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Study on spinel - typed catalyst $NiCo_2O_4$ for total oxidation of toluene

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ABSTRACT

Toluene is a component of volatile organic compounds which need to be converted into non-poisonous one. Thus, we study the spinel-typed catalyst as $NiCo_2O_4$ for total oxidation of toluene because the advantage of spinel catalyst is multi- defective. Based on the sol-gel method, the catalysts $NiCo_2O_4$ were successfully prepared with different ratios of Ni/Co. The characteristic properties of catalysts were evaluated by XRD, BET, H_2-TPR and EPR experiments. Amongst these ratios, the catalyst with ratio Ni/Co as 0.5 had the best activity in the total oxidation of toluene, as 100% conversion reached at 250 °C.

Introduction

In the world today, toluene is one hazardous compound which was called VOCs which emitted from many kinds of industrial materials. It can cause environmental and health problems [1].

An effective way to treat toluene is catalytic combustion. Both noble metal (Pt, Pd and Ru) and transition metal (Cu, Co, Mn, Fe, Zr …) have been investigated to catalytically convert toluene. In case of noble metals, generally, high surface area materials are often used to disperse noble metals such as Pd, Pt. In the investigation of Yuan T. Lai et al. [1], the Pt-catalysts were prepared on SBA15 and SiO_2 to study the key factor influencing the catalytic activity in the total oxidation of toluene. Combining the experimental results with Density Functional Theory (DFT) calculation, it was found that the formed Pt nanoparticles on SBA15 was able to strongly dissociate toluene to benzene, hydrocarbon fragments (CH_x) and H_2 at low temperature. Not only Pt but also Pd was applied on toluene oxidation in the report of Jiafu Qu et al. [4], owing to hollow $NiCoO_x$ nanospheres (h-$NiCoO_x$) with numerous surface hydroxyl groups and large surface areas together with oxygen vacancies, 2.0 wt% Pd/h-$NiCoO_x$ sample exhibited the highest activity, achieving approximately 100% toluene conversion at 190°C. However, during the process of toluene oxidation, the formation of coke leading to the deactivation of active sites, combined with the high cost of noble metals cause the researchers to look for new active phases such as the transition metallic oxides. Manganese oxides have received significant interest due to their encouraging catalytic performance for the decomposition of volatile organic compounds. Much work is carried out by doping other transition metals to improve the low temperature reducibility and mobility of oxygen species. For example, the Ni – Mn complex oxide catalyst with 0.5 mol ratio of Ni/Mn showed the activity as T100 at 200°C [2] because of the presence of an effective $NiMnO_3$ phase.

Owing to ultrasonic treatment combined with complexation reaction, the La-Co with the highest level of the Co^{2+}/ Co^{3+} and the O_{lat}/O_{ads} resulted in the value of T98 at 165°C [3]. In the publication of Jiafu Qu [4], hollow $NiCo_2O_4$ is a promising catalyst because of

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multi-defects, high stability during catalytic oxidation. Another type of $NiCo_2O_4$ as double- shell nanocages was also prepared for use in non radical oxidation of phenol [11]. However, these types of $NiCo_2O_4$ were quite difficult to produce, thus our aim is focused on simple but effective preparation of $NiCo_2O_4$ for the total oxidation of toluene.

In Viet Nam, toluene was degraded by ultrasound in the presence of hydro peroxide (H_2O_2). The advantage of this method is low investment cost. However, the concentration of toluene treatment is limited (<100 ppm), resulting in low amounts of toluene decomposition. N.T Ha et al. reported that up to 90% of toluene was decomposed at low concentration (11 ppm), but only 28% of toluene was degraded at a higher concentration (94 ppm) [5]. A photocatalytic method with titanium dioxide as a catalyst can be applied to the treatment of toluene at normal temperature and pressure conditions. N.T. Hue et al showed that toluene treatment efficiency was about 70% in the visible light spectrum by using nitrogen doped TiO_2 (N-TiO_2) covered on alumina (Al_2O_3) [6].

