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Correlation between the characteristics and catalytic performance of Ni–V–O catalysts in oxidative dehydrogenation of propane

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Ni–V–O series catalysts for the oxidative dehydrogenation (ODH) of propane were prepared and characterized by BET, XRD, H_2-TPR, O_2-TPD-MS and electrical conductivity. At 425 °C a C_3H_6 selectivity of 49.9% was observed on $Ni_{0.9}V_{0.1}O_Y$ at a C_3H_8 conversion of 19.4%, and the obtained selectivity is almost two times higher than that over NiO at the roughly same conversion of C_3H_8. The mobile oxygen species created by the interaction of NiO and V_2O_5 has been found in the composite catalysts by O_2-TPD-MS and electrical conductivity studies, which seems to be responsible for the enhanced selectivity of the propane oxidative dehydrogenation.

KEY WORDS: propane; oxidative dehydrogenation; Ni–V–O catalysts.

1. Introduction

Oxidative dehydrogenation (ODH) of propane to propene is one of the most challenging problems of utilizing light alkanes, which are relatively abundant in natural gas or in liquefied petroleum gas. There has been great interest in the development of highly selective catalysts for propane ODH to propene, due to its potential application as a source of cheap raw material. A wide variety of catalysts have been used as being effective in the propane ODH [1–14]. The catalysts are usually used to activate the propane and dioxygen, and are believed to play more important roles in activating the dioxygen. The nature of the activated oxygen species of the catalysts directly influences the propane conversion and propene selectivity. The formation and properties of the oxygen species are strongly related to the character of the metal cation, the structure and redox properties of the metal oxide catalysts [8–10,12,14]. On the basis of the nature of the oxygen species involved, two types of oxygen species for ODH of light alkanes are considered. One type is lattice oxygen [8], in this reaction mechanism, the ODH reaction is performed at higher temperature. The other one is nonstoichiometric oxygen [15,16], in this reaction mechanism, the ODH reaction is performed at a relatively low temperature. However, it is very difficult to control the rate of reaction and propene formation because of the oxidation of propane and propene into CO_X [12,13]. It is quite important to develop selective catalysts capable of activating propane and dioxygen at low or intermediate temperatures and to study the fundamental relationship between characteristics of the catalysts and their catalytic behavior for propane ODH.

Indeed, our previous studies on propane ODH over the Ni–V–O system showed that the adding of a small amount of vanadium significantly improved the catalytic performance of NiO, which could run this reaction at relatively low temperature (425 °C) [11,17]. It was suggested that there is a synergetic effect between NiO and V_2O_5. The objective of the present study is to further demonstrate the relationship between the characteristics of the Ni–V–O bicomponent catalyst and the catalytic performance of propane ODH.

2. Experimental

2.1. Catalyst preparation

The $Ni_XV_{1-X}O_Y$ ($X = 0.9$–0.6 molar) catalysts used in this study were prepared by an evaporation method. Aqueous solutions of stoichiometric amounts of $Ni(NO_3)_2 \cdot 6H_2O$ with ammonium vanadates [NH_4VO_3] were evaporated to dryness under stirring, the dried materials were calcined in air at 350 °C for 1 h and pulverized, then calcined at 600 °C in air for 6 h.

NiO and V_2O_5 were obtained from the decomposition of $Ni(NO_3)_2 \cdot 6H_2O$ and NH_4VO_3 respectively, calcined at 600 °C (heating rate 2 °C/min) for 6 h.

2.2. Catalyst characterization

The BET surface areas of the catalysts were measured by N_2 adsorption using a Coulter SA3100 equipment.

X-ray diffraction (XRD) patterns were obtained by using a Siemens D5000 X-ray diffractometer working

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with Ni-filtered CuK_α radiation ($\lambda = 1.5406$ Å). The voltage was 40 kv and the current was 30 mA. The data accumulated from 15 to 90, 2θ are in accordance with the corresponding JCPDS powder diffraction files.

