Partial oxidation of ethane to syngas over nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide

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The catalytic activity, thermal stability and carbon deposition of various modified NiO/γ-Al_2O_3 and unmodified NiO/γ-Al_2O_3 catalysts were investigated with a flow reactor, XRD, TG and UVRRS analysis. The activity and selectivity of the NiO/γ-Al_2O_3 catalyst showed little difference from those of the modified nickel-based catalysts. However, modification with alkali metal oxide (Li, Na, K) and rare earth metal oxide (La, Ce, Y, Sm) can improve the thermal stability of the NiO/γ-Al_2O_3 and enhance its ability to suppress carbon deposition during the partial oxidation of ethane (POE). The carbon deposition contains graphite-like species that were detected by UVRRS. The nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide have excellent catalytic activities (C_2H_6 conversion of $\sim$100%, CO selectivity of $\sim$94%, 7×10^4 l/(kg h), 1123 K), good thermal stability and carbon-deposition resistance.

Keywords: partial oxidation of ethane, syngas, nickel-based catalysts, modification, alkali metal oxide, rare earth metal oxide, thermal stability, carbon deposition

1. Introduction

Although natural gas is predominantly CH_4, it also contains from 5 to 30% C_2H_6, C_3H_8 and C_4H_{10}. Commonly, C_2H_6 is the most abundant secondary component in natural gas [1]. The partial oxidation of methane (POM) to syngas ($CO + H_2$) reaction over nickel-based catalysts has received intensive attention [2,3], and many researches have been devoted to the conversion of ethane to ethylene [4]. Ethylene has been shown to be formed from ethane by thermal dehydrogenation ($C_2H_6 \rightleftharpoons C_2H_4 + H_2$) and oxidative dehydrogenation ($C_2H_6 + (1/2)O_2 \rightleftharpoons C_2H_4 + H_2O$). Thermal dehydrogenation of ethane exhibits a high selectivity to ethylene ($\sim$80%) with a fairly high conversion ($\sim$60% per pass), and these reactions represent the main processes for commercial olefin production. The oxidative dehydrogenation of ethane over oxide catalysts such as V_2O_5/SiO_2 has also been shown to be fairly selective to ethylene at low conversions [5]. These catalysts are 100% selective to ethylene at conversions of ethane <1%. However, at a conversion of only 5% C_2H_6, the ethylene selectivity falls to only 80%. Since these processes are operated under severely fuel-rich conditions, carbon deposition and, consequently, deactivation can be the major problems, and this contributes to the poor conversions of many processes. At higher conversions, not only does selectivity decrease but also coke formation becomes an issue [6]. Provided that syngas can be produced from C_2H_6 over nickel-based catalysts with high selectivity and conversion, it can be directly obtained from mixture gases containing CH_4, C_2H_6 from natural gas, FCC (fluidized catalytic cracking) tail gas, etc. (Syngas can be produced from CH_4 over nickel-based catalysts with high selectivity and conversion [3].) This may lead to better utilization of the light fractions from natural gas and refineries, etc. Schmidt et al. [7,8] reported that syngas can be produced from CH_4, C_2H_6 and C_3H_8 over a supported Rh catalyst with high selectivity and conversion, and the presence of C_2H_6 in natural gas will not lead to catalyst deactivation by carbon deposition. However, little work about partial oxidation of ethane (POE) to syngas over nickel-based catalysts has been reported.

Previously, we reported the partial oxidation of methane to syngas over nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide, and pointed out that ABNiO/γ-Al_2O_3 ($A = \mathrm{Li, Na, K}$; $B = \mathrm{La, Sm, Ce, Y}$) were excellent POM reaction catalysts [3,9,10]. On the basis of these results, the partial oxidation of ethane to syngas over nickel-based catalysts was investigated. One of the aims for this investigation on the POE reaction is to search for a catalyst that is not only suitable for the POE reaction, but also for the POM reaction, hence enabling mixture gases containing CH_4 and C_2H_6 from natural gas and FCC tail gas to be converted to syngas with high conversion and selectivity. In the present work, the catalytic activity, thermal stability and carbon deposition over the nickel-based catalysts were discussed in detail.

