to 973 K from room temperature within 10 min and the gas–solid reaction was started by adding methane to the system. Only a trace of oxygen was observed in the gas phase at the first analysis of the gas composition in the system by gas chromatographic technique.

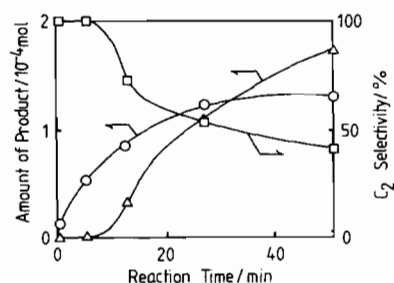
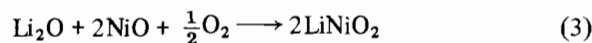
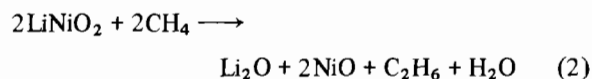


Fig. 3. Gas-solid reaction between CH₄ and LiNiO₂ at 973 K. Kinetic curves of products: ○, C₂H₆ + C₂H₄; △, CO₂; □, C₂ selectivity. Initial CH₄ pressure was 5.3 kPa.

However, no gaseous oxygen was observed after then. The CO₂ evolved in the gas phase during the reaction was only a trace probably because of absorption of the CO₂ formed by the catalyst or of reaction with the Li₂O produced in eqn. (2). Therefore, the amount of CO₂ plotted in Fig. 3 was calculated from the difference in the amount of carbon between the methane reacted and the ethane and ethylene produced. The experimental error in the amount of CO₂ thus calculated was of $\pm 0.05 \times 10^{-4}$ mol. As can be seen in Fig. 3, C₂ compounds (mainly C₂H₆) were produced very selectively (100%) at the early stage of the reaction. The formation of CO₂ commenced after 5 min, decreasing the C₂ selectivity. Similar kinetic curves to those in Fig. 3 were also observed in the case of the reaction of CH₄ with Li(20%)-NiO.

Figure 4 shows the XRD patterns observed for LiNiO₂ after different treatments. The spectrum for the fresh LiNiO₂ before the reaction was already shown in Fig. 1b. The change in the spectra from Fig. 1b to (a) in Fig. 4 indicates that LiNiO₂ is reduced to NiO by CH₄. Oxidation of the reduced sample regenerates LiNiO₂ (spectrum (b)), though some peaks are missing compared to the original sample (Fig. 1b). The results in Figs. 3 and 4 strongly suggest that the oxidative coupling of CH₄ proceeds via the redox of LiNiO₂ as follows



The desorbable oxygen observed in the TPD experiments (Fig. 2) must be responsible for reaction (2). The induction period observed for the formation of CO₂ in Fig. 3 can be explained by the idea that the deep oxidation of CH₄ is caused by the NiO formed according to eqn. (2). In fact, the gas-solid reaction between CH₄ and NiO at 973 K produced only CO₂. Thus, the role of Li doped in NiO is to generate the active lattice oxygen atoms of LiNiO₂

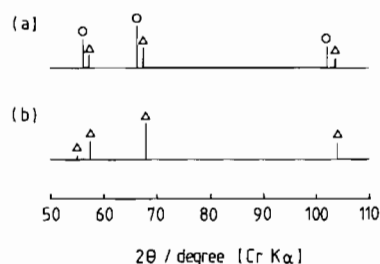


Fig. 4. XRD spectra for the LiNiO₂ after the following treatment: (a) after the reaction with CH₄ (13.3 kPa) at 973 K for 160 min; (b) after oxidation of the sample (a) with oxygen (13.3 kPa) at 1023 K for 60 min. ○, NiO; △, Li-NiO solid solution.

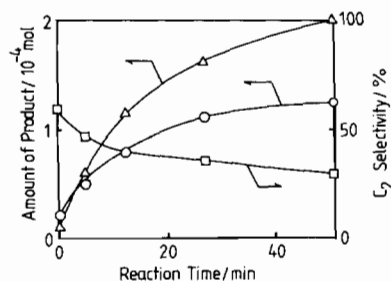


Fig. 5. Gas-solid reaction between CH₄ and LiNiO₂ in the presence of gaseous oxygen at 973 K. Kinetic curves of products: ○, C₂H₆ + C₂H₄; △, CO₂; □, C₂ selectivity. Initial pressures of CH₄ and O₂ were 5.3 and 0.53 kPa, respectively.

for the formation of C₂ compounds according to eqn. (2).

Figure 5 shows the kinetic curves observed in the presence of gaseous oxygen at the early stage of the reaction. The experimental procedure and conditions are the same as those for Fig. 3 except for the presence of gaseous oxygen (initial partial pressure was 0.53 kPa). In contrast to the results in Fig. 3, fast production of CO₂ was observed at the initial stage of the reaction when gaseous oxygen was present. However, very similar kinetic curves of C₂ formation were observed in the presence and absence of gaseous oxygen, indicating that the formation rates of C₂ compounds are approximately the same in the two cases. This observation supports the idea that the formation of C₂ compounds is caused by the lattice oxygen atoms of LiNiO₂ according to eqn. (2). The adsorbed oxygen on the surface supplied from the gaseous oxygen must oxidize methane mainly to CO₂. The gaseous oxygen added was consumed within 15 min for the formation of CO₂ in Fig. 5. This explains the observation that the quantity of CO₂ was not increased sharply at the later stage of the reaction in Fig. 5.

Gaseous oxygen decreases the C₂ selectivity due to deep oxidation of CH₄ to CO₂. However, the presence of gaseous oxygen, of course, is necessary

to regenerate LiNiO_2 (eqn. (3)) under steady state catalytic reactions. The XRD analysis for the LiNiO_2 used in the steady state catalytic reaction at 1023 K in the gas mixture of CH_4 (10.1 kPa) and O_2 (5.1 kPa) showed strong XRD peaks of LiNiO_2 and very small peaks due to NiO , indicating only a slight decomposition or reduction of the catalyst during the reaction.

The 1:1 mixture of NaNO_3 and NiO calcined in air at 1023 K gave a similar complex oxide NaNiO_2 . However, this complex oxide was unstable and was reduced to NiO under steady state catalytic reactions. The 1:1 mixture of KNO_3 and NiO did not produce any complex oxide. These facts explain why the Na- and K-doped NiO were poor catalysts in oxidative coupling of methane compared to the Li-doped NiO (Table I). As described above, good stability of the solid solution compounds under steady state reaction conditions is an important factor for the alkali metal-doped transition metal oxides to be effective in oxidative coupling of methane.

Since NiO exerts an unfavorable effect enhancing deep oxidation of methane, the fast oxidation of NiO into LiNiO_2 (eqn. (3)) must be essential for the catalyst to be selective in the formation of C_2 compounds. It is reasonable to assume that the reaction is initiated by oxidative abstraction of hydrogen of CH_4 [3, 4d]. The reactive oxygen atoms of LiNiO_2 must play an important role in this hydrogen abstraction reaction. The fast reduction of LiNiO_2 (eqn. (2)) is also essential for the catalyst to be active in the oxidative coupling of methane.

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