

The Study on Characterization, Adsorption and Oxidation Properties of M-Xylene over AC-5%Co Material

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ARTICLE INFO

Article history:

Received: 9 March 2016;

Received in revised form:
14 April 2016;

Accepted: 20 April 2016;

Keywords

Activated carbon,
M-xylene,
VOCs,
Adsorption.

ABSTRACT

AC-5%Co has been synthesized successfully by impregnation method using Tra Bac activated carbon (AC) and cobalt chloride as precursors. The characterization of prepared materials showed that Co species which exists in oxide form (denoted as CoO_x) distribute on surface of AC with the size ranging from 20 to 25 nm. The CoO_x almost does not affect to the m-xylene adsorption of AC and m-xylene adsorption processes occurred mainly at micropores with two types of AC adsorption sites. The study on the catalytic activity revealed that the oxidation of m-xylene by oxygen in the air occurred mainly at cobalt oxide sites with the conversion degree ranging from 23.2 to 51.8% at the temperature range of 180-250°C with the WHSV of 1941.75 hour^{-1} and relatively low activation energy (21.16 $\text{kJ mol}^{-1} \approx 5 \text{ kcal mol}^{-1}$).

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Introduction

Air pollution caused mainly by volatile organic compounds (VOCs) [1] which is ubiquity in the environment and may produce risk to human health. Therefore, VOCs have been considered intensively in term of environmental treatment. The use of porous materials, such as activated carbon, for VOCs adsorption has been suggested as a new method to control the emission of VOCs [2]. However, it has been revealed that using activated carbon as an adsorbent faces with several disadvantages, such as fire risk at high temperature, hygroscopicity and some problems related to regeneration [3]. Hence, there is still a need to improve technology, which actually oxidizes the pollutants at low temperature, rather than removing them for recycling elsewhere in the other atmosphere [2]. The advantage of the low oxidation temperature is reduced fuel consumption particularly for large volumes of dilute VOC polluted air [1]. Catalytic oxidation can destroy VOCs in air effectively to meet requirements of environmental regulation. In order to reduce oxidation temperature, catalytic oxidation using activated carbon as support is a widely used method to decrease VOCs emission, especially at low concentration [3]. Pt, Pd and transition metal oxides have been used as catalyst on the activated carbon support [4, 5]. However, Pt and Pd are rare and expensive metals. In addition, though they have high catalytic activity in the combustion reaction of VOCs at low temperature, they are easy to be poisoned by sulfur containing compounds and accumulated at high temperature.

The transition metal oxides are cheap compared to Pt and Pd metals. Even though they have lower catalytic activity in comparison to rare metals, they are stable at high temperature and rarely poisoned.

In this study, we report the catalytic activity of the supported CoO_x activated carbon prepared by impregnation method in the oxidation reaction of m-xylene. The morphology and surface characteristics of materials are also reported.

Experiment Part

Chemicals: Activated carbon with a size of 0.65 – 1.00 nm produced from coconut husk was purchased at Tra Bac province in Vietnam. CoCl_2 and m-xylene were purchased from China chemical company.

Preparation of materials: Activated carbon (AC) was washed with a plenty of distilled water and then dried at 110°C in 3 hours to remove all adsorbed water. The obtained activated carbon (AC) was impregnated several times with 0.20 M cobalt chloride solution to produce activated carbon samples with 5.0 wt.% of Co. The obtained samples were dried at 110°C in 4 hours and at 250°C in 3 hours, then cooled down and kept in vacuum.