Besides, oxidation is a common method used to treat toluene. Vanadium-containing catalysts are applied to the selective oxidation of toluene. The research by P.T. Huyen et al has published the maximum toluene metabolism is 45% at the reaction temperature of 600°C when using the VaPo catalyst [7]. On the other hand, the Au/Zeoli Y catalyst is also used to study toluene completely oxidation, the conversion efficiency of toluene reaches 90% in the temperature range from 300 to 350 °C [8].

In order to seek the potential catalysts which are able to apply in industry, the toluene concentration is much higher than in the study of N.T Ha et al. Moreover, the utilization of noble metal like in the paper of P. T. Huyen et al. is not in our purpose as well. Thus, in this paper, we have synthesized transition metal oxides such as Ni, Co by the simple but effective method as sol– gel method for the toluene oxidation at low temperature by varying the Ni: Co ratio.

Experimental

Preparation of the catalysts

A series of different mole ratios of Ni/Co catalysts were synthesized via the citric acid assisted sol-gel method. The samples prepared with a molar ratio of Ni: Co = 1:4, 2:4 and 3:4 are NCO-0.25, NCO-0.5, NCO-0.75. Firstly, the desired amount of $Ni(NO_3)_2.6H_2O$ and $Co(NO_3)_2.6H_2O$ were dissolved together in a distilled water until forming a homogeneous solution. At the same time, based on theoretical calculation, the equal molar of citric acid with a total metal precursor was also dissolved in distilled water to make a transparent solution. Secondly, the solution of acid citric was added to a solution of Ni-Co precursors slowly during thorough stirring. After 1 hour, the heat was provided to increase the temperature of solution Ni-Co- acid citric to 60°C and kept for 4 hours. At high temperatures, evaporation occurred resulting formation of gel. The transparent gel was transferred to the oven at 80 °C for 24h. Finally, the as-prepared powder was ground and calcined in air at 550 °C for 5h with the heating rate of 0.5 °C/min.

Characterization of catalyst

The crystalline phase of catalysts was characterized by powder X–ray diffraction (XRD) using a D8 Advance Bruker instrument with Cu Kα radiation, λ = 0,15406 nm. The specific surface area of the samples was determined by nitrogen adsorption and desorption on a Micromeritics Gemini VII 2390 instrument. Before measurement, the samples were degassed at 300°C for 1 hour. The experiment was carried out under the conditions as: adsorption at -196°C (77K), 770 mmHg pressure, carrying gas flow 25 ml/min.

In order to investigate the reducibility, the temperature-programmed reduction (TPR) experiment was measured by the AutoChem II 2920 V5.02 instrument. The pretreatment was started with heating up to 250 °C in He to clean out the sample's surface. Before changing to flow H_2 in Ar, the temperature of the sample was decreased to 50 °C owing to the cooling system. At the same time, the cold traps were prepared by mixing propanol in N_2 liquid to absorb water as byproduct. During the experiment, the Thermal Conductivity Detector was utilized to detect the signal induced from the transformation of catalyst when raising the temperature from 50 – 700°C (10 °C/ min). The total consumed H_2 would determine the reductibility of the catalysts.

The electronic states of element in catalysts would be studied by Electron Paramagnetic Resonance (EPR) spectra recorded with a continuous wave X-band by Bruker EMX- Micro EPR spectrometer with a microwave power of 6.3 mW, modulation frequency 100 kHz and amplitude 0.5 mT at 100K, the magnetic field was full range.

Measurement of catalytic activity

A schematic diagram of the total oxidation of toluene is shown in Fig 1. The N_2 flow of 9.5 ml/min went through toluene tank to bring the toluene vapor to the reactor. Then toluene flow was mixed with an O_2 flow of 20 ml/min to reduce the concentration of saturated toluene vapor. As the inlet concentration of toluene reached a steady state at 9000 ppm, the valve would be switched from bypass line to reaction line, as a result the toluene would go to the fixed bed reactor. In the middle of ¼ inch reactor having 60 cm length, 0.1 gram the catalyst (particle sizes are within the range of 300-450 μm) was loaded. The catalytic measurements was performed from 150 to 400 ^{o}C. The remained reactants and products (O_2, CO_2 and toluene) were analyzed by an online Focus-Thermo Scientific gas chromatography with a thermal conductivity detector (TCD).

