

# The effect of K and Al over NiCo<sub>2</sub>O<sub>4</sub> catalyst on its character and catalytic oxidation of VOCs

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## Abstract

NiCo<sub>2</sub>O<sub>4</sub>, K-NiCo<sub>2</sub>O<sub>4</sub>, and Al-NiCo<sub>2</sub>O<sub>4</sub> spinel oxides were prepared by co-precipitated method. The properties of these three samples were investigated by X-ray powder diffraction (XRD), temperature-programmed reduction (TPR), Brunauer–Emmett–Teller (BET) measurement, and X-ray photoelectron spectroscopy (XPS) technologies. The catalytic activity of volatile organic compounds (VOCs) oxidation was found to be decreased after adding aluminum and increased after adding potassium in NiCo<sub>2</sub>O<sub>4</sub> sample. The small particle size of NiCo<sub>2</sub>O<sub>4</sub> was responsible for VOCs oxidation. The potassium was the most effective in promoting NiCo<sub>2</sub>O<sub>4</sub> sample in reducibility and surface area. XPS analysis indicated that the electrophonic oxygen species on the catalyst surface is the main active oxygen and plays an important role in total oxidation of VOCs.

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## 1. Introduction

Volatile organic compounds (VOCs) are main air pollution because of their toxic properties. Recently, catalytic combustion presents many advantages, such as high combustion efficiency and low emission of unburnt hydrocarbons [1–3]. The combustion catalysts are also based on the noble metal (such as Pd, Pt, and Rh) catalysts. [4,5]. Moro-oka and co-workers [6] studied the catalytic properties of various metal oxides in the oxidation of VOCs and found that the activity of noble metals was higher than that of non-noble metal oxides. But, the application of noble metals catalyst was limited by the high cost and the supply. Transition metal oxides were the other series of catalysts. Finding transitional metal element catalyst to replace or partly replace the noble metal catalyst was attracted many scientist's attention [7–9]. It has been previously reported that transitional metal-spinel structure oxide can be achieved in CH<sub>4</sub> oxidation, but Ni and Co spinel oxide catalyst used in VOCs oxidation have not be reported. In this paper, we

reported a new series of NiCo<sub>2</sub>O<sub>4</sub> catalysts for the oxidation of VOCs (ethanol, toluene, acetone, and acetic ether). The results indicated that K-NiCo<sub>2</sub>O<sub>4</sub> catalyst has been found to be very active in the oxidation of tested VOCs among the three catalysts. The structure characteristics, reducibility, surface area, and surface oxygen state of these samples were studied by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), Brunauer–Emmett–Teller (BET), and TGA–DTG techniques.

## 2. Experimental

### 2.1. Catalyst preparation

NiCo<sub>2</sub>O<sub>4</sub> spinel structure oxide catalyst was prepared by co-precipitation method. 3N NaOH was added into the aqueous solution containing the required amount of Ni(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> until the pH of the solution was 12. The resultant precipitate was filtered and washed with deionized water until the pH of the solution was below 8, then the samples were dried at 100 °C for 4 h, followed by calcination at 800 °C for 6 h in an air stream to obtain Ni-Co-O composite

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oxide catalysts. The K-NiCo<sub>2</sub>O<sub>4</sub> and Al-NiCo<sub>2</sub>O<sub>4</sub> catalysts were prepared by impregnate method with an aqueous solution of KOH and Al(OH)<sub>3</sub> under incipient wetness condition. The catalyst precursor was washed several times (until disappearance of OH<sup>-</sup>) then dried under 120 °C for 2–4 h and calcined in an air atmosphere at 500 °C for 2 h. The potassium and aluminum loading of the K-NiCo<sub>2</sub>O<sub>4</sub> and Al-NiCo<sub>2</sub>O<sub>4</sub> catalysts were 2.0 wt. %.

## 2.2. Activity measurements

The catalytic activity test for total oxidation of ethanol, toluene, acetone, and acetic ether were performed in a flow reactor containing a fixed-bed with 150 mg of catalyst. The temperature was raised from room temperature to 500 °C. A space velocity of 5000 h<sup>-1</sup> was used. The temperature was measured both before and after the catalyst bed. The analysis of the reactor effluent was performed with an on-line SP-2304 model vapor chromatograph with a FID. The catalytic activity was denoted by *T*<sub>98</sub> (*T*<sub>98</sub> indicated that temperature at which the indicated substance conversion levels were 98%, respectively).