Temperature programmed reductions (TPR) of the catalysts were performed by using an $Ar + H_2$ (96/4) gas mixture. The flow rate of the carrier gas was 50 mL/min. A 25 mg sample was used and heated (rate 15 °C/min) to a final temperature of 900 °C. The H_2 consumption was measured by a thermal conductivity detector, which connected to a data acquisition computer.

O_2-TPD-MS test was performed on a QTMD Spectrometer. 0.5 g of sample was used and pretreated under He atmosphere (45 mL/min) at 300 °C for 1 h and cooled down to room temperature, then heated (rate 15 °C/min) to a final temperature. Oxygen desorption was recorded on line mass spectrometer.

Electrical conductivity measurement: 0.3 g of sample was compressed at 5 MPa during 1 min, and placed between a couple of special designed platinum electrodes. The electrical resistance of the sample was measured with a Fluke 8840A Multi-meter under different atmospheres and temperatures. The electrical conductivity $\sigma(S \cdot m^{-1})$ was then determined by the formula:

$$\sigma = L/(R \cdot A)$$

where R is the measured electrical resistance (Ω), A is the cross sectional area of the electrodes (m^2), L is the thickness of the sample (m).

2.3. Catalytic test

The ODH reaction was performed at atmospheric pressure in a fixed bed quartz reactor (14.7 mm o.d., 13.3 mm i.d., 28.0 cm long) containing 0.5 g of catalyst. Under standard conditions, the reactants consisted of $V(C_3H_8) = 10$ mL/min, $V(O_2) = 5$ mL/min and $V(He) = 35$ mL/min with a total flow rate of 50 mL/min. The reaction temperatures were ranged from 300 to 500 °C at 25 °C intervals. The reaction products were analyzed on line by GC.

3. Results and discussion

3.1. XRD results

XRD analysis (table 1) indicated that only two phases were detected: NiO and $Ni_3V_2O_8$ in the Ni–V–O system, and a pure phase of $Ni_3V_2O_8$ were observed in the adding of 40 mol% vanadium. The two phases are coexisted and the molar ratio of them is changed as shown in table 1 in the range of vanadium content from 40 mol% to 10 mol%.

3.2. Catalytic performance

The C_3H_8 conversion and the C_3H_6 selectivity observed for the reactions on $Ni_{0.9}V_{0.1}O_Y$ catalyst are strongly dependent on the reaction temperatures. With reaction temperature rising, the propane conversion and total oxidation products are increased, the propene selectivity is decreased, and cracking products are not observed (figure 1). This is due to the further oxidation of propene to CO_X being the more thermodynamically

Table 1
XRD phase of the $Ni_XV_{1-X}O_Y$ catalysts

	Sample				
	NiO	$Ni_{0.6}$-$V_{0.4}O_Y$	$Ni_{0.7}$-$V_{0.3}O_Y$	$Ni_{0.8}$-$V_{0.2}O_Y$	$Ni_{0.6}$-$V_{0.1}O_Y$
XRD phase	NiO	P	NiO + P	NiO + P	NiO + P
NiO : $Ni_3V_2O_8$ (molar ratio)	1 : 0	0 : 1	15 : 9	15 : 3	15 : 1

P : $Ni_3V_2O_8$.

