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Acid–base properties and the directions of oxidative transformation of methane over nickel-based catalysts

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Two completely different behaviors of the oxidative transformation of methane (OTM) were performed on nickel-based catalysts because of different acid–base properties of those catalysts. The relatively acidic LaNiOx and LiNiLaOx/Al_2O_3 catalysts exhibit excellent performances in the partial oxidation of methane to syngas (POM). However, the relatively basic LiNiLaOx catalyst has a good performance in the oxidative coupling of methane to C_2 hydrocarbons (OCM). The redox behaviors of those catalysts and the states of the nickel present were investigated by TPR techniques. TPR results indicated that the active component nickel of the working LaNiOx and LiNiLaOx/Al_2O_3 catalysts existed in the reduced state, and that of the working LiNiLaOx catalyst existed in the oxidized state under the same reaction conditions. It can be concluded that the acidic property favors keeping the reduced nickel and the reduced nickel is necessary for the POM reaction, whereas the basic property favors keeping the oxidized nickel and the oxidized nickel is necessary for the OCM reaction.

Keywords: acid–base properties; oxidative transformation of methane; nickel-based catalysts; oxidative coupling of methane; C_2 hydrocarbon; partial oxidation of methane; syngas

1. Introduction

Catalytic transformation of methane has received intensive attention due to the large amounts of natural gas (mainly methane) found worldwide. Although many routes are conceptually possible, the oxidative transformation of methane is one of the most important methods [1–4].

The oxidation of methane over transition metal oxides is always highly active, but its products are CO and CO_2, namely the products of deep oxidation. Therefore, they were usually used as the main components of catalysts for the complete oxidation of alkanes [5]. The strong oxidative activity of CH_4 over transition metal oxides such as NiO indicated that the activation of a C–H bond over transition metal oxides is much easier than over alkaline-earth metal oxides and/or rare-earth metal oxides. Furthermore, the activation of a C–H bond is the key step of the OCM reaction [6]. This is the reason that we use transition metal oxides as the main component of the OTM catalysts. However, we have to realize that the selectivity of OTM reaction over transition metal oxides is poor. We expected to control the direction of the OTM reaction over NiO by surface modification, namely making use of the interactions between NiO and other components to beget a synergistic effect in order to get the desired products selectively. A good OCM performance over NaCl/B_2O_3/Fe_2O_3 [7] due to a synergistic effect of NaCl and B_2O_3 on Fe_2O_3 had been reported. Another good OCM catalyst $LiNiO_2$ was also reported by Otsuka [8]. In this paper, we describe two completely different behaviors of the oxidative transformation of methane performed on nickel-based catalysts due to different acid–base properties of those catalysts. The effects of acid–base properties on the catalytic performances, the redox behaviors and the states of nickel present in the working nickel-based catalysts are discussed in detail.

2. Experimental

The LiNiLaOx catalysts were prepared by the impregnation method. Appropriate amounts of $LiNO_3$ and $Ni(NO_3)_2$ were impregnated on La_2O_3 for 24 h, dried at 393 K and then calcined in air at 823–1173 K for 4 h. The LiNiLaOx supported catalysts were also prepared by the impregnation method. Here appropriate amounts of $LiNO_3$, $Ni(NO_3)_2$ and $La(NO_3)_3$ were impregnated on γ-Al_2O_3 support for 24 h, dried at 393 K and then calcined in air at 823–1073 K for 4 h.

Catalysts were tested by the flow-reaction at atmospheric pressure in a fixed-bed microreactor. Products of the reaction were analyzed by gas chromatography using a TCD detector. The conversion of methane, the selectivity and yield of the products were calculated on the basis of carbon numbers of the methane reacted. The usual OTM reaction was carried out under the following conditions: $CH_4 : O_2 : He = 3 : 1 : 4$, weight of sample $= 200$ mg, $CH_4 + O_2 + He = 40$ ml/min. The POM reaction over the LiNiLaOx/Al_2O_3 sample was per-

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formed under the following conditions: $CH_4 : O_2 = 2 : 1$, GHSV = 2.7×10^4 ℓ/kg h.