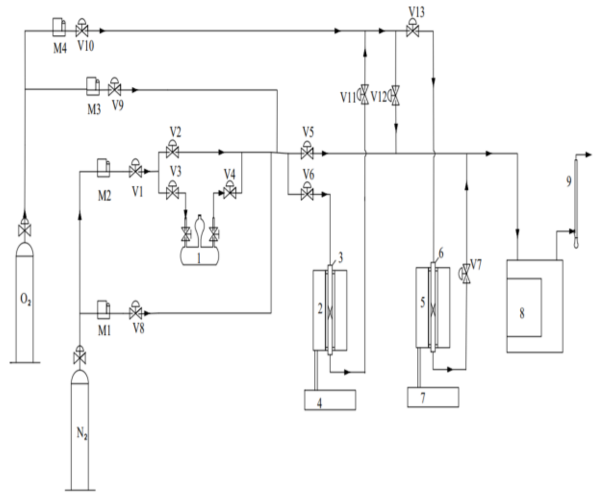

Figure 1: Schematic diagram of toluen Oxidation experiment

1.Toluene tank
2, 5. Heating furnace
3,6. Internal diameter tube
4,7. The temperature controller of the furnace
8. GC with TCD detector
9. Soap bubbler flow meters
V1÷V13. Valve
M_1÷M_3. Mass flow controller

The program of the analysis method of GC are shown in table 1:

Table 1: Specification of GC

Detector	TCD	Oven	
Block temperature (^{o}C)	180	Oven run time (min)	8.5
Trans temperature (^{o}C)	180	Initial Temperature (^{o}C)	60
The flow rate of N_2 (ml/min)	35	Initial Time (min)	1
The flow rate of He (ml/min)	20	Ramp (^{o}C/min)	60
		Final temperature ((^{o}C))	210
		Final Time (min)	5

Based on the concentration of toluene at different temperatures, the conversion of toluene is determined as:

$$\text{Conversion of toluene (\%)} = \left(1 - \frac{C_{toluene,out}}{C_{toluene,bypass}}\right) \times 100$$

Where $C_{toluene,\ bypass}$ (ppm), $C_{toluene,\ out}$ (ppm) are the concentrations of toluene in the bypass and outlet gas, respectively.

Results and discussion

Catalytic activity

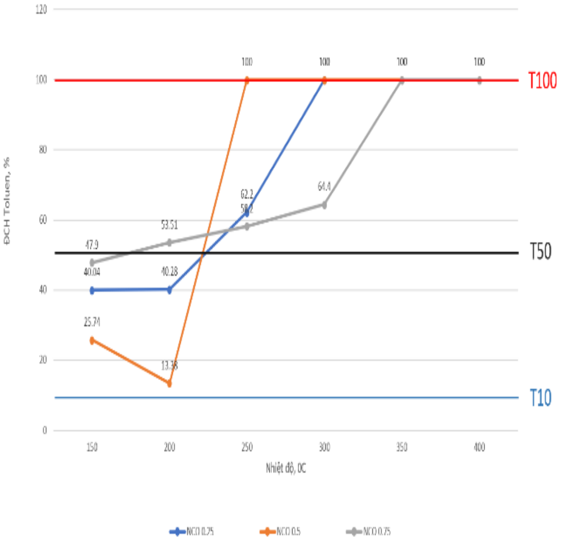

Figure 2: Toluene conversion on $NiCo_2O_4$ samples with different ratios

The catalytic performances of all catalysts were illustrated on figure 2. It was divided into three parts as T10, T50 and T100 to evaluate more accurately the activity of each catalyst. The experiments were set up from 150 ^{0}C to 400 ^{0}C and all catalyst reached higher than 10% conversion at 150 ^{0}C, the catalysts NCO – 0.5 was the one with the lowest conversion of 25%, while the other catalysts had the better conversion as 40%.