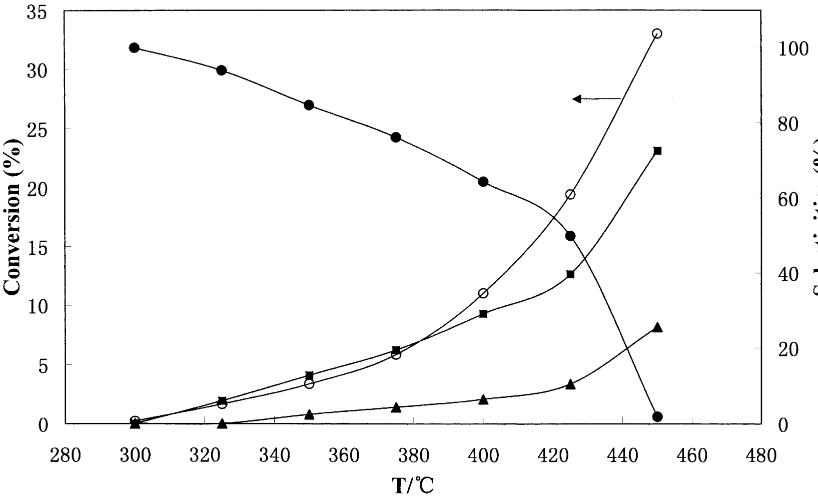

Figure 1. Conversion of C_3H_8 (○) and selectivities to C_3H_6 (●), CO (▲) and CO_2 (■) as a function of temperature for $Ni_{0.9}V_{0.1}O_Y$ sample.

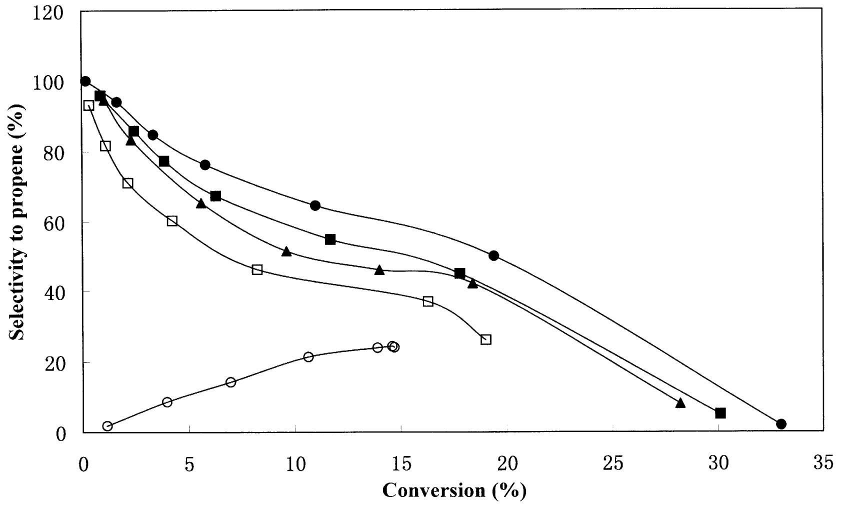

Figure 2. Variation in selectivity to C_3H_6 with C_3H_8 conversion for NiO (○), $Ni_{0.9}V_{0.4}O_Y$ (●), $Ni_{0.8}V_{0.2}O_Y$ (■), $Ni_{0.7}V_{0.3}O_Y$ (▲), $Ni_{0.6}V_{0.4}O_Y$ (□) samples.

Table 2
Propane ODH over the $Ni_XV_{1-X}O_Y$ catalysts

Catalyst	BET (m^2/g)	Conversion of C_3H_8 (mol%)	Specific activity (mol%/m^2)	Selectivity to C_3H_6 (mol%)
NiO	3.3	14.6	4.4	24.2
$Ni_{0.6}V_{0.4}O_Y$	13.1	16.3	1.2	36.9
$Ni_{0.7}V_{0.3}O_Y$	13.4	18.4	1.4	42.1
$Ni_{0.8}V_{0.2}O_Y$	11.6	17.8	1.5	44.9
$Ni_{0.9}V_{0.1}O_Y$	11.2	19.4	1.7	49.9

Reaction conditions: $C_3H_8/O_2/N_2$ = 10/5/35 mL/min, total feed 50 mL/min for 0.5 g catalyst, T = 425 °C.