2. Experimental

NiO/γ-Al_2O_3, NiO/SiO_2 and NiO/MgO catalysts were prepared by impregnating γ-Al_2O_3, SiO_2 and MgO, respectively, with an appropriate amount of $Ni(NO_3)_2$ for

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24 h then drying at 393 K, and calcining in air at 823–1073 K for 4 h. Preparation of the ABCO/γ-Al_2O_3 (A = Li, Na, K; B = La, Sm, Ce, Y; C = Fe, Co, Ni) catalysts was described previously [3].

Heat treatment of the samples was carried out at 1123, 1373, 1423, 1523 and 1573 K, respectively, under a flow of air. Temperature was slowly brought to the final value with a variable current automatic controller, then set at the predetermined reading for the desired temperature. At this temperature, the catalysts were activated for 5 h. After that, the samples were slowly cooled to room temperature under a flow of air. The sample calcined at 1373 K for 5 h was labelled as "catalyst"-1373, e.g., NiO/γ-Al_2O_3-1373, etc.

Catalysts were tested in an atmospheric pressure fixed-bed flow microreactor. Reaction performance was tested using a microreactor with an internal diameter of 4 mm, and 50 mg of catalyst with an average particle size of 0.37–0.25 mm was employed, giving a catalyst bed length of 7 mm (no dilution). An EU-2 type thermocouple fixed with the quartz reactor was placed at the exit of the catalyst bed to control the electric furnace temperature, which was taken as the reaction temperature. The catalyst was reduced at 1123 K with H_2 (20 ml/min) for 1 h *in situ* before it was used for the POE reaction. Products of the reaction were analyzed by gas chromatography using a TCD detector. The conversion of ethane and the selectivity were calculated on the basis of carbon numbers of the ethane reacted. The amount of H_2 was corrected by the external standard method.

TG tests were recorded and treated by a Perkin–Elmer 3600 workstation at a programmed temperature velocity of 10 K/min in air, with a flow rate 25 ml/min. XRD characterization was performed with a Riguku D/Max-RB X-ray diffractometer using a copper target at 40 kV × 100 mA and scanning speed of 8°/min.

UV resonance Raman spectra (UVRRS) characterization was performed in air at room temperature, using an UV resonance Raman spectroscope. The ultraviolet laser beam for exciting UV Raman spectra was generated by frequency doubling of the 488 nm output of an Ar^+ ion laser to 244 nm using a BBO crystal. The Raman scattering from the sample surface was collected by an $AlMgF_2$-coated ellipsoidal reflector using back-scattering geometry, and then focused into a 0.32 nm single grating spectrograph through a notch filter.

3. Results and discussion

The effect of reaction temperature on the activity of the LiLaNiO/γ-Al_2O_3 catalyst is shown in figure 1. Ethane and oxygen were almost converted completely (not shown). When the reaction temperature was subsequently increased from 973 to 1123 K, the CO selectivity increased gradually, while the CH_4 selectivity decreased. Under the constant space velocity by keeping the flow rate of C_2H_6 (10 ml/min) and the total flow rate (50 ml/min) of O_2 and He constant, the respective flow rates of O_2 and He were changed to obtain different C_2H_6/O_2 ratios. The effect of the C_2H_6/O_2 ratio on the activity of the LiLaNiO/γ-Al_2O_3 was investigated (figure 2). As the C_2H_6/O_2 ratio changed from 0.56 to 0.94, the CO selectivity increased from 80 to 94%, and the CH_4 selectivity changed slightly. However, with the C_2H_6/O_2 ratio increasing from 0.94 to 1.54 the CO selectivity decreased slowly, while the CH_4 selectivity increased drastically. There exists an optimum value at C_2H_6/O_2 ratio of 0.94, where the CO selectivity is 94%. Under 1123 K and an O_2/C_2H_6/He ratio of 1.06/1/4, the influence of space velocity on the activity of the LiLaNiO/γ-Al_2O_3 was also studied (figure 3). The results indicated that the influence of space velocity was not appreciable, e.g., the LiLaNiO/γ-