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In the second part of T50, the catalytic activities were approximately the same with all the catalysts. At 225 ^{0}C, the catalyst NCO – 0.75 had a little higher conversion than the others, at 53%. While both catalysts with Ni/Co as 0.25 and 0.5 had the same toluene conversion as 50%. Thus, increasing reaction temperature definitely reduced the differences in the catalytic capacity of catalysts with various ratio Ni/Co even though the catalyst NCO- 0.75 was still better than the remainings.

The big differences were obviously seen at the T100 part. Only the catalyst NCO – 0.5 was able to convert toluene completely at 250^{0}C. While the others must go up to higher temperature to get 100% conversion, for instance, the T100 of NCO – 0.25, NCO – 0.75 were at 300^{0}C, 350^{0}C, respectively. At high reaction temperature, the top catalyst as NCO- 0.75 was replaced by NCO – 0.5 may be caused by the compositional change of catalysts.

In conclusion, in the low temperature range below 200^{0}C, the catalyst NCO-0.25, and NCO- 0,75 had a good performance. However, in the high temperature range from 250^{0}C, the NCO – 0.5 exhibited better activity than the others. And catalyst NCO – 0.5 was the best amongst the three samples because it can totally oxidize toluene at the lowest temperature.

Catalyst characterization

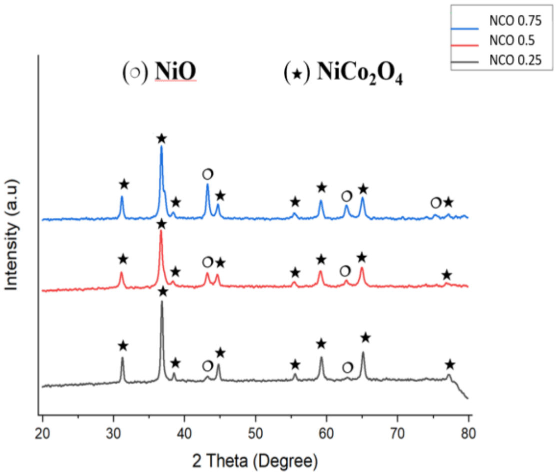

Figure 3: XRD patterns of different catalysts

The crystalline phases of catalysts were detected by XRD, and the XRD patterns were shown on figure 3. The characteristic peaks of spinel $NiCo_2O_4$ was noticed at 2-theta of 18^{o}, 31^{o}, 36^{o}, 38^{o}, 44^{o}, 55^{o}, 59^{o}, 64^{o} and 77^{o} assigned to (111), (220), (311), (222), (400), (422), (511) (440) and (533) planes of $NiCo_2O_4$, respectively [9]. The less intensity of NCO – 0.5's peaks than those of the remainings indicating decreased crystallinity of $NiCo_2O_4$ phase or smaller $NiCo_2O_4$ crystallite [10]. Besides, the appearance of NiO crystallite was also recognized due to the appearance of typical peaks of 2-theta of 37^{o}, 43.4^{o}, 63.4^{o} corresponding to (111) (200) and (220) planes, respectively [9]. The larger amount of Ni was, the higher these typical peaks' intensities were, proving more NiO distributed on the surface of catalysts. Thus, when increasing the ratio of Ni/Co, the phase $NiCo_2O_4$ maybe was affected by the competition of higher Ni content, particularly the larger coverage of NiO on the surface, lowering the crystallite size. This phenomenon can influence catalytic activity as well. As the ratio Ni/Co raised from 0.25 to 0.5, the catalytic activity went up even though the intensity of $NiCo_2O_4$ decreased, perhaps, the reason was the smaller $NiCo_2O_4$ resulting better activity, and the number of active sites still dominated on the surface of the catalyst. However, when the Ni/Co ratio increased from 0.5 to 0.75, the coverage of Ni was so large that it caused the decrease of catalytic activity.

