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Oxygen species on NiO/Al_2O_3 and their reactivities

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Abstract

Oxygen species on fresh and treated NiO/Al_2O_3 and their activities for oxidation of ethane and ethylene were investigated using catalytic property measurements, ethane and ethylene pulse experiments and O_2–TPD–MS experiments. The results revealed that there are two kinds of active oxygen species (the more active one and the less active one) on fresh NiO/Al_2O_3 catalyst, but there is only one active oxygen species, the less active one, on treated NiO/Al_2O_3 catalyst. The more active oxygen species can convert ethane or ethylene to carbon dioxide by one step while the less active one can only convert ethane to ethylene, but cannot convert ethane and/or ethylene to carbon dioxide. The more active oxygen species can be removed from the catalyst by heating from 350 to 850 °C. The amounts of desorption oxygen on the catalysts are proportional to their selectivity to carbon dioxide. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oxygen species; Ethane; Ethylene; Oxidative dehydrogenation; NiO/Al_2O_3

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1. Introduction

Oxidative dehydrogenation of light alkanes is one of the most important topics in catalysis [1,2]. Among them, oxidative dehydrogenation of ethane (ODE) to ethylene at low temperature is the most challenging one because of its significant industrial application. In 1978, Union Carbide reported their MoVNbOx catalysts for low temperature ODE [3]. From that time, a lot of catalysts have been tested for the low temperature ODE, but no catalysts gave both higher yield to ethylene and better life span than the catalysts developed by Union Carbide [4–13]. Recently, we developed a new type of low temperature catalyst, NiO/Al_2O_3 [14], which gives a high yield to ethylene.

In this paper, oxygen species on the fresh and treated NiO/Al_2O_3 catalyst and their activities were investigated by catalyst property tests, ethane and ethylene pulse experiments and O_2–TPD–MS experiments.

2. Experimental

2.1. Catalyst preparation

Al_2O_3 with surface area of 126 m^2/g was prepared by hydrolysis of aluminum alkoxide and calcination at 900 °C for 5 h. The catalysts, NiO/Al_2O_3, were prepared by impregnation of Al_2O_3 powders with aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. The slurry was dried at 140 °C overnight followed by calcination at 450 °C in air for 5 h. The catalysts, NiO-K/Al_2O_3 (Ni:K = 10:2 (mol:mol)) and NiO-W/Al_2O_3 (Ni:W = 10:2 (mol:mol)), were prepared by adding KNO_3 and $(NH_4)_6W_{12}O_{39} \times H_2O$ into the solution of $Ni(NO_3)_2 \cdot 6H_2O$, respectively. For the above three catalysts, the amount of NiO on Al_2O_3 is 0.24 g/g cat. NiO, which is obtained by decomposition

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of $Ni(NO_3)_2{\cdot}6H_2O$ at 450 °C for 5 h, was used for comparison. The catalysts were crushed and sieved to 40–80 meshes before use.

The fresh catalyst, NiO/Al_2O_3, is the catalyst just taken out of the oven before use. The treated NiO/Al_2O_3 catalysts is obtained by treating the fresh catalyst at 400 °C in a gas mixture (C_2H_6:O_2:N_2 = 10.0:10.0:80.0 (volume)) for 5 h. The space velocity is 338 ml C_2H_6/g cat·h (GHSV at STP).

2.2. Catalytic property measurement

The catalytic property measurements were carried out at atmospheric pressure in a fixed-bed flow quartz glass microreactor filled with 0.5 g catalysts. The reaction temperature ranged from 300 to 450 °C. The feed gas consisted of 10.0 vol.% C_2H_6, 10.0 vol.% O_2 and 80.0 vol.% N_2. The space velocity is 338 ml C_2H_6/g cat·h (GHSV at STP). The products were analyzed using an on-line gas chromatography with a 4 m Poropak Q column and a hydrogen flame ionization detector. A methanator of Ni catalyst was equipped to the GC to convert carbon dioxide to methane for analysis.

2.3. Pulse experiments

Pulse experiments of ethane and ethylene were carried out at 1.4 atm on an automatic system with an on-line GC. The schematic diagram was plotted in Fig. 1. High purity nitrogen, which was used as carrier gas, first went through deoxidant (MnO). A total of 1.0 ml ethane/nitrogen mixture (C_2H_6:N_2 = 20:80 (volume)) or 1.0 ml ethylene/nitrogen mixture (C_2H_4:N_2 = 20:80 (volume)) was fed into this carrier gas through a six-way valve, and then this nitrogen carried ethane (or ethylene) to the catalyst bed (0.5 g catalyst) and then carried the reagent and the products to the online GC.