favorable reaction at higher temperatures. For the sake of comparison, the catalytic activities of NiO and $Ni_XV_{1-X}O_Y$ ($X = 0.8$–0.6 molar) catalysts were also evaluated at different temperatures. The similar results are obtained on all of the other catalysts. Moreover, in figure 2, propene selectivity is reported as a function of propane conversion on NiO and $Ni_XV_{1-X}O_Y$ catalysts. With NiO as catalyst, C_3H_6 selectivity is increased with increasing C_3H_6 conversion. Finally, C_3H_6 selectivity is remained 24% at 14.6% of C_3H_8 conversion. $Ni_XV_{1-X}O_Y$ catalysts all show similar behavior, with high selectivity to C_3H_6 at low propane conversion dropping off with increasing conversion. With increasing Ni content in the catalysts, the catalytic behaviors for propane ODH are improved. It is shown in table 2 that 36.9% C_3H_6 selectivity at 16.3% C_3H_8 conversion is obtained on $Ni_3V_2O_8$ under given reaction conditions. Compared with NiO, a 12.7% of enhancement of C_3H_6 selectivity is observed, while a slight increase in C_3H_8 conversion is detected too. A maximum selectivity to C_3H_6 (49.9%) is obtained on $Ni_{0.9}V_{0.1}O_Y$ (a mixture of NiO and $Ni_3V_2O_8$), which is much higher than that of NiO alone or of $Ni_3V_2O_8$ at the same C_3H_8 conversion. Obviously, there is a synergetic effect beneficial for the selective formation of C_3H_6 occurred between NiO and $Ni_3V_2O_8$.

3.3. O_2-TPD-MS studies

The O_2-TPD-MS curves for NiO and $Ni_XV_{1-X}O_Y$ samples are shown in figure 3. Two peaks of oxygen desorption on NiO appear at about 450 and 740 °C respectively. For $Ni_3V_2O_8$, two peaks of oxygen desorption are also observed at < 450 °C and at 740 °C. However, the area of the first peak is larger than that of the second peak is smaller than that of NiO. With the amount of $Ni_3V_2O_8$ decreases, the peak areas of $Ni_XV_{1-X}O_Y$ catalysts around 400°C are increased, the areas of the second peak is also smaller than that of NiO. And the desorption temperatures of the second peaks are shifted to high temperatures. It is noticed that a shoulder peak is observed on the first oxygen desorption peak at about 500 °C for the $Ni_{0.9}V_{0.1}O_Y$ catalyst. One thing most interesting is that the second

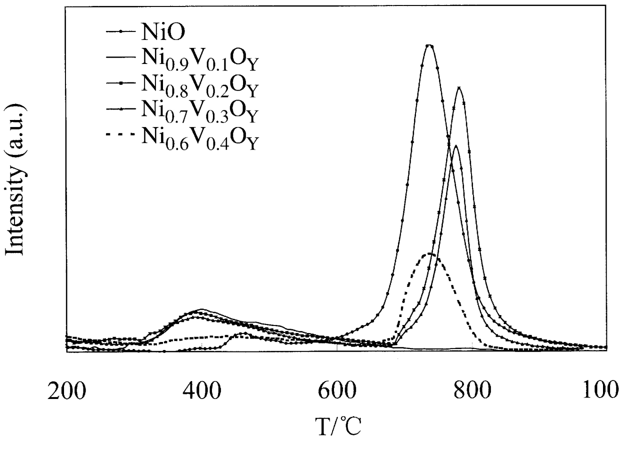

Figure 3. Curves of O_2-TPD-MS for NiO and $Ni_XV_{1-X}O_Y$ catalysts.

desorption peak of oxygen in the $Ni_{0.9}V_{0.1}O_Y$ to be nearly disappeared. It can be explained that the second oxygen species of the $Ni_{0.9}V_{0.1}O_Y$ catalyst may have a more strong interaction with metal cation, therefore, their desorption temperatures are shift to higher, and it is not observed in our experimental conditions.

The desorption temperature of the first peak seems to coincide with the reaction temperature. This result indicates that more oxygen species in $Ni_XV_{1-X}O_Y$ catalysts are much easy accessible to reactants than that of NiO, and it may be related to their catalytic performance. Combined with the catalytic results in figure 2 and table 2, it can be found that the more oxygen desorption at reaction temperature, the higher the catalytic performance of the catalysts. According to Chen *et al.* [15], the first desorption is related to α oxygen species, and the second one is due to desorption of β oxygen species, the former seemed most probably to be the nonstoichiometric oxygen (or mobile oxygen) desorption. From this suggestion, it could be deduced that the propane ODH would be realized by using nonstoichiometric oxygen species at low temperature.