Table 2: The total H_2 consumption of the samples

Sample	Peak number	Temperature at Maximum (^{0}C)	Quantity (mmol/g)
NCO 0.25	1	252.2	0.40
	2	325.9	11.88
NCO 0.5	1	236.3	1.58
	2	323.1	13.68
NCO 0.75	1	240.0	0.95
	2	303.4	13.13

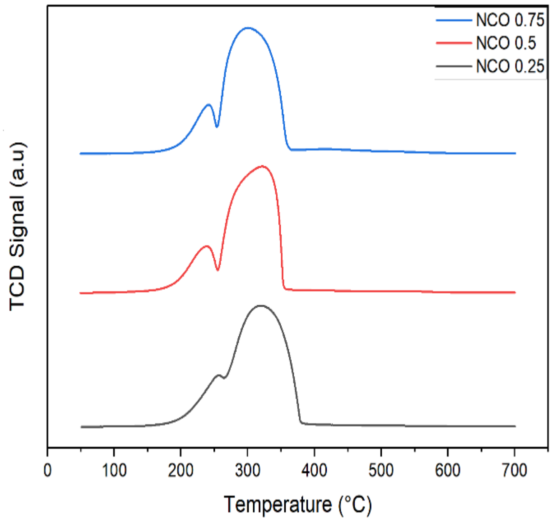

Figure 4: TPR- H_2 profile of $NiCo_2O_4$ at different ratio

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In order to understand the catalyst nature, it is necessary to investigate the redox properties. In this paper, the reducibility of $NiCo_2O_4$ catalysts was studied using H_2- TPR experiments. As shown on table 2, there were two desorption peaks at 236°C -240 °C, and the other at 296 °C – 325.9 °C. From observing in the paper of Jianrui Niu [9], the lower desorption peak was correlated with the change of Co^{3+} to Co^{2+}, and Ni^{3+} to Ni^{2+}. The higher desorption peak was associated with the reduction of Co^{2+} to Co^0 and Ni^{2+} to Ni^0. Amongst three catalysts, at the lower region, the NCO – 0.5 had the sooner desorption than the others, at 230 ^{0}C, which proved that catalyst NCO– 0.5 had better reducibility than the others. This was similar to recorded phenomena in the work of Jianrui Niu. Because there was a reduction in the redox potential of Co species, which means that better redox property was achieved. Due to better redox property, the lattice oxygen became more labile and more vacancies were generated, so the better redox property and higher intensity of desorption of lattice oxygen resulted in promoting catalytic reaction rate. This may be explained for the better catalytic activity of NCO – 05 than other ratios.

The total H_2 consumption of catalysts was listed on table 2. In both low and high temperature regions, the quantities of consumed H_2 of catalyst NCO – 0.5 was greater than the others. This also evidenced that the reducible ability of NCO – 0.5 was the main factor to elucidate the significant catalytic activity in the total oxidation of toluene.

The BET surface area of catalysts was displayed on table 3. All the catalysts were quite as same as each other with about 14.5 m^2/g. That means the BET surface area was not main factor to determine the catalytic performance in this paper. Nevertheless, the change in BET surface area may be related to the composition of catalysts. As discussed about XRD results, the particle size of $NiCo_2O_4$ was smaller, and the coverage of NiO enlarged when ratio Ni/Co going up.

Table 3: BET surface areas of the samples

Sample	Ni^{2+}/ Co^{2+} ratio	BET (m^2/g)
NCO 0.25	0.25	14.10
NCO 0.5	0.50	15.97
NCO 0.75	0.75	13.90

Therefore, catalyst NCO – 0.5 had a higher BET surface area than that of NCO – 0.25 because of the increase of smaller particle $NiCo_2O_4$. However, due to the broad coverage of NiO on surface, the BET area of NCO-0.75 was the lowest amongst the three catalysts.