## 2.3. Characterization of the catalysts

XRD patterns were recorded by using CuKα radiation on a Rigaku D/max-III B diffractometer for phase identification.

XPS spectra was obtained using a PHI-550 model ESCA/SAM system. The binding energy was adjusted to the C1s peak at 284.6 eV which existed in all measurements.

TPR was described in our previous paper [10]. TGA–DTG analysis was carried on a PE-TG-7 instrument. The sample was investigated according to the following experiment conditions: catalyst weight: 100 mg; gas composing: 5% H<sub>2</sub> in N<sub>2</sub>; temperature raising rate: 15 °C/min; temperature range: 20–800 °C.

The surface area was measured with an OMNISORP-100CX instrument by adsorption of nitrogen at 77 K. The surface area was obtained base the BET (Brunauer–Emmett–Teller) procedure.

Electric properties of the samples were performed on a DDS-11A type instrument to detect the conductance.

## 3. Results and discussion

### 3.1. Catalytic activity for ethanol, toluene, acetone, and acetic ether combustion

The results of total oxidation of ethanol, toluene, acetone, and acetic ether on samples of NiCo<sub>2</sub>O<sub>4</sub>, K-NiCo<sub>2</sub>O<sub>4</sub>, and Al-NiCo<sub>2</sub>O<sub>4</sub> are shown in Table 1. It was found that the catalytic activity of K-NiCo<sub>2</sub>O<sub>4</sub> is higher than those of NiCo<sub>2</sub>O<sub>4</sub> and Al-NiCo<sub>2</sub>O<sub>4</sub> sample. For example, in K-NiCo<sub>2</sub>O<sub>4</sub> catalyst, the *T*<sub>98</sub> of toluene was 50 °C and 100 °C lower compared with that of in NiCo<sub>2</sub>O<sub>4</sub> and in

Table 1

Temperature of oxidation activity of the indicated substances over three catalysts

Catalyst	<i>T</i> <sub>98</sub> (toluene)/°C	<i>T</i> <sub>98</sub> (acetone)/°C	<i>T</i> <sub>98</sub> (alcohol)/°C	<i>T</i> <sub>98</sub> (acetic ether)/°C
NiCo <sub>2</sub> O <sub>4</sub>	300	340	280	370
K-NiCo <sub>2</sub> O <sub>4</sub>	250	270	220	330
Al-NiCo <sub>2</sub> O <sub>4</sub>	350	350	300	400

Space speed = 5000 h<sup>-1</sup>.

Al-NiCo<sub>2</sub>O<sub>4</sub> catalyst. The optimize result of the conversion of alcohol was at 220 °C in K-NiCo<sub>2</sub>O<sub>4</sub>, suggesting that VOCs oxidation activity was virtually influenced in the NiCo<sub>2</sub>O<sub>4</sub> by adding of potassium. It might be due to the fact that potassium and NiCo<sub>2</sub>O<sub>4</sub> was made a strong interaction which influenced the catalytic activity of VOCs oxidation. Meanwhile, from Table 1, a clear order was observed that ethanol was most readily oxidized, followed by toluene, than acetone and acetic ether in all catalysts.

### 3.2. Characterization of Ni-Co-O catalyst

The XRD spectra of Ni-Co-O, K-Ni-Co-O and Al-Ni-Co-O catalysts are shown in Fig. 1. Characteristic lines of XRD due to NiCo<sub>2</sub>O<sub>4</sub> spinel phase were observed in all catalysts. However, in NiCo<sub>2</sub>O<sub>4</sub> catalyst, only the characteristic lines due to NiCo<sub>2</sub>O<sub>4</sub> were appeared (*d* = 2.439, 2.862, 1.429, 1.556, and 2.021). It should be noticed that the intensity of NiCo<sub>2</sub>O<sub>4</sub> spinel oxides peaks was stronger after adding potassium and weaker after adding aluminum. Based on the catalytic activity, result is shown in Table 1, it can be found that the more the NiCo<sub>2</sub>O<sub>4</sub> spinel oxides phase were, the high the catalyst activity was. It may be due to the fact that NiCo<sub>2</sub>O<sub>4</sub> spinel phase are active phase for VOCs oxidation. In addition, there were any crystal lines due to potassium phase or any compound of the same oxide compounds in K-NiCo<sub>2</sub>O<sub>4</sub> catalyst. The absence of the characteristic peaks of potassium indicated that potassium was well dispersed on the NiCo<sub>2</sub>O<sub>4</sub> surface or in microcrystalline state. The XRD