2.4. O_2–TPD–MS experiments

The O_2–TPD–MS experiments were carried out at atmosphere by combination of a TPD system and a MS system. The temperature is ranged from room temperature to 1000 °C. Argon is used as a carrier gas. It first goes through the deoxidant (MnO), and then passes the catalyst bed and carries any gases escaping from the samples, and then sends the gas mixture to MS (Anelva 100) for recording the signal (mass = 32).

3. Results and discussion

3.1. Catalytic property measurements

The catalytic properties of the catalysts NiO, NiO/Al_2O_3, NiO-K/Al_2O_3 and NiO-W/Al_2O_3 were presented in Table 1.

In Table 1, bulk NiO has very high activity compared to the supported catalysts. At 300 °C, while the supported catalysts showed small or no activities, conversion of ethane on bulk NiO was >20%. At 350 °C, the activity of NiO is still the highest among these four catalysts; ethane conversion on it was 46.3% while ethane conversion on other catalysts was only 20% or less. The selectivity to ethylene on bulk NiO is medium; it is lower than that on NiO/Al_2O_3 and NiO-W/Al_2O_3, but higher than that on NiO-K/Al_2O_3. For bulk NiO catalyst, further increasing reaction temperature from 400 °C resulted in the total consumption of oxygen in the feed. When there is no oxygen in the back part of the catalyst bed and there is still some ethane, NiO is reduced by ethane to metal Ni. This metal Ni will produce a total different product distribution, which was not presented here.

After supported on Al_2O_3, the activity of NiO was decreased, but the selectivity to ethylene is greatly

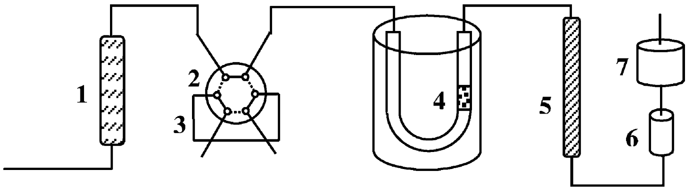

Fig. 1. The schematic plot of pulse experiments: (1) deoxidant, (2) six-way valve, (3) pulse tube, (4) catalyst bed, (5) GC column, (6) Ni methane converter, (7) detector.

Table 1
The catalytic properties of the NiO-based catalysts for ODE

Catalyst	T (°C)											
	300			350			400			450		
	C (%)[a]	S (%)[b]		C (%)	S (%)		C (%)	S (%)		C (%)	S (%)	
		C_2H_4	CO_2		C_2H_4	CO_2		C_2H_4	CO_2		C_2H_4	CO_2
NiO	22.3	48.6	51.4	46.3	46.4	53.6	–	–	–	–	–	–
NiO/Al_2O_3	5.3	75.4	24.6	20.4	72.1	27.9	41.9	69.1	30.9	61.7	64.2	35.8
$NiO-K/Al_2O_3$	1.2	8.7	91.3	10.6	9.9	90.1	26.0	9.6	90.4	34.0	15.9	84.1
$NiO-W/Al_2O_3$	–	–	–	5.01	86.3	13.7	14.3	84.1	15.9	29.0	76.9	23.1

[a] C (%): conversion of ethane (mol%).

[b] S (%): selectivity (mol%).

increased. As we see in Table 1, at an ethane conversion of 20%, the selectivity to ethylene is <50% on bulk NiO, but the selectivity is 72.1% on NiO/Al_2O_3. For NiO/Al_2O_3 catalyst, the highest yield to ethylene of 39.6% can be obtained at 450 °C with an ethane conversion of 61.7% and selectivity to ethylene of 64.2%.

$NiO-K/Al_2O_3$ and $NiO-W/Al_2O_3$ catalysts show completely different behaviors compared with NiO/Al_2O_3 catalyst. For $NiO-W/Al_2O_3$ catalyst, the activity of the catalyst was decreased, but the selectivity to ethylene was increased. For $NiO-K/Al_2O_3$ catalyst, the activity of the catalyst decreased, but at the same time, the selectivity to ethylene was also decreased. The decrease of the selectivity is so great that it is <20% on $NiO-K/Al_2O_3$ catalyst.