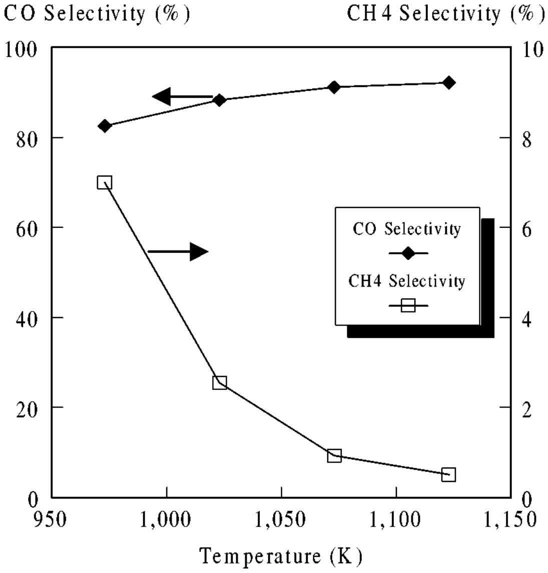

Figure 1. Catalytic activity of LiLaNiO/γ-Al_2O_3 catalyst at different temperatures (O_2/C_2H_6/He = 1.06/1/4, GHSV = 7 × 10^4 l/(kg h)).

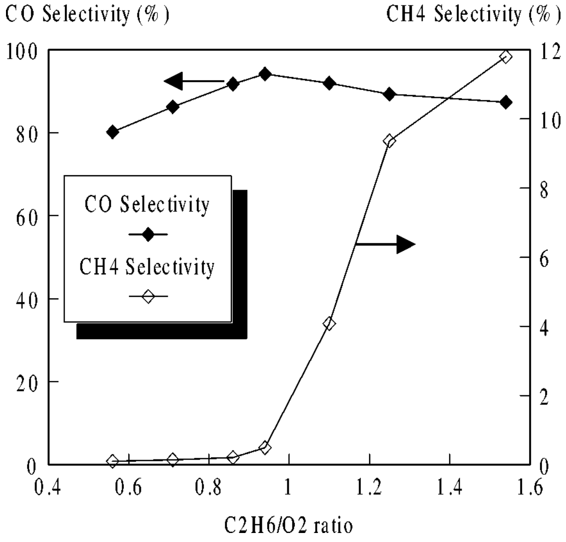

Figure 2. Influence of C_2H_6/O_2 ratio on the catalytic activity of LiLaNiO/γ-Al_2O_3 catalyst (at 1123 K).

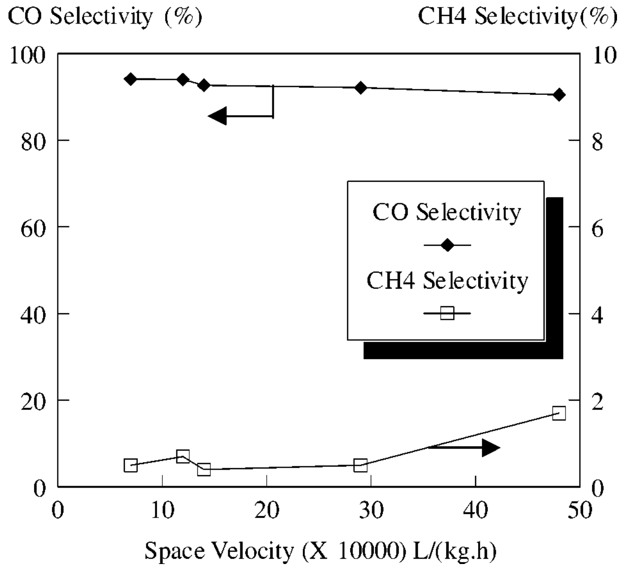

Figure 3. Catalytic activity of LiLaNiO/γ-Al_2O_3 catalyst at different space velocities (at 1123 K).