Characterization: Microstructure of samples was taken by transmission electron microscope at 200 kV using TECNHL G2 F20, TEM instrument. The structural characterization of the AC and AC-5%Co was based on the N_2 adsorption isotherms at 77K using a Micromeritics model TriStar 3000 analyzer. The samples were degassed in nitrogen stream for 24h at 573K to remove moisture or adsorbed contaminants that may present on surface of samples. The specific surface area (S_{BET}) was calculated by applying the BET equation to the adsorption data [6]. The microporous surface area (S_{micro}) and external surface area (S_{ex}), as well as the micropore volume (V_{micro}) were evaluated by the t-plot method [7]. The total pore volume (V_{tot}) was evaluated by summation of microporous and mesoporous volumes. The diameter of micropore (D_{micro}) can be calculated from volume and area of micropore. Temperature programmed desorption of oxygen (TPD- O_2) was performed by means of an automated catalyst characterization system (AutoChem II RS232 model, Micromeritics, UAS). The adsorption-oxidation of m-xylene on catalytic materials was carried out in a quartz tube of a micro-flow system as shown in Figure 1.

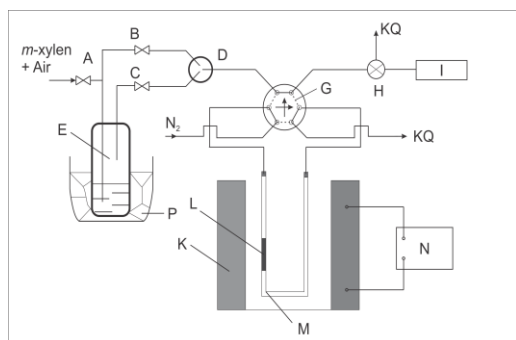


Figure 1. Microflow system used in this study. A, B, C: flow controller, D: mixed compartment, E: aeration section, G: 6-way valve, H: 3-way valve, I: gas chromatography, K: furnace, L: catalyst, M: quartz tube, N: temperature controller, P: isotherm bath.

Results and Discussion

TEM image: shown in figure 2 is TEM image of AC-5%Co sample. It is clear that Co species in form of CoO_x distribute homogeneously on the AC surface (black dots on TEM image) with the size ranging from 20 to 25 nm.

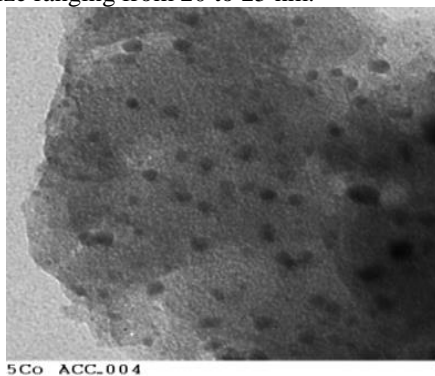


Figure 2. TEM image of AC-5%Co sample.

Adsorption isotherm of N_2 : structural information, such as S_{BET} , S_{mi} , V_{tot} , V_{micro} , and D_{micro} , can be obtained from adsorption isotherm measurements. Table 1 lists results related to structural properties of materials, obtained from adsorption isotherm measurement.

As can be seen from Table 1, the micropore diameter (D_{micro}) is relatively unchanged (1.87 nm) in two samples AC and AC5%Co. The AC exhibits a developed BET surface area and a high pore volume, mostly contributed by micropore. The BET surface area and the microporous surface area are $1090 \text{ m}^2 \text{ g}^{-1}$ and $1038 \text{ m}^2 \text{ g}^{-1}$ for AC sample, $836 \text{ m}^2 \text{ g}^{-1}$ and $805 \text{ m}^2 \text{ g}^{-1}$ for AC-5%Co, respectively. The lower specific surface area of AC-5%Co compared to AC sample may be explained because the CoO_x species with the size from 20-25 nm can only distribute on AC surface and therefore cover a small portion of external surface area (S_{ex}), reduce slightly volume of micropore (V_{micro}) and small micropores (S_{micro}). This result is in good agreement with result obtained from TEM image.