3.2. O_2–TPD–MS experiments

As is noticed above, these four catalysts show significant difference in catalytic properties. The O_2–TPD–MS experiments were designed to characterize their differences. The catalysts used here are fresh catalysts without pre-treatment. The results are presented in Fig. 2a–d.

For these four catalysts, there is oxygen escaping from the catalyst in the temperature range of 350–850 °C when the catalysts were heated gradually. The amounts of oxygen escaping from the catalyst are very different. It is interesting to notice that the amounts of oxygen escaping from the catalysts are related to their selectivities to carbon dioxide as shown in Table 1. The exact relationship was presented in Fig. 3. The selectivity to carbon dioxide was the one at ethane conversion of 30%. The conclusion is clear that the selectivity to carbon dioxide is proportional to the amount of desorption oxygen on the fresh catalysts.

The color change of the catalysts was also observed before and after the O_2–TPD–MS experiments. Before the experiments, all the catalysts are deep black, a typical color of non-stoichiometric form of NiO. After the experiment, the color of NiO catalyst is light yellow, NiO/Al_2O_3 light green, $NiO-K/Al_2O_3$ light blue and $NiO-W/Al_2O_3$ light green. For bulk NiO catalyst, the color changes means oxygen associated with non-stoichiometric form of NiO was taken away in the TPD-MS experiment. For other catalysts, the change of the color is partially due to the loss of oxygen associated with the non-stoichiometric form of NiO [15] and partially due to the formation of some new structures.

3.3. Ethane and ethylene pulse experiment

From the above experiments, it is noticed that the oxygen species, which can desorb from the catalysts at high temperature (350–850 °C), may play an important role in the formation of carbon dioxide. Ethane and/or ethylene pulse experiments without oxygen in the feed were designed to test the activities of oxygen species on the catalyst.

The catalyst was heated from room temperature at 10 °C/min and maintained at 400 °C for 1 h, and then small amount of ethane and/or ethylene were introduced into the system. When passing the catalysts, ethane and/or ethylene may react with the oxygen species on the catalyst (from the most active one to

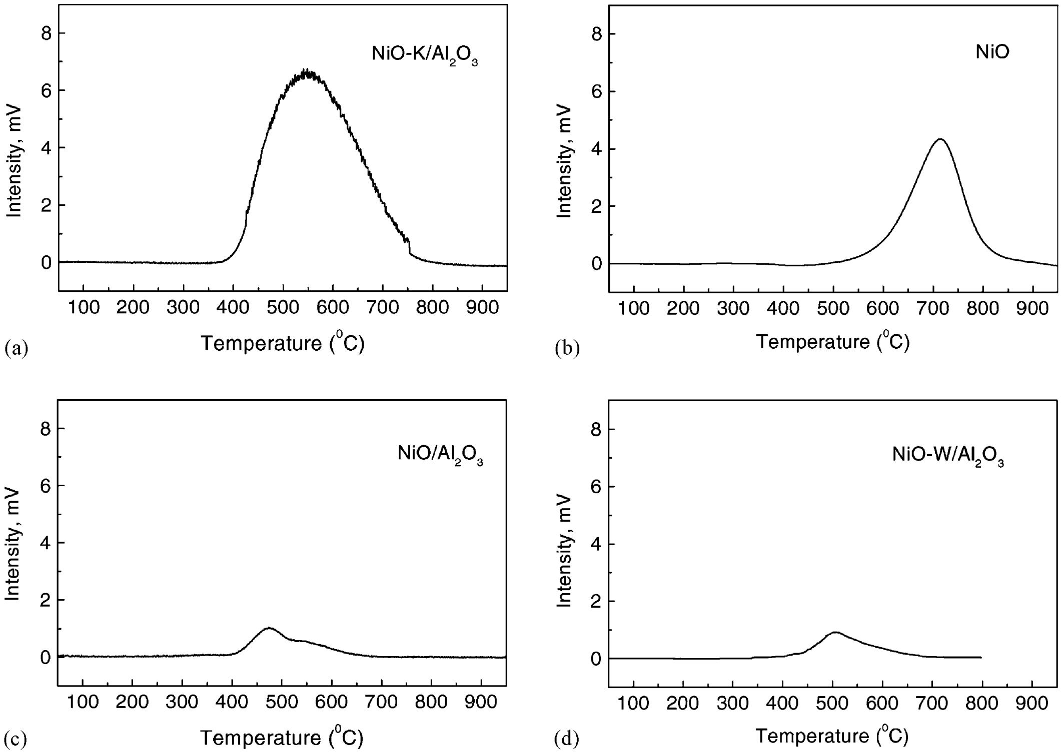

Fig. 2. O_2–TPD–MS spectra of fresh NiO, NiO/Al_2O_3, $NiO\text{-}K/Al_2O_3$, $NiO\text{-}W/Al_2O_3$.