Table 1
Comparison of activities of different supported catalysts.[a]

Catalyst	Selectivity (%)			
	CO	CH_4	CO_2	C_2H_4
NiO/γ-Al_2O_3	89.0	0.2	10.8	0
NiO/MgO	87.3	2.0	10.7	0
NiO/SiO_2	72.6	11.8	11.5	4.1

[a] $O_2/C_2H_6/He = 1.15/1/4$, GHSV $= 3 \times 10^5$ l/(kg h), $T = 1123$ K.

Al_2O_3 catalyst kept excellent catalytic activity over a wide range of high space velocity.

The catalytic activities of the partial oxidation of ethane to syngas over NiO/γ-Al_2O_3, NiO/MgO and NiO/SiO_2 were studied. The results are shown in table 1. Ethane and oxygen were almost converted completely (not shown), and CO selectivities under the same reaction conditions were as follows: NiO/γ-Al_2O_3 > NiO/MgO > NiO/SiO_2. Some C_2H_4 was produced over the NiO/SiO_2 catalyst. Miao [11] investigated the catalytic activity of the POM reaction over the same catalysts. The results showed that the sequence of CH_4 conversions was as follows: NiO/γ-Al_2O_3 > NiO/SiO_2 $\gg$ NiO/MgO, while that of the CO selectivities as follows: NiO/SiO_2 > NiO/γ-Al_2O_3 $\gg$ NiO/MgO. Some C_2H_4 was produced over NiO/MgO (for POM), but not NiO/SiO_2 (for POE). These results indicate that the behaviour of the POE reaction is different from that of the POM reaction over the three different nickel-based catalysts, and the activated behaviour of ethane is not the same as that of methane. So it is necessary to study the reaction of partial oxidation of ethane over the nickel-based catalysts.

A series of ABCO/γ-Al_2O_3 (A = Li, Na, K; B = La, Sm, Ce, Y; C = Fe, Co, Ni) catalysts were prepared with the same preparation method and conditions in order to investigate the action of different components. The results are present in table 2. There were strikingly different performances when Fe displaced the Ni component in the LiLaNiO/γ-Al_2O_3 catalyst. The CO selectivity of the Fe-containing catalyst was much lower than that of the Ni-containing catalyst, and some C_2H_4 was produced over LiLaFeO/γ-Al_2O_3. However, the CO selectivity of the Co-containing catalyst was only slightly lower than that of the LiLaNiO/γ-Al_2O_3. The different behavior of Fe may possibly be attributed to the differences in structure, ability to remove hydrogen, redox ability and the interaction between transition metal and Al_2O_3 support. Nickel is most suitable for the POE reaction according to the results listed in table 2.

Table 2
Comparison of activities of different catalysts.[a]

Catalyst	Selectivity (%)			
	CO	CH_4	CO_2	C_2H_4
NiO/γ-Al_2O_3	94.2	0.6	5.2	0
LiNiLaO/γ-Al_2O_3	94.1	0.5	5.4	0
LiCoLaO/γ-Al_2O_3	93.7	0.8	5.5	0
LiFeLaO/γ-Al_2O_3	64.4	14.3	8.5	12.8
NaNiLaO/γ-Al_2O_3	94.2	0.6	5.2	0
KNiLaO/γ-Al_2O_3	94.0	0.5	5.5	0
LiNiCeO/γ-Al_2O_3	94.8	0.7	4.5	0
LiNiYO/γ-Al_2O_3	94.7	0.6	4.7	0
LiNiSmO/γ-Al_2O_3	95.1	0.7	4.2	0

[a] $O_2/C_2H_6/He = 1.06/1/4$, GHSV $= 7 \times 10^4$ l/(kg h), $T = 1123$ K.

The activity and selectivity of the NiO/γ-Al_2O_3 showed little difference from those of the catalysts with different alkali metal oxides ALaNiO/γ-Al_2O_3 (A = Li, Na, K) and rare earth metal oxides LiBNiO/γ-Al_2O_3 (B = La, Sm, Y, Ce). Ethane and oxygen were almost converted completely (not shown), the selectivities of CO and CH_4 kept at about 94 and 0.6%, respectively. The results indicate that modification with alkali and rare earth metal oxides does not significantly influence the activity and the selectivity of the POE reaction over the NiO/γ-Al_2O_3 under these conditions.