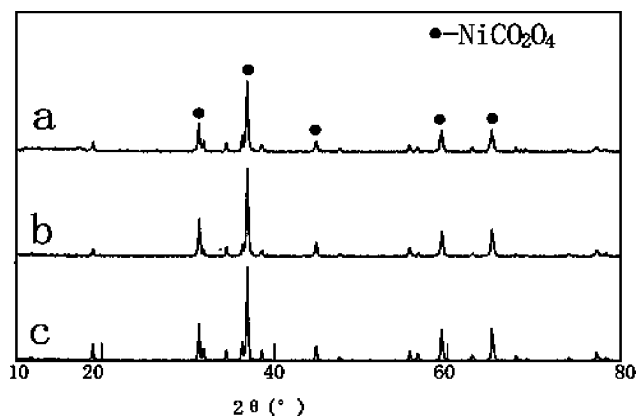


Fig. 1. XRD patterns of K-NiCo<sub>2</sub>O<sub>4</sub>, NiCo<sub>2</sub>O<sub>4</sub>, and K-NiCo<sub>2</sub>O<sub>4</sub> (a) Al-NiCo<sub>2</sub>O<sub>4</sub>, (b) NiCo<sub>2</sub>O<sub>4</sub>, (c) K-NiCo<sub>2</sub>O<sub>4</sub>.

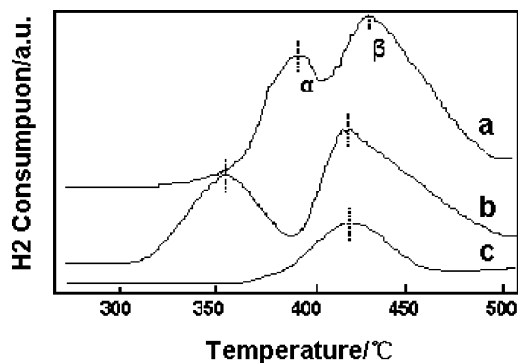


Fig. 2. TPR profiles of three catalysts (a)  $\text{NiCo}_2\text{O}_4$ , (b)  $\text{K-NiCo}_2\text{O}_4$ , (c)  $\text{Al-NiCo}_2\text{O}_4$ .

result may be explained by the interaction between the active potassium phase and  $\text{NiCo}_2\text{O}_4$ . The larger the interface between the potassium and  $\text{NiCo}_2\text{O}_4$ , the more prominent catalytic activity was shown. The good dispersion of potassium, giving an intimate contact with the  $\text{NiCo}_2\text{O}_4$  support, leads to a stronger tendency for stabilize  $\text{NiCo}_2\text{O}_4$  spinel oxides, which was an active phase for VOCs oxidation.

### 3.3. TPR measurement

In order to investigate the reducibility of the series of  $\text{NiCo}_2\text{O}_4$  catalysts, the  $\text{H}_2$ -TPR experiment has been carried out and the result is shown in Fig. 2. The TPR profile of  $\text{NiCo}_2\text{O}_4$  catalyst was shown by two reduction peaks of  $\alpha$  and  $\beta$  in the experiment temperature range of 350–500 °C, indicating that there were two kinds of  $\text{NiCo}_2\text{O}_4$  spinel oxides with different chemical environments in  $\text{NiCo}_2\text{O}_4$  catalyst. Among them,  $\alpha$  peak was ascribed to the reduction of the dispersed and small particle size of  $\text{NiCo}_2\text{O}_4$  and they were reduced at lower temperature. The  $\beta$  peak was ascribed to the reduction of the big or combined particle size of  $\text{NiCo}_2\text{O}_4$  and they were reduced at higher temperature. In the profile of  $\text{K-NiCo}_2\text{O}_4$  catalyst, it changed a lot compared with that of in  $\text{NiCo}_2\text{O}_4$  sample. It appeared a largest peak area and a lowest peak temperature, indicating that  $\text{NiCo}_2\text{O}_4$  sample can be easily reduced by adding potassium. It was interesting that the  $\alpha$  peak disappeared and the  $\beta$  peak areas became small in  $\text{Al-NiCo}_2\text{O}_4$  catalyst, indicating that adding aluminum in  $\text{NiCo}_2\text{O}_4$  restrained the reduction of small particle size of  $\text{NiCo}_2\text{O}_4$ . The results indicated that  $\text{NiCo}_2\text{O}_4$  sample can be easily reduced by adding potassium. Combined the results of XRD and catalytic activity, we propose that the small particle size of  $\text{NiCo}_2\text{O}_4$  was responsible for VOCs oxidation.