the less active one), which provides us a method to understand the activity of the oxygen species on the catalysts.

Two catalysts, a fresh NiO/Al_2O_3 catalyst and a treated NiO/Al_2O_3 catalyst were used and the results were presented in Fig. 4a–d. The difference of this fresh catalyst and this treated catalyst was also characterized by O_2–TPD–MS experiments that were shown in Fig. 5. As we knew before, only ethylene and carbon dioxide are the products on NiO-based catalyst, so only selectivity to ethylene was shown in Fig. 4a and b.

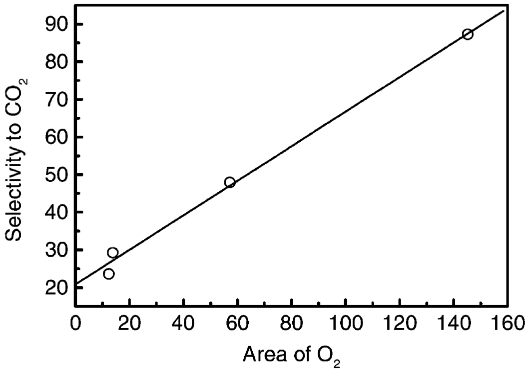

Fig. 3. Relationship of selectivity to CO_2 and amount of oxygen desorbed in TPD–MS.

From Fig. 4, it is noticed that in the ethane pulse experiment on fresh catalyst (Fig. 4a), for the first three ethane pulses, all the product is carbon dioxide and no ethylene was produced. For the fourth ethane pulse, both ethylene and carbon dioxide was formed. But for the fifth ethane pulse, the product is only ethylene and no carbon dioxide was observed. From the fifth pulse, the only product is ethylene while ethane conversion maintains a high level. Even for the twelfth pulse, ethane conversion is >10%, which means that there is still some oxygen on the catalyst that has the ability to react with ethane to form ethylene.

From Fig. 4c, it is noticed that the ethylene pulse experiment on fresh catalyst shows similar results with that of ethane pulse experiment. For the first four