The introduction of alkali and rare earth metal oxides can increase the thermal stability of the NiO/γ-Al_2O_3 catalyst and prevent the sintering of nickel. Stability is one of the most important criteria to evaluate catalysts. Nickel-based catalysts supported on γ-Al_2O_3 are usually unstable at high temperatures. It is well known that the stability of γ-Al_2O_3-supported catalysts during high-temperature reactions is due to the thermal deterioration of the γ-Al_2O_3 support, which causes sintering and leads to pore closing and reduction in surface area as well as phase transformation into α-Al_2O_3, which changes the active surface layer and promotes a low surface area structure. Preventing the alumina support from thermal deterioration is studied by many authors [12,13], and a large number of additives to the γ-Al_2O_3 support have been shown to inhibit sintering and phase transformation. In the papers published by Schaper et al. [14,15], lanthanum was introduced as lanthanum nitrate on the γ-Al_2O_3. The author concluded that the stabilization proceeds via the formation of a lanthanum aluminate surface layer. More recently, Oudet et al. [16] concluded that the stabilization of alumina by lanthanum occurs be-

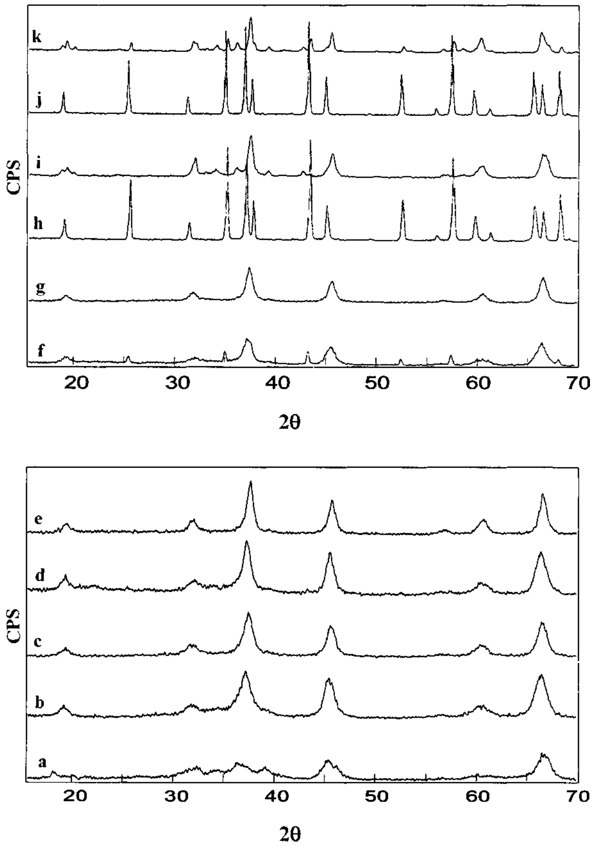

Figure 4. XRD spectra of samples after the thermal treatment: (a) γ-Al_2O_3-1123, (b) NiO/γ-Al_2O_3-1123, (c) LiLaNiO/γ-Al_2O_3-1123, (d) NiO/γ-Al_2O_3-1373, (e) LiLaNiO/γ-Al_2O_3-1373, (f) NiO/γ-Al_2O_3-1423, (g) LiLaNiO/γ-Al_2O_3-1423, (h) NiO/γ-Al_2O_3-1523, (i) LiLaNiO/γ-Al_2O_3-1523, (j) NiO/γ-Al_2O_3-1573, (k) LiLaNiO/γ-Al_2O_3-1573. Note: NiO/γ-Al_2O_3-1373 means NiO/γ-Al_2O_3 calcined at 1373 K for 5 h, etc.

cause of the nucleation of a cubic $LaAlO_3$ structure on the surface of the alumina support, inhibiting the surface diffusion of species responsible for sintering. Levy et al. [17] reported that it is possible to optimize the stability of a transition alumina through appropriate incorporation of doping agents to selectively control various physical properties of the alumina. The thermal stability is a complex parameter sensitive to factors such as inhomogeneities or strains in lattice constants, ionic radii of impregnates, and the relation of the latter to oxygen coordination. Lithium stabilizes a spinel alumina by the formation of a mixed bulk phase, while potassium ions give even greater stabilization and reside predominantly in pore mouths. So, the addition of Li_2O and La_2O_3 should be beneficial to the improvement of the thermal stability of the NiO/γ-Al_2O_3.