TPR profiles were recorded by an on-line computer at a programmed temperature velocity of 14 K/min in 5% H_2/Ar flow after the samples had been pretreated in Ar flow at 873 K for 30 min. When the programmed temperature reached 1173 K, it was held for 30 min.

The acidities of the catalysts were tested by measuring the ammonia uptakes at 373 K after the catalysts had been pretreated with helium at 873 K for 1 h, followed by a temperature-programmed desorption of ammonia (NH_3-TPD) at a programmed temperature velocity of 16 K/min.

3. Results and discussion

A series of LiNiLaOx catalysts with different Li content were prepared in order to investigate the effects of acid–base properties on the directions of the oxidative transformation of methane. The dependence of the performance of LiNiLaOx catalysts on Li content at 1073 K is shown in fig. 1. The performance of LiNiLaOx catalysts with different Li content and acid–base properties at 1073 K was different. When the Li/Ni mole ratio was 0, the relatively acidic LaNiOx had the highest CH_4 conversion (92.0%), but no C_2 yielded. The products were CO, CO_2 and H_2, and CO selectivity is 98.3%. It is not an OCM catalyst but a good catalyst for partial oxidation of methane (POM). With Li content and the basic property of LiNiLaOx catalysts increasing, CH_4 conversion and CO selectivity decreased, but there was still no C_2 formed until the Li/Ni mole ratio was 0.4. When the Li/Ni mole ratio was 0.2, CH_4 conversion was 34.6%, and C_2 selectivity was 0 and CO selectivity was 63.4%. However, when the Li/Ni mole ratio was 0.4, CH_4 conversion was 28.8%, and C_2 selectivity was 46.0% and CO selectivity decreased to 0.2%, C_2 and CO_2 being the main products. There is a turnpoint of catalytic behaviors between 0.2 and 0.4 (Li/Ni mole ratio). Beyond Li/Ni mole ratio of 0.4, C_2 and CO_2 were the main products and CO selectivity was almost zero. CH_4 conversion, C_2 selectivity and $C_2^=/C_2$ increased with increasing Li content. There is an optimum C_2 yield at the Li/Ni mole ratio of 1.6, namely CH_4 conversion is 34.7%, and C_2 selectivity is 60.1% and CO selectivity is 0.0%. Furthermore, when the LiNiLaOx sample with good OCM performance was supported on the acidic support Al_2O_3, it was changed to an excellent POM catalyst ($CH_4 : O_2 = 2 : 1$, CH_4 conversion of 91.5% and CO selectivity of 99.2%) again. The catalyst acidity was measured by NH_3-TPD. The results (see fig. 2) indicate that the strength of acidity increased according to the following sequence: LiNiLaOx (Li/Ni = 1.6) < LaNiOx < LiNiLaOx/Al_2O_3. It was shown that the acid–base properties of the nickel-based catalysts resulted in the radical change of the behaviors of the OTM reaction.

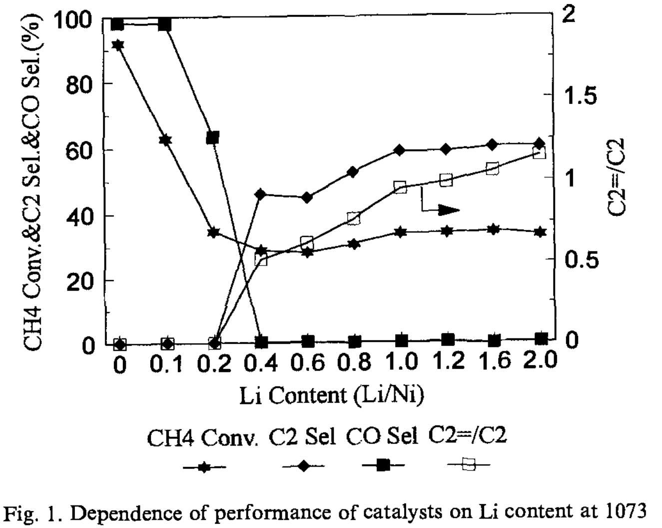

Fig. 1. Dependence of performance of catalysts on Li content at 1073 K. $CH_4 : O_2 : He = 3 : 1 : 4$, weight of sample = 200 mg, $CH_4 + O_2 + He = 40$ ml/min.