3.4. H_2-TPR studies

Figure 4 shows the H_2-TPR diagrams of NiO and $Ni_XV_{1-X}O_Y$ catalysts. According to H_2 consumption, it can be estimated that in H_2-TPR reaction conditions, $Ni_XV_{1-X}O_Y$ catalysts are reduced to Ni and V_2O_3, which is furthermore confirmed by XRD analysis. This result suggested that mobile oxygen species and a part of lattice oxygen would be reduced. Compared with the H_2-TPR curves of pure NiO, the reduction curves of $Ni_3V_2O_8$ was shifted to high temperatures. It means that oxygen species in $Ni_3V_2O_8$ are less active than that in NiO, and this may be attributed to the C_3H_6 selectivity on $Ni_3V_2O_8$ is higher than that on NiO. With the decrease of $Ni_3V_2O_8$ amount in the $Ni_XV_{1-X}O_Y$ catalysts, the activity of oxygen species increases and H_2-TPR reaction occurs at 300–500 °C, which is in accordance with the temperature of ODH reaction. Comparison of the yield of propene over the catalysts, it can be found that a moderate activity of oxygen species in the catalyst is beneficial to C_3H_6 formation.

3.5. In situ electrical conductivity

Figure 5 gives the electrical conductivity of $Ni_XV_{1-X}O_Y$ catalysts in pure oxygen and reaction mixture atmospheres at 425 °C. NiO has the highest electrical conductivity and $Ni_3V_2O_8$ shows the lowest one. Chen *et al.* [15] suggested that the desorption peaks of NiO before 700 °C seemed to be desorption of the nonstoichiometric oxygen. From the comparison to electrical conductivity and the results in figure 3, it can be noticed that the peak areas have a good correlation with electrical conductivity of the $Ni_XV_{1-X}O_Y$ catalysts. It may be proposed that desorption peaks before 600 °C seem to be nonstoichiometric oxygen desorption. These results strongly suggested that the ratio of NiO and $Ni_3V_2O_8$ in the catalysts plays an important role in the formation of mobile oxygen species.

Combined with the results obtained about the relationship between mobile oxygen species and electrical conductivity, it may be deduced that the more mobile oxygen species, the higher the C_3H_6 formation on the $Ni_XV_{1-X}O_Y$ catalysts. However, NiO has the highest electrical conductivity but its catalytic performance is the lowest. This could be explained by the absence of $Ni_3V_2O_8$ that favors to propene formation. In conclusion, *in situ* electrical conductivity can be used to estimate the catalytic performance of the catalyst like TPR studies and acidity-basicity of the catalyst.

3.6. Reaction mechanism

All of the active and selective catalysts tested in this study were composed of NiO and $Ni_3V_2O_8$. These kinds of p-type semiconductor catalysts [18] have positive holes h^+ as the main charge carriers. According to the suggestion of Herrmann *et al.* [19], O^- may be produced in $Ni_XV_{1-X}O_Y$ catalysts by the positive holes. Electrochemical equilibrium can be assumed:

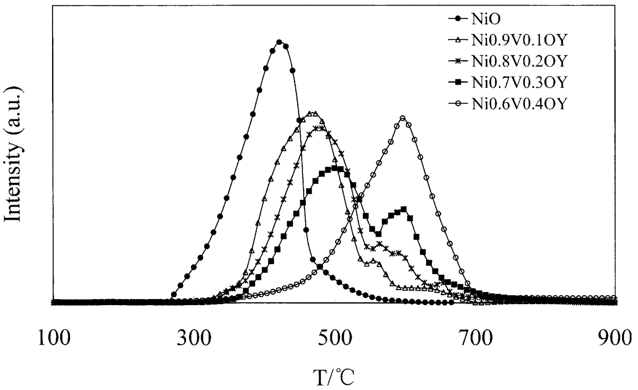

Figure 4. H_2-TPR spectra of the NiO and $Ni_XV_{1-X}O_Y$ catalysts.