Table 3
Comparison of carbon deposition of different catalysts.[a]

Catalyst	Amount of carbon deposition (wt%)	Decreasing percentage
NiO/γ-Al_2O_3	2.5	0
LaNiO/γ-Al_2O_3	0.9	62.9
LiLaNiO/γ-Al_2O_3	0.4	84.3

[a] $C_2H_6/O_2/He = 1.15/1/4$, $C_2H_6 = 10$ ml/min, 1123 K, 5 h.

In order to demonstrate that the addition of Li_2O and La_2O_3 can improve the thermal stability of the NiO/γ-Al_2O_3, NiO/γ-Al_2O_3 and LiLaNiO/γ-Al_2O_3 with the same nickel loading were employed for examing the differences in their high-temperature phase transformation. The results are shown in figure 4. γ-Al_2O_3 phase (d: 0.4600, 0.2800, 0.2398, 0.1983 and 0.1403 nm) was present in samples with calcination temperatures below 1373 K (figure 4 (a)–(e)). After treatment in air at 1423 K for 5 h, the γ-Al_2O_3 phase almost completely disappeared over the NiO/γ-Al_2O_3 catalyst, while the α-Al_2O_3 phase (d: 0.3482, 0.2555, 0.2410, 0.2086, 0.1744, 0.1603, 0.1404 and 0.1374 nm) was clearly present (figure 4(f)). However, phase transformation of γ-Al_2O_3 to α-Al_2O_3 did not occur over the LiLaNiO/γ-Al_2O_3 catalyst in such case (see figure 4(g)). The γ-Al_2O_3 phase did not begin to transform to the α-Al_2O_3 phase over the LiLaNiO/γ-Al_2O_3 until the temperature was increased to 1573 K (figure 4(k)). The results indicate that the γ-Al_2O_3 phase can be stabilized by the addition of Li_2O and La_2O_3. Previously, we compared the stability of LiLaNiO/γ-Al_2O_3 and NiO/γ-Al_2O_3 for the CH_4/O_2 to syngas reaction at 1123 K. The results revealed also that the addition of Li_2O and La_2O_3 could stabilize the γ-Al_2O_3 phase during the high-temperature reaction [18].

The introduction of Li and La not only improves the thermal stability of the NiO/γ-Al_2O_3, but more importantly, also enhances the ability of carbon-deposition resistance. The deposition of surface carbon over the NiO/Al_2O_3 catalyst during the POM reaction was undesirable and resulted in the deactivation of the NiO/Al_2O_3 [19]. A hydrocarbon with higher C/H ratio favors carbon deposition on the surface of a catalyst in comparison with lower C/H ratio. Therefore, it is reasonable that the amount of carbon deposition for the POE reaction is more than for the POM reaction over the NiO/Al_2O_3, and carbon deposition also results in the deactivation of the NiO/Al_2O_3 for the POE reaction. It is well known that the acidity of the catalyst surface favors carbon deposition, while the basicity of the catalyst surface prevents carbon deposition [20]. So, the addition of Li_2O and La_2O_3 should be beneficial to the prevention of carbon deposition over the catalyst surface. The TG results of the samples after the POE reaction for 5 h indicated that the resistant ability for carbon deposition of the LiLaNiO/γ-Al_2O_3 was much better than that of the NiO/γ-Al_2O_3 (table 3). The amount of carbon deposition over the LiLaNiO/γ-Al_2O_3 was only 1/6 of that over the NiO/γ-Al_2O_3 under 1123 K, $C_2H_6/O_2/He$ ratio of 1.15/1/4 and space velocity of 7×10^4 l/(kg h). It was shown that the introduction of Li and La could obviously suppress carbon deposition of the nickel-based catalysts. Xiong et al. [3] studied carbon deposition of the nickel-based catalysts for the POM reaction. They reported also that the incorporation of Li and La could improve the ability of carbon-deposition resistance.