Fig. 3 shows TG–DTG profiles. From Fig. 3, it can be seen that there are three stages of weight loss at temperatures below 700 °C, the corresponding DTG curves appeared three peaks, indicating there were three different oxygen species in the samples. The top temperature of DTG was as following,  $\text{K-NiCo}_2\text{O}_4$  sample appeared at 320 °C, 390 °C, and 640 °C,  $\text{NiCo}_2\text{O}_4$  sample appeared at 330 °C, 390 °C,

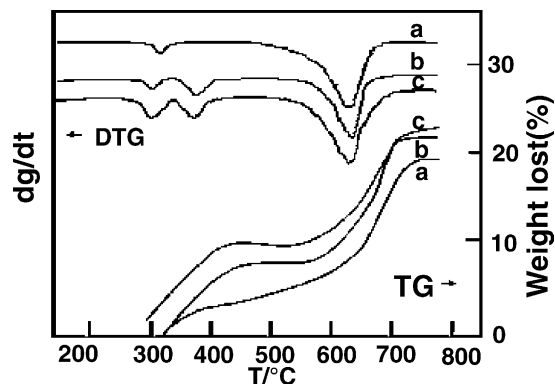
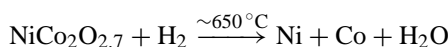
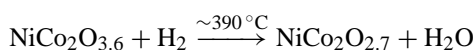
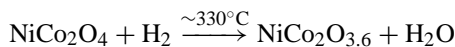
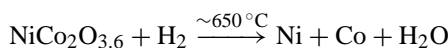
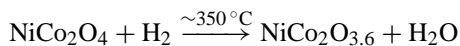


Fig. 3. TG–DTG curve of three samples (a)  $\text{Al-NiCo}_2\text{O}_4$ , (b)  $\text{NiCo}_2\text{O}_4$ , (c)  $\text{K-NiCo}_2\text{O}_4$ .

and 650 °C. Compared with  $\text{NiCo}_2\text{O}_4$  and  $\text{K-NiCo}_2\text{O}_4$ ,  $\text{Al-NiCo}_2\text{O}_4$  showed difference in the profiles; there were only two weight loss stages and two peaks in DTG curve, at about 350 °C, 660 °C, suggesting aluminum additive effect the reducibility of oxygen in  $\text{NiCo}_2\text{O}_4$  catalyst. Calculating the reduced compounds during the different temperature stage, the  $\text{K-NiCo}_2\text{O}_4$  and  $\text{NiCo}_2\text{O}_4$  samples process three steps:



The reducibility process of  $\text{NiCo}_2\text{O}_4$  in  $\text{Al-NiCo}_2\text{O}_4$  sample is as following:



Based on the results indicated in Figs. 2 and 3, the order of the active oxygen in the three samples was:  $\text{K-NiCo}_2\text{O}_4 > \text{NiCo}_2\text{O}_4 > \text{Al-NiCo}_2\text{O}_4$ . Hence, it was apparent that catalytic activity was related to the active oxygen properties of the three samples.

### 3.4. BET surface area

The BET surface areas of these three samples are reported in Table 2. Adding potassium leads to increase the surface area of sample  $\text{NiCo}_2\text{O}_4$  from 35.81 to 58.92  $\text{m}^2/\text{g}$  whereas adding aluminum leads  $\text{NiCo}_2\text{O}_4$  sample decreased specific

Table 2  
Date of surface area of the three samples

Sample	$\text{NiCo}_2\text{O}$	$\text{K-NiCo}_2\text{O}_4$	$\text{Al-NiCo}_2\text{O}_4$
Surface area ( $\text{m}^2/\text{g}$ )	35.81	58.92	27.14

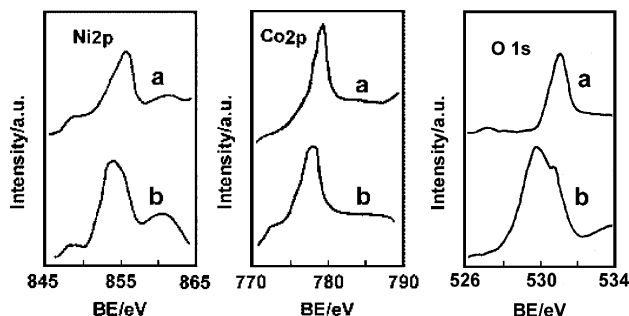


Fig. 4. XPS profiles of Ni2p, Co2p, and O1s spectra for NiCo<sub>2</sub>O<sub>4</sub> and K-NiCo<sub>2</sub>O<sub>4</sub> catalysts: (a) NiCo<sub>2</sub>O<sub>4</sub> (b) K-NiCo<sub>2</sub>O<sub>4</sub>.