Table 1. The specific surface area ($S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$), microporous surface area ($S_{\text{micro}}/\text{m}^2 \text{ g}^{-1}$), external surface area ($S_{\text{ex}}/\text{m}^2 \text{ g}^{-1}$), micropore volume ($V_{\text{micro}}/\text{cm}^3 \text{ g}^{-1}$), total pore volume ($V_{\text{tot}}/\text{cm}^3 \text{ g}^{-1}$) and diameter of micropore ($D_{\text{micro}}/\text{nm}$) of AC and AC5%Co samples

Sample	S_{ex}	S_{micro}	S_{BET}	V_{tot}	V_{micro}	D_{micro}
AC	52	1038	1090	0.510	0.4848	1.87
AC-5%Co	31	805	836	0.4184	0.3768	1.87

TPD- O_2 measurement: Figure 3 shows TPD- O_2 profiles of AC and AC-5%Co samples in the temperature range from

120°C to 300°C. As shown in figure 2, there is no peak, which can be observed in the studied range of temperature for AC sample. This means that AC is not able to adsorb oxygen gas at the temperature range from 120-300°C. Whilst, AC-5%Co exhibits a peak at about 198°C. The appearance of the peak proves that AC-5%Co is able to adsorb oxygen gas in the form of $\text{O}_{2,\text{ad}}$ in the temperature range of 150-250°C and can favor the reaction [8, 9, 10]:

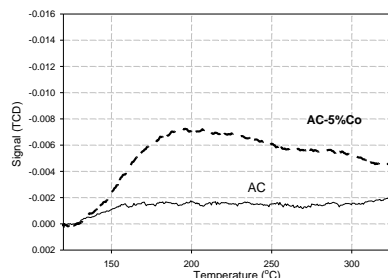
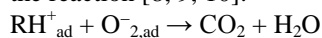


Figure 3. TPD- O_2 profiles of AC and AC5%Co.

Adsorption study: dynamic m-xylene adsorption of AC and AC-5%Co was performed with a system shown in figure 1, where nitrogen was used as carrier gas with the m-xylene concentration of 2240 ppm, catalyst mass of 0.62 g and flow rate of 2.0 L/hour.

Figure 4 shows the breakthrough curves of m-xylene adsorption of AC and AC-5%Co at different temperatures. From these curves, adsorption capacities AC and AC-5%Co at different temperatures can be determined using a method described by P. Le Cloirec[11]. The obtained capacities are listed in table 2.

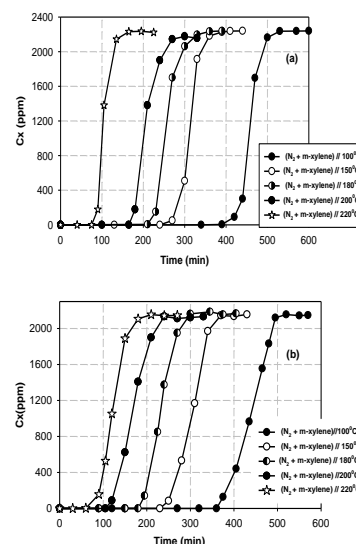


Figure 4. Breakthrough curves of dynamic m-xylene adsorption of AC (a) and AC-5%Co (b) at different temperatures.

As a method described in reference [12], the adsorption heat of adsorption sites can be determined using an equation expressed as following:

$$q = q_0 \times \exp(-\Delta H H / RT) \quad (1)$$

Where: q (mg g^{-1}) is adsorption capacity of catalyst materials, ΔH (kJ mol^{-1}) is adsorption heat at temperature T , R is universal gas constant and q_0 is a constant proportional to number of adsorption sites.

Table 2. Adsorption capacity (q) of AC and AC-5%Co at different temperatures (T).

T/ °C	q/ mmol g ⁻¹	
	AC	AC-5%Co
100	2.94	2.11
115	2.56	1.94
135	2.23	1.78
150	1.91	1.51
165	1.48	1.37
180	1.31	1.23
200	0.93	0.87
220	0.71	0.69

The equation (1) can be also expressed in the a linear form as follow:

$$\ln q = -\frac{\Delta H}{RT} + \ln q_0 \quad (2)$$

By fitting data listed in table 2 to equation (2), the linear relationship between $\ln q$ and $1/T$ can be depicted as shown in figure 5.