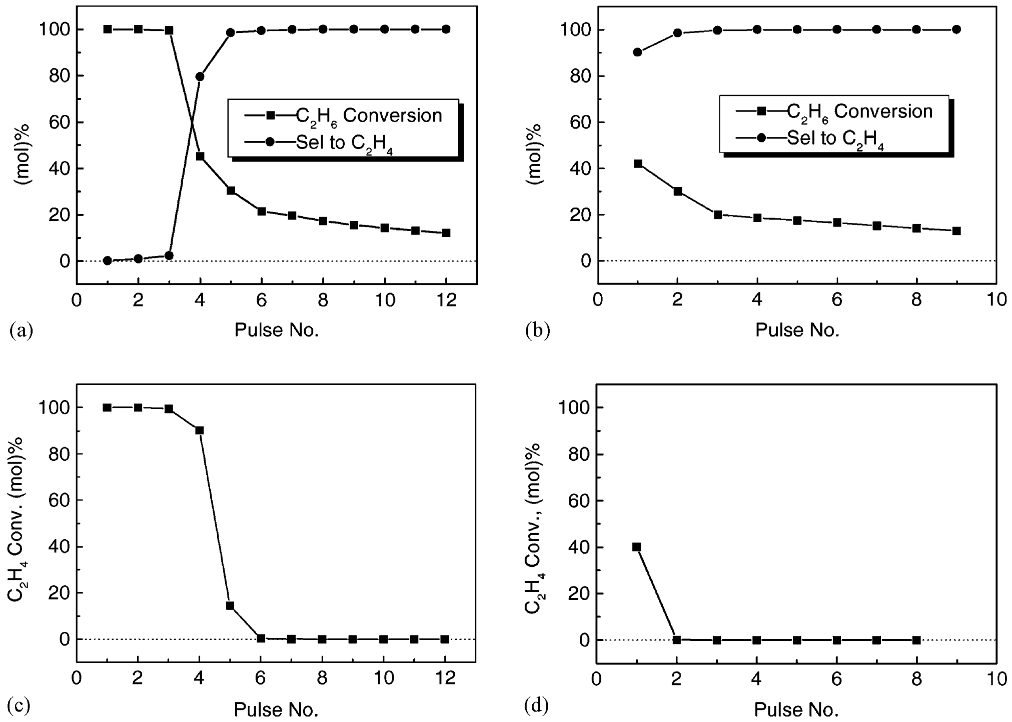

Fig. 4. Pulse experiments of ethane and ethylene on fresh and treated NiO/Al_2O_3: (a) ethane pulse on fresh NiO/Al_2O_3; (b) ethane pulse on treated NiO/Al_2O_3; (c) ethylene pulse on fresh NiO/Al_2O_3; (d) ethylene pulse on treated NiO/Al_2O_3.

pulses, all the product is carbon dioxide. But from the fifth pulse, ethylene did not react, the conversion of ethylene is zero, which indicated that there is no oxygen active enough to react with ethylene to form product.

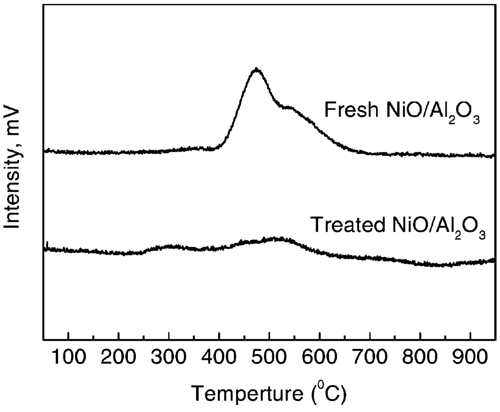

Fig. 5. O_2–TPD–MS spectra of fresh and treated NiO/Al_2O_3.

The sharp change of ethane conversion and product distribution is surprising because always we assume the activity of oxygen species on the catalysts changes gradually, which means that we should see the gradual change of the product distribution. This sharp change means that the activities of oxygen species are absolutely different. We can assume that there are at least two different active oxygen species on the fresh NiO/Al_2O_3 catalyst. The more active one can change ethane to carbon dioxide by one step without forming ethylene, and it can also change ethylene to carbon dioxide by one step. The less active one can convert ethane to ethylene without forming carbon dioxide, but it cannot change ethylene to carbon dioxide.

For the ethane pulse experiment on treated NiO/Al_2O_3 catalyst, only in the first pulse, small amount of carbon dioxide can be seen, and from the second pulse, the only active oxygen species is the less active oxygen that converts ethane to ethylene. Fig. 4b is just the second part of Fig. 4a. For ethylene pulse on treated catalyst (Fig. 4d), it is just the second part of Fig. 4c.

By comparing Fig. 4a and b, and Fig. 4c and d, we concluded that on the treated catalyst, there is one active oxygen species, the less active oxygen, which can convert ethane to ethylene, but can not convert ethylene to carbon dioxide.

From O_2–TPD–MS experiments of fresh and treated NiO/Al_2O_3 catalysts shown in Fig. 5. We know that the on the treated NiO/Al_2O_3 catalyst, there is almost no desorption oxygen compared with fresh NiO/Al_2O_3 catalyst. So the more active oxygen species is just the oxygen that can be taken away from the catalyst in TPD–MS experiment.

4. Conclusions

There are two kinds of active oxygen species (the more active one and the less active one) on the fresh NiO/Al_2O_3 catalysts, but there is only one active oxygen species (the less active one) on the treated NiO/Al_2O_3 catalyst. The more active oxygen species can convert ethane and ethylene to carbon dioxide by one step and the less active species can only convert ethane to ethylene, but cannot convert ethylene to carbon dioxide. The more active oxygen species can be taken away from the fresh catalyst by heating from 350 to 850 °C. Doping different metal oxide can change the amount of oxygen species that can be taken away from the fresh catalyst, and can greatly change the selectivity to ethylene. The amount of desorption oxygen species on the fresh catalysts is proportional to their selectivity to carbon dioxide.

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