areas to 27.14 m<sup>2</sup>/g. It indicated that surface area of the three catalysts also depend on the adding of different additive. Associating with the result of Table 1, it can be found that the sample with the higher surface area is superior in the catalytic activity.

### 3.5. XPS characterization of catalysts

In order to explain the good effect of potassium in NiCo<sub>2</sub>O<sub>4</sub> sample, X-ray photoelectron spectrum were measured. Fig. 4(a) and (b) are the Ni and Co XPS spectra of catalysts with and without potassium. It can be seen that the binding energy of Ni2p<sub>3/2</sub> shifts from 856 to 854 eV and the binding energy of Co2p<sub>3/2</sub> shifts from 779 to 777 eV after adding potassium. Thus, the chemistry shift is reasonable to consider that there is a direct interaction of the internal donor with the potassium species in the NiCo<sub>2</sub>O<sub>4</sub> catalyst.

The surface oxygen species in the catalyst also plays an important role. Fig. 4(c) is the O1s spectrum of NiCo<sub>2</sub>O<sub>4</sub> and K-NiCo<sub>2</sub>O<sub>4</sub> catalysts. Obviously, the peak area of electrophilic oxygen increased after adding potassium. Sokolovskii reported that nucleophilic oxygen species(O<sup>2-</sup>) located in 529 eV was mainly responsible for partial oxidation and while electrophilic oxygen species (O<sup>-</sup>, O<sub>2</sub><sup>-</sup>) located in 532 eV was relation with total oxidation, respectively [11]. Therefore, we propose the electrophilic oxygen species(O<sup>-</sup>, O<sub>2</sub><sup>-</sup>) located in 532 eV in K-NiCo<sub>2</sub>O<sub>4</sub> catalyst was the main active oxygen and performed an important role in total oxidation of VOCs.

### 3.6. Test of electric properties

It was reported that p-type semiconductor has excellent ability of providing oxygen, it can decrease the activation energy and resulted high catalytic activity [12]. Table 3 lists the results of electric activation energy of these three samples in two different moods (air and nitrogen), in which calculated by the data of tested electric conduction band

Table 3

Comparing of the electric activation energy of the three samples in the different mood

Sample	In air	In nitrogen
NiCo <sub>2</sub> O <sub>4</sub>	1.1	1.2
K-NiCo <sub>2</sub> O <sub>4</sub>	0.65	0.88
Al-NiCo <sub>2</sub> O <sub>4</sub>	1.5	2.7

potential. The results indicated that the electric conduction band potential was larger in air than in nitrogen mood, suggesting all the catalysts were p-type semiconductor. In other words, we found that the lower the electric activation energy of the catalysts was, the higher the catalytic activity is. The order of electric activation energy was: Al-NiCo<sub>2</sub>O<sub>4</sub> > NiCo<sub>2</sub>O<sub>4</sub> > K-NiCo<sub>2</sub>O<sub>4</sub>. This finding indicated the high oxidation activity to VOCs in K-NiCo<sub>2</sub>O<sub>4</sub> may be connected with the electron property.

## 4. Conclusions

Potassium as additive considerably improved the activity of NiCo<sub>2</sub>O<sub>4</sub>, in which the excellent function to the total oxidation of VOCs was obtained. The XRD indicated that the spinel phase of NiCo<sub>2</sub>O<sub>4</sub> was observed in all samples and potassium was well dispersed on the NiCo<sub>2</sub>O<sub>4</sub> surface. The small particle size of NiCo<sub>2</sub>O<sub>4</sub> was the active sites for VOCs oxidation. The order of reducibility of the three samples was found to be K-NiCo<sub>2</sub>O<sub>4</sub> > NiCo<sub>2</sub>O<sub>4</sub> > Al-NiCo<sub>2</sub>O<sub>4</sub>, which was consistent with the order of to the catalytic oxidation for VOCs. The surface area of NiCo<sub>2</sub>O<sub>4</sub> catalyst was enhanced by adding of potassium.

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