XRD characterizations were performed to determine the crystal phases of those samples (see fig. 3). When the Li/Ni mole ratio was 0, the dominant crystal phase was $LaNiO_3$. With Li addition, the peak intensity of crystal phases increased and the dominant crystal phase was changed to $La_2Ni_{1-y}Li_yO_{4-\lambda}$ (*d*: 0.2823, 0.2652, 0.1563 nm). When the Li/Ni mole ratio was 0.4, its dominant phase was $La_2Ni_{1-y}Li_yO_{4-\lambda}$. Beyond the Li/Ni mole ratio of 0.8, the crystal phases of LiNiLaOx catalysts were almost completely $La_2Ni_{1-y}Li_yO_{4-\lambda}$. Other results [9] demonstrated that the $La_2Ni_{1-y}Li_yO_{4-\lambda}$ crystal phase with oxygen vacancy was the active phase of the LiNiLaOx catalyst for OCM reaction and its lattice oxygen might be the active oxygen species. CH_4 was activated by the active oxygen species and produced $CH_3\cdot$ free radical. Yu and his co-workers also think that the $La_2Ni_{1-y}Li_yO_{4-\lambda}$ crystal phase is the active phase of LiNiLaOx catalysts [10]. It is shown that the Li addition affects the formation and structure of crystal phases of LiNiLaOx catalysts. It is the difference of crystal phases

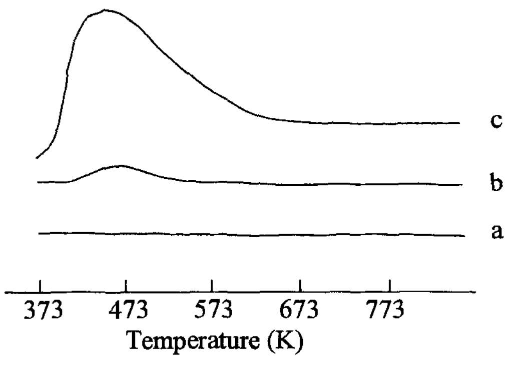

Fig. 2. NH_3-TPD profiles of LaNiOx, LiNiLaOx (Li/Ni = 1.6) and LiNiLaOx/Al_2O_3 catalysts. (a) LiNiLaOx (Li/Ni = 1.6); (b) LaNiOx; (c) LiNiLaOx/Al_2O_3.