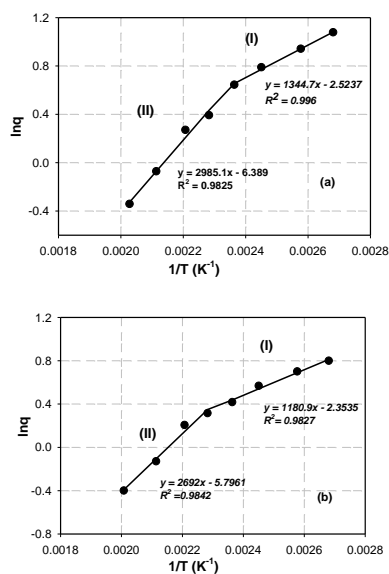


Figure 5. Linear relationship between $\ln q$ and $1/T$ and AC (a) and AC-5%Co (b).

As shown in figure 5, both curves contain two linear parts, (I) and (II). The first part is corresponding to the temperature range from 100 to 150°C and the second part is referred to the temperature range from 165 to 220°C. From the slopes of linear curves, the adsorption heat (ΔH_{ad}) of samples can be calculated. The obtained results are listed in table 3.

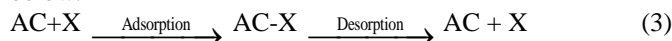
Table 3. The adsorption heat at part I (ΔH_{ad}^I /kJ mol⁻¹) and part II (ΔH_{ad}^{II}), and number of adsorption sites at part I (q_{o}^I) and part II (q_{o}^{II}).

Sample	AC	AC-5%Co
ΔH_{ad}^I	-11.18	-10.00
ΔH_{ad}^{II}	-24.82	22.00
$q_{o}^I/10^{18}$	48.16	57.10
q_{o}^{II}	1.02	2.10

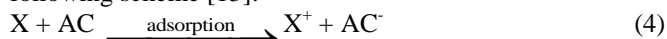
As the obtained results listed in table 3, it is concluded that both AC and AC-5%Co samples possess two types of adsorption sites, (i) the site of physical adsorption corresponding to low value of adsorption heat (-11.2 kJ mol⁻¹ for AC and 10.00 kJ mol⁻¹ for AC-5%Co) and (ii) the site of activated adsorption corresponding to higher value of

adsorption heat (- 24.82 kJ mol⁻¹ for AC and 22.00 kJ mol⁻¹ for AC-5%Co).

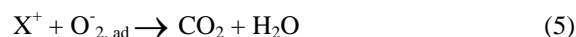
For site (i), the adsorption of m-xylene obeys the mechanism of physical adsorption which can be represented as below:



In the case of site (ii), the adsorption of m-xylene takes place with the activated mechanism, where electrons are transferred from organic compound to adsorbent according to the following scheme [13]:



If there are $O_{2, ad}^-$ species, there may have another reaction as follow:



The presence of some Co sites (in form of CoO_x) on Tra Bac AC does not affect to property as well as the number of adsorption sites of AC in the m-xylene adsorption. The explanation for this is that the adsorption of m-xylene on AC or AC-5%Co occurs mainly in micropores at two site types as mentioned above.

The catalytic properties of AC-5%Co: The m-xylene oxidation of AC and AC-5%Co was performed with a system shown in figure 1, where the air was used as carrier gas with the m-xylene concentration of 2240 ppm, catalyst mass of 0.62 g and flow rate of 2.0 L/hour. Reactor is a quartz tube with a diameter of 10 nm. The oxidation was carried out at 180°C. The observed data are illustrated by a breakthrough curves shown in figure 6. In order to investigate the role of oxygen in the oxidation of m-xylene, the similar experiment was carried out using nitrogen as the carrier gas.

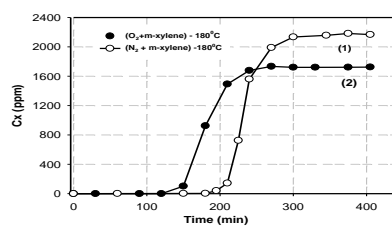


Figure 6. Breakthrough curves of oxidation of m-xylene on the AC-5%Co catalyst with carrier gas of nitrogen (1) and oxygen (2).