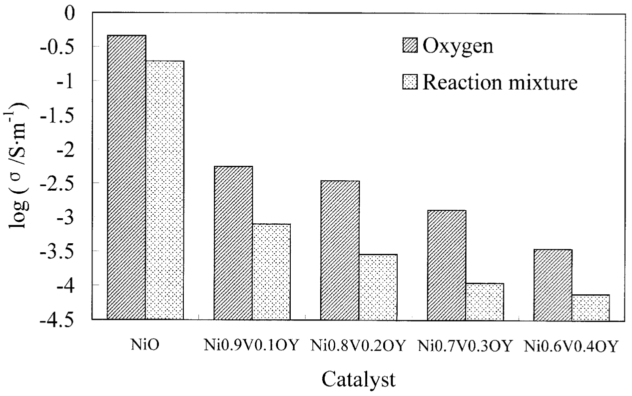

Figure 5. Electrical conductivity of NiO and $Ni_XV_{1-X}O_Y$ catalysts in different atmospheres.

$$V^{5+} \Leftrightarrow V^{4+} + h^+$$

Electrons transferred from O^{2-} ion would neutralize this kind of positive hole and produce O^-

$$O^{2-}(l) + h^+ \Leftrightarrow O^-(s) \tag{1}$$

From above two equations, it can be obtained

$$V^{5+} + O^{2-}(l) \Leftrightarrow V^4 + O^-(s)$$

In various oxygen species on the metal oxides, O^- species has a suitable energy [20], and its potential energy is lower than that of surface O^{2-} favorable to total oxidation and higher than that of lattice oxygen species. It means that O^- species is more active than lattice oxygen species and less active than surface O^{2-} species. For n-type semiconductors, many authors [1] suggested that the formation of propene was performed *via* the reaction of propane with surface lattice O^{2-}s of the catalysts:

$$C_3H_8 + O^{2-}s \rightarrow C_3H_6 + H_2O + V_0 + 2e^-$$

where V_0 is oxygen vacancy.

However, according to the work on ethane ODH by Lunsford et al. [21,22] and Martin et al. [16], and the researches on the partial oxidation of n-butane by Herrmann *et al.* [19] on p-type semiconductor oxides, it can be proposed that the propane ODH reaction can be initiated by the abstraction of a hydrogen atom with a very active O^- species on p-type Ni–V–O catalysts. The reaction mechanism of initiation of dehydrogenation may be suggested as follows:

$$C_3H_8 + O^-(s) \Leftrightarrow C_3H_7 \cdot (s) + OH^-(s) \tag{2}$$

$$\text{propene formation:} \quad \begin{aligned} &C_3H_7 \cdot (s) + O^-(s) \\ &\quad \rightarrow C_3H_6 + OH^-(s) \end{aligned} \tag{3}$$

$$\text{water elimination:} \quad \begin{aligned} &OH^-(s) + OH^-(s) \\ &\quad \rightarrow H_2O + O^2(l) + V_0 \end{aligned} \tag{4}$$

$$\text{positive hole formation:} \quad V_0 + 1/2O_2(g) \rightarrow O^{2-}(l) + 2h^+ \tag{5}$$

from (1) to (5) we have

$$C_3H_8 + 1/2O_2(g) \rightarrow C_3H_6 + H_2O$$

From the above discussion, it could be concluded that the presence of the positive holes in the catalysts makes O^- species production. Therefore, propane ODH reaction can be realized at low temperature on the $Ni_XV_{1-X}O_Y$ catalysts *via* the recycling of the reaction

$$V^{5+} + O^{2-}(l) \Leftrightarrow V^{4+} + O^-(s)$$

4. Conclusion

$Ni_XV_{1-X}O_Y$ catalysts with NiO and $Ni_3V_2O_8$ phases show better catalytic performance for propane ODH due to their more mobile oxygen species to reactant, moderate strengthening redox properties.

Propane ODH reaction is initiated by the abstraction of hydrogen atom using very active O^- species and realized on $Ni_XV_{1-X}O_Y$ catalysts *via* recycle of the reaction $V^{5+} + O^{2-} \Leftrightarrow V^{4+} + O^-$ at low temperature.

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