In order to determine the carbon-deposition species formed on the catalysts, the samples performed under the same reaction conditions were characterized by UVRRS,

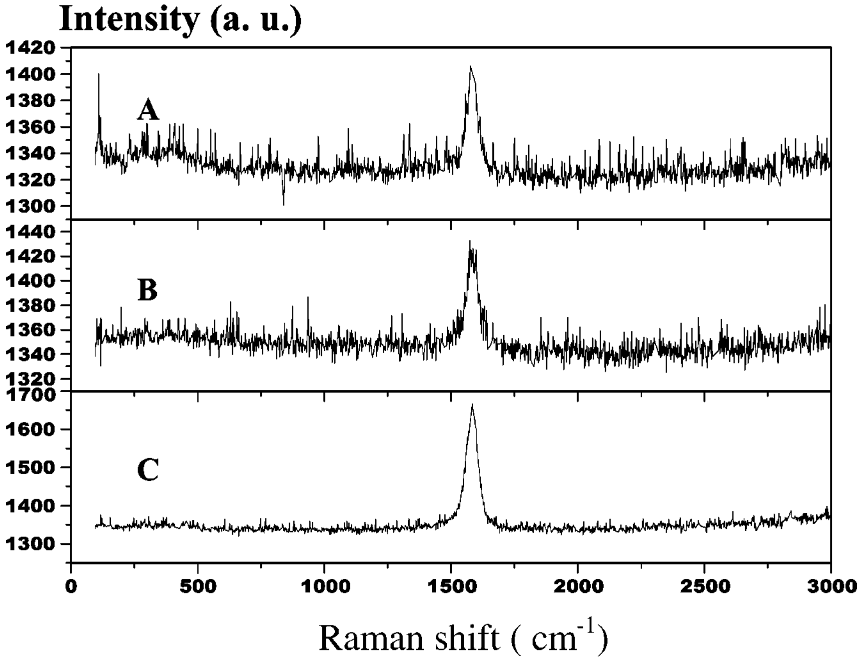

Figure 5. UV Raman spectra of carbon deposition formed on catalysts LiLaNiO/γ-Al_2O_3 (A), LaNiO/γ-Al_2O_3 (B), NiO/γ-Al_2O_3 (C).

which has been demonstrated to be a powerful tool for catalysis and surface science studies, with the advantage of avoiding the surface fluorescence which frequently occurs in visible Raman spectra of many catalysts [21]. The samples used for the UVRRS were manipulated in air prior to the analysis. The results are shown in figure 5. Only one band at 1580 $cm^{-1}$was present clearly in the spectra, which is close to the characteristic band of graphite at 1575 cm^{-1} [22]. The intensity of the band for the NiO/γ-Al_2O_3 was far stronger than that for the LiLaNiO/γ-Al_2O_3, while the intensity of the band for the LaNiO/γ-Al_2O_3 was stronger than that for the LiLaNiO/γ-Al_2O_3. The results reveal that the carbon deposition formed on the nickel-based catalysts contains graphite-like species (amorphous forms of carbon may not be detected by UVRRS), and the unmodified NiO/γ-Al_2O_3 favors the formation of carbon deposition.

4. Conclusion

Modification with alkali and rare earth metal oxides does not significantly influence the activity and selectivity of the POE reaction over NiO/γ-Al_2O_3. However, the introduction of alkali metal oxide (Li, Na, K) and rare earth metal oxide (La, Ce, Y, Sm) can improve the thermal stability of the NiO/γ-Al_2O_3 and enhance the ability to suppress carbon deposition that contains graphite-like species over the NiO/γ-Al_2O_3 during the POE reaction. The nickel-based catalysts modified by alkali metal oxide and rare earth metal oxide have excellent catalytic activity, good thermal stability and carbon-deposition resistance.

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