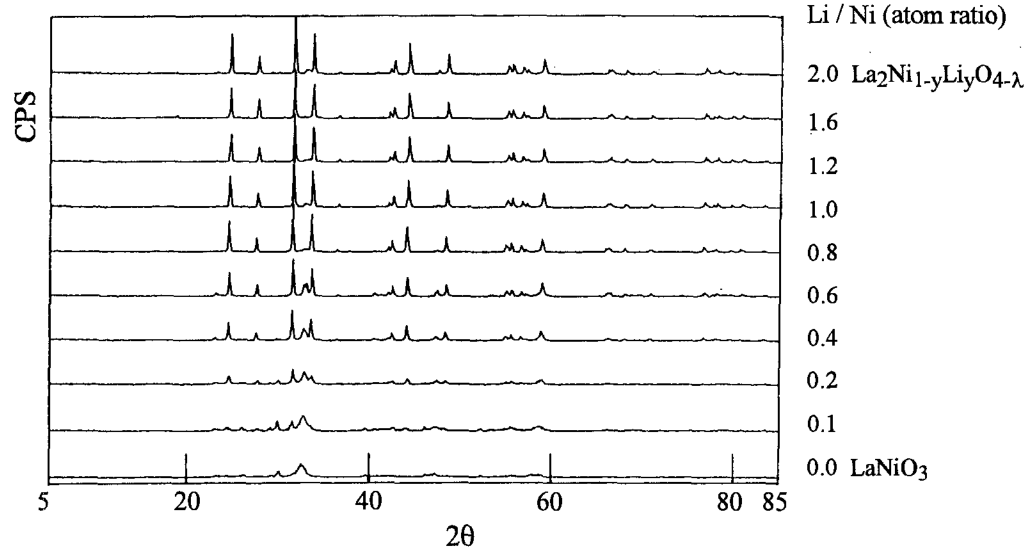

Fig. 3. XRD spectra of LiNiLaOx catalysts with different Li content.

that results in the different behaviors of the oxidative transformation of methane.

The states of nickel present in the different LiNiLaOx catalysts with different Li content were investigated by TPR techniques (see fig. 4). It was shown that the nickel-based catalysts modified by alkali metal oxides and rare-earth metal oxides were more difficult to be reduced than NiO. With Li content increasing, the states of LiNiLaOx catalysts present were changed. The more Li content and the stronger the basic property of LiNiLaOx catalysts, the more difficult they are to be reduced by H_2. An obvious high temperature reducing peak appeared according to the TPR profiles of LiNiLaOx (Li/Ni = 1.6) catalyst. That high temperature reducing peak is attributed to the existence of fixed-form NiO [11], which may be related to the $La_2Ni_{1-y}Li_yO_{4-\lambda}$ crystal phase.

In order to imitate the redox process in the oxidative transformation of methane and compare the redox behaviors of those catalysts, the LaNiOx, LiNiLaOx (Li/Ni = 1.6) and LiNiLaOx/Al_2O_3 catalysts under O_2 pretreatment for 30 min at different temperature were also investigated by TPR technique. It is shown that the reduced LaNiOx catalyst under O_2 treatment can produce crystal NiO [11] that is easily to be reduced (see fig. 5). The reduced LiNiLaOx catalyst under the same O_2 treatment can produce the well-dispersed NiO [11]

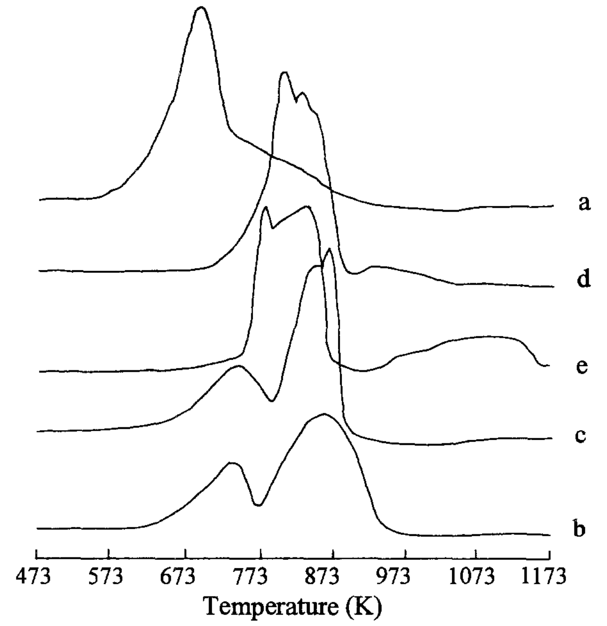

Fig. 4. TPR profiles of LiNiLaOx catalysts with different Li content. (a) NiO; (b) LaNiOx; (c) Li/Ni = 0.2; (d) Li/Ni = 0.4; (e) Li/Ni = 1.6.