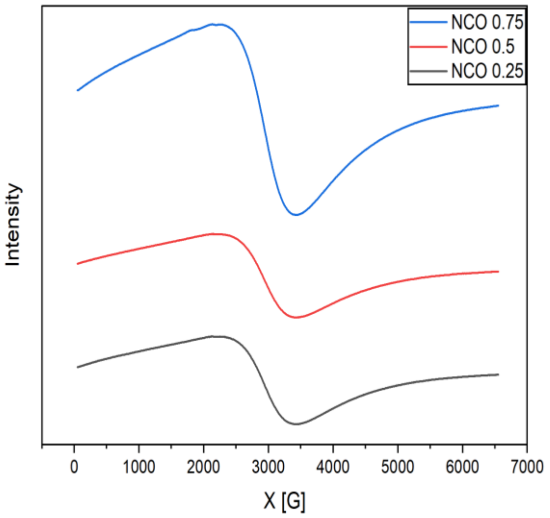

Figure 5: EPR spectra of $NiCo_2O_4$ at different ratio

To examine the surface electronic states, low-temperature electron paramagnetic resonance (EPR) was conducted. As displayed in figure 5, the signal peak at a g value of 2.27 attributed to Co^{2+}, according to the investigation of Yinxiang Zeng [10], because the Co^{3+} species reduced to Co^{2+} thus, the more Co^{2+} species, the greater oxygen vacancies, and the weaker bond of Metal - Oxygen. The strongest signal peak was belonged to NCO -0.5, meaning this catalyst had the highest number of Co^{2+} species, and the largest oxygen vacancies as well. This result was consistent with the redox property as discussed H_2-TPR results.

Among three catalysts with various ratios of Ni/Co, the NCO-0.5 had the best activity in the total oxidation of toluene because it can totally oxidize toluene at the lowest temperature at 250^{0}C. In the lower reaction temperature, the NCO – 0.5 was not the one having the greatest conversion of toluene, but the high temperature maybe was the important factor to accelerate the catalytic activity of NCO – 0.5. All of the catalysts had $NiCo_2O_4$ crystallite and NiO phases. However, when the ratio Ni/Co increased from 0.25 to 0.75, the $NiCo_2O_4$ crystallite became smaller or the crystallinity decreases, and more NiO distributed on the surface. This insight was supported not only by XRD patterns but also the change in BET surface area. Generally, the smaller particles, possibly the higher specific surface area was. As verified in XRD, the lowest intensity of NCO – 0.75 was probably indicated for the smallest $NiCo_2O_4$ particles but BET surface area of NCO – 0.75 was not as high as other catalysts. These results only can be caused by the growth of NiO led overlapping small $NiCo_2O_4$ particles. It is well-known that $NiCo_2O_4$ is the active phase for the total oxidation of toluene in this case because of its multi-defects, hence, the tiny particles with proper number would benefit catalytic efficiency, and that is the definite reason explaining the significant capacity of NCO-0.5. Other results in H_2-TPR, EPR experiments were confirmed the better properties of NCO-0.5 compared with NCO – 0.25 and NCO -0.75. The NCO – 0.5 had lowest reduction peak at 236 ^{0}C indicating the maximum oxygen vacancy, which also noticed from EPR spectra.

Conclusions

In conclusion, the spinel-typed catalysts with three molar ratios of Ni/Co as 0.25, 0.5 and 0.75 were prepared successfully by sol-gel method. The catalysts NCO- 0.5 had best activity in the total oxidation of toluene as T100 at 250 ^{0}C. This is also consistent with the H_2-TPR experiments showed that it had better redox property than the others. In addition, the same observation was noticed in the EPR spectrum. However, when the ratio of Ni/Co was increased to 0.75, in the XRD patterns, the highest intensity of typical peak NiO in catalyst NCO- 0.75 illustrated the largest distribution of NiO on the surface catalyst, perhaps covered the active Co site leading to lower catalytic performance.

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