As shown in figure 7, m-xylene was almost not oxidized when nitrogen is used as a carrier (in output flow is approximately equal to 2240 ppm, the concentration of m-xylene in input flow). In contrast, m-xylene was oxidized when the air is used as a carrier. The concentration of m-xylene in the output flow reduces 23% in comparison to the concentration of m-xylene in input flow. The decrease of concentration of m-xylene means that 23% of it was oxidized. In the oxidation of m-xylene, the volume hourly space velocity (VHSV) can be calculated according to expression (6) reported by Y.M. Lin [14], using data obtained from experiment presented in figure 7.

$$VHSV = \frac{\text{Flow rate of reactant gas}}{\text{Volume of catalyst}} \quad (6)$$

The VHSV value obtained from calculation in our experiments is of 1941.75 hour⁻¹. Thus, contact time, τ , between adsorbent and adsorbate before the oxidation reaction occurring is equal to $VHSV^{-1}$ (about 1.85 second).

From the experimental data, it can conclude that catalytic sites for oxidation reaction between m-xylene and oxygen (in the air) are cobalt particles (in form of cobalt oxide) distributed on Tra Bac AC.

Activation energy: In order to determine activation energy of oxidation reaction of m-xylene, the reaction was carried out at different temperatures. The corresponding conversion degree (percentage of m-xylene, which was oxidized after reaction) and rate of reaction can be also determined and are listed in table 4. The rate (r) can be calculated using the following expression:

$$r = \frac{r_f}{22.4} \times \frac{273}{T} \times \frac{P_x}{P_{air}} \times \frac{\alpha}{m} \text{ mmole g}^{-1} \text{ hour}^{-1} \quad (7)$$

Where: r , r_f and T are the rate of reaction, flow rate of input mixture gas and absolute temperature, respectively. P_{air} , P_x and m are pressure of the air, saturated pressure of m-xylene at 273 K ($P_x = 1.69$ mmHg, $\hat{\sigma}$ 273 K) and mass of catalyst.

Table 4. Conversion degree (α %) and rate (r /mmol/g h) of oxidation reaction of m-xylene on AC-5%Co at different temperatures ($T^\circ\text{C}$)

Temperature	α	r
180	23.20	4.42
200	28.69	5.24
220	40.33	7.09
250	51.80	8.64

The activation energy, E_a , can be calculated from reaction rate at different temperatures using Arrhenius equation in the form of natural logarithm as follow:

$$\ln r = -\frac{E_a}{R} \times \frac{1}{T} + \ln A \quad (8)$$

Where A is pre-exponential factor. By plotting “ $\ln r$ versus $1/T$ ” line, E_a can be calculated from the slope of “ $\ln r$ versus $1/T$ ” line (see figure 7) and has value of $21.16 \text{ kJ mol}^{-1}$ ($\approx 5 \text{ kcal mol}^{-1}$).

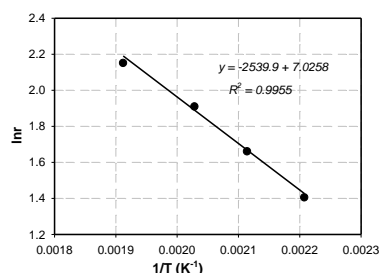


Figure 7. The “ $\ln r$ versus $1/T$ ” curve of the oxidation reaction on AC-5%Co.

Conclusion

Cobalt in form of cobalt oxide (CoO_x) has been successfully introduced onto Tra Bac activated carbon with the size ranging from 20 to 25 nm and accounting for 5% of material mass. The presence of cobalt oxide does not affect the adsorption of m-xylene on AC because the adsorption occurs mainly at two types of adsorption types of micropores.

At 180°C - 250°C , conversion degree of m-xylene is 23.2 – 51.8% with the WHSV of $1941.75 \text{ hour}^{-1}$ and relatively low activation energy ($21.16 \text{ kJ mol}^{-1} \approx 5 \text{ kcal mol}^{-1}$).

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