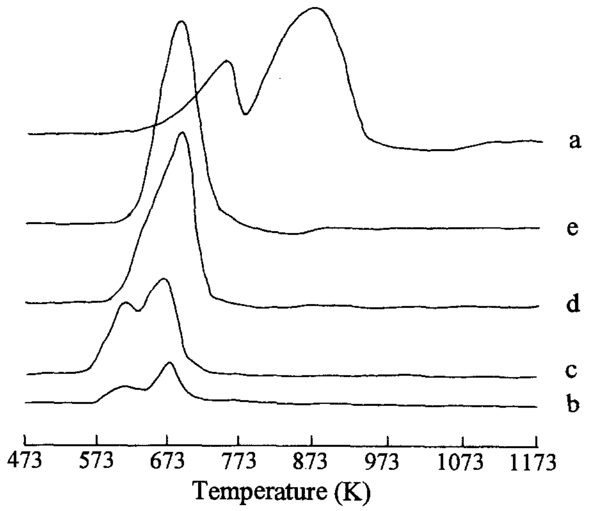

Fig. 5. TPR profiles of LaNiOx catalysts after O_2 pretreatment. (a) Without O_2 pretreatment (the precursor of LaNiOx catalysts); after O_2 pretreatment for 30 min at (b) 323 K; (c) 423 K; (d) 573 K; (e) 773 K.

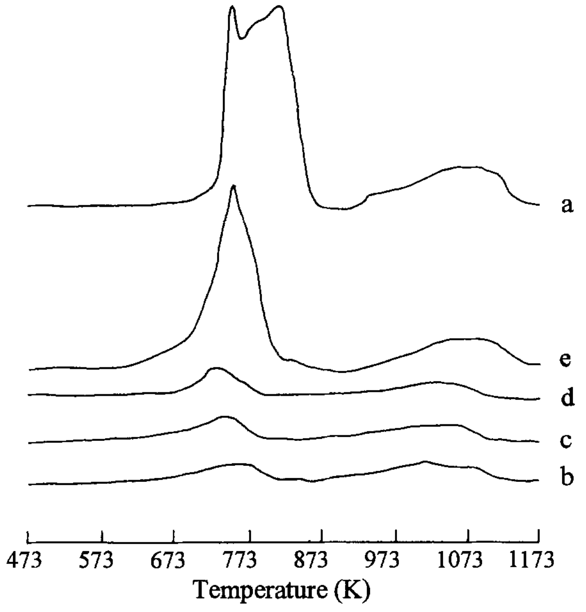

Fig. 6. TPR profiles of LiNiLaOx (Li/Ni = 1.6) catalyst after O_2 pretreatment. (a) Without O_2 pretreatment (the precursor of LiNiLaOx catalyst); after O_2 pretreatment for 30 min at (b) 323 K; (c) 423 K; (d) 573 K; (e) 773 K.

and fixed-form NiO [11] that are more difficult to be reduced than crystal NiO (see fig. 6). The result of LiNiLaOx/Al_2O_3 (fig. 7) is similar to that of LaNiOx catalysts (see fig. 5) and contrary to that of LiNiLaOx (see fig. 6). The reduced LiNiLaOx/Al_2O_3 sample under O_2 pretreatment also produced crystal NiO that was easily reduced (fig. 7). These results indicate that the LaNiOx and LiNiLaOx/Al_2O_3 catalysts are more easily to be reduced under the same redox reaction conditions than the LiNiLaOx catalyst (Li/Ni = 1.6). It can be inferred that the nickel in the working and LaNiOx and LiNiLaOx/Al_2O_3 catalysts under the OTM reaction conditions maybe exist in a reduced state. The difference between the TPR results of LiNiLaOx and LiNiLaOx/Al_2O_3 catalysts is that the nickel present in the precursor of LiNiLaOx/Al_2O_3 catalyst was much more difficult to be reduced than that in the precursor of LiNiLaOx catalyst (see figs. 6 and 7). It was also shown by the TPR results that nickel existed in a uniform state over the Al_2O_3 support and the high temperature reducing peak was due to the formation of $NiAl_2O_4$, which was confirmed by XPS results [9]. Those indicated that there existed a strong interaction between LiNiLaOx and Al_2O_3, and this strong interaction resulted in the formation of $NiAl_2O_4$. This metal–support interaction improved the dispersity of the active component nickel and the high dispersion of the nickel over the Al_2O_3 support was beneficial to obtain an excellent performance for the POM reaction. Ross [12] also pointed out that the unreduced NiO/Al_2O_3 catalysts used in the steam reforming reaction contained surface nickel aluminate phases which, on reduction, gave monodispersed nickel atoms closely associated with alumina sites in addition to metallic crystallites arising from the reduction of nickel oxide, and the monodispersed nickel atoms probably participated in the $CH_4 + H_2O$ reaction.

In order to prove the above-mentioned inference, the LaNiOx, LiNiLaOx and LiNiLaOx/Al_2O_3 catalysts after OTM reactions for a period of 5 h were investigated by TPR techniques to observe the state of nickel present in the working catalysts. The TPR results of the working LaNiOx, LiNiLaOx and LiNiLaOx/Al_2O_3 catalysts (see fig. 8) indicated that the nickel in the working LaNiOx and LiNiLaOx/Al_2O_3 sample existed in the reduced state, but the nickel in the working LiNiLaOx sample existed in the oxidized state and had two kinds of existing states, namely well dispersed NiO [11] and fixed-form NiO [11]. The high temperature reducing peak is attributed to the existence of fixed-form NiO, which may be related to the $La_2Ni_{1-y}Li_yO_{4-\lambda}$ crystal phase (*d*: 0.2823, 0.2652, 0.1563 nm). The XRD results of

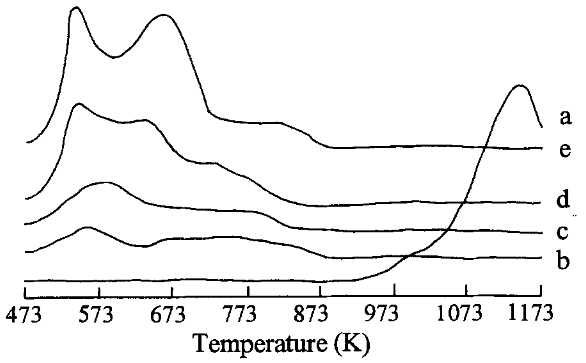

Fig. 7. TPR profiles of LiNiLaOx/Al_2O_3 catalyst after O_2 pretreatment. (a) Without O_2 pretreatment (the precursor of LiNiLaOx/Al_2O_3 catalyst); after O_2 pretreatment for 30 min at (b) 323 K; (c) 423 K; (d) 573 K; (e) 773 K.

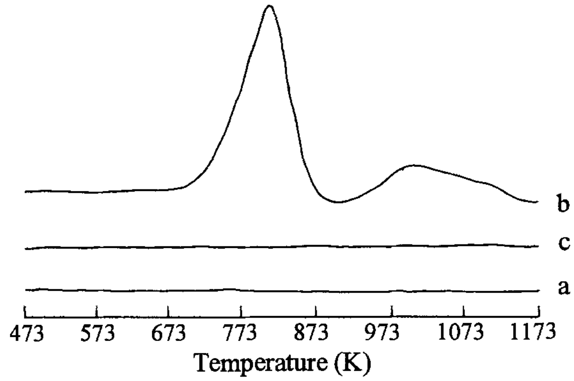

Fig. 8. TPR profiles of LaNiOx, LiNiLaOx (Li/Ni = 1.6) and LiNiLaOx/Al_2O_3 catalysts after OTM reaction. (a) LaNiOx; (b) LiNiLaOx (Li/Ni = 1.6), (c) LiNiLaOx/Al_2O_3. (The reaction conditions for LaNiOx and LiNiLaOx samples are as follows: $CH_4 : O_2 : He = 3 : 1 : 4$, weight of sample = 200 mg, $CH_4 + O_2 + He$ = 40 ml/min. The reaction conditions for LiNiLaOx/Al_2O_3 sample are as follows: $CH_4 : O_2 = 2 : 1$, GHSV = 2.7×10^4 ℓ/kg h).

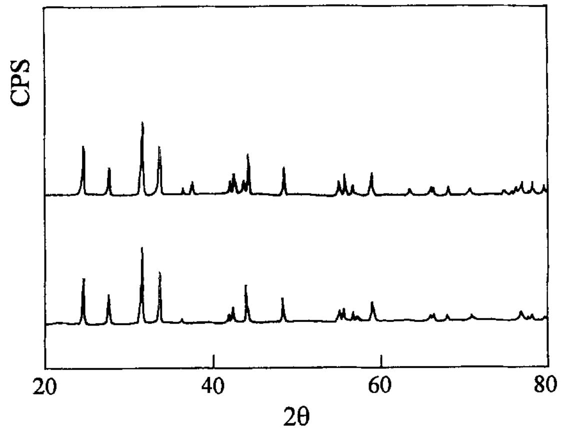

Fig. 9. XRD spectra of LiNiLaOx (Li/Ni = 1.6) catalyst after OCM reaction.

LiNiLaOx catalyst after OCM reaction (see fig. 9) indicated that its main crystal phase was still the $La_2Ni_{1-y}Li_yO_{4-\lambda}$ crystal phase (*d*: 0.2823, 0.2652, 0.1563 nm). It was found that the $La_2Ni_{1-y}Li_yO_{4-\lambda}$ crystal phase with oxygen vacancy was the active phase of LiNiLaOx catalysts for OCM reaction and its lattice oxygen may be the active oxygen species [9,10]. The effects of Li_2O on the performance of the LiNiLaOx catalysts include two aspects: (1) the addition of Li_2O enhances the basic property of the catalyst and makes nickel difficult to be reduced, and keeps it in the oxidized state; (2) the addition of Li_2O favors the formation of $La_2Ni_{1-y}Li_yO_{4-\lambda}$ crystal phase and oxygen vacancy, and enhances the mobility of oxygen anion and C_2 selectivity.

It was inferred that the acidic property favors keeping the reduced nickel and the reduced nickel is necessary for the POM reaction, and the basic property favors keeping the oxidized nickel and the oxidized nickel is necessary for the OCM reaction. According to the results of the pulse-reaction experiments for the POM reaction over the $LiNiLaOx/Al_2O_3$ catalyst [13], it was found that CH_4 dissociatively adsorbed on the reduced nickel and produced H_2 and surface carbon. The surface carbon reacted with the lattice oxygen on the $LiNiLaOx/Al_2O_3$ catalyst to produce CO. That conclusion agrees with other reports [14–17]. However, for OCM reaction, CH_4 was activated by the oxygen species of the $La_2Ni_{1-y}Li_yO_{4-\lambda}$ crystal phase on the surface of LiNiLaOx catalysts to produce a $CH_3\cdot$ free radical and the $CH_3\cdot$ free radicals were coupled in the gas phase to form C_2 hydrocarbons [9,10,18,19]. Otsuka [8] found that the lattice oxygen atoms of $LiNiO_2$ play an important role in the activation of methane which is dissociatively adsorbed on Ni^{3+}–O^{2-} sites, the rate-determining step being the coupling of adsorbed $CH_3\cdot$. POM and OCM reactions proceed at different active sites with different reaction intermediates and reaction mechanisms.

4. Conclusions

In a word, the acid–base property is one of important factors that determine the states of nickel present in the working catalysts and the direction of oxidative transformation of methane over LiNiLaOx catalysts. It was concluded that the acidic property favors keeping the reduced nickel and the basic property favors keeping the oxidized nickel. The reduced nickel is necessary for the POM reaction and the oxidized nickel is necessary for the OCM reaction. POM and OCM reactions possibly proceed at different active sites with different reaction intermediates and reaction mechanisms. The effect of Li_2O on the performance of the LiNiLaOx catalysts is that the addition of Li_2O enhances the basic property of the catalyst and makes nickel difficult to be reduced and keeps it in the oxidized state.

Acknowledgement

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