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STUDY ON THE ADSORBENT - CATALYTIC PROPERTIES OF BI-FUNCTIONAL MATERIAL ON THE BASIS OF Co_3O_4 / ACTIVATED CARBON IN THE META-XYLENE TREATMENT

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INTRODUCTION

Pollution by volatile organic compounds (VOCs) has a great influence on the atmospheric environment, on human health and aquatic life.

Catalytic oxidation has been considered as one of the most advanced techniques to thoroughly convert VOCs to CO_2 and H_2O. The noble metal catalysts having high catalytic activity in the oxidation reaction of VOCs in air are Pt and Pd Due to their instability at high temperature and easily poisoned by the impurities containing sulfur, chlorine and their high cost, the application of precious metal catalysts in environmental treatment is notreally economically feasible. Transition metal oxide catalysts which possess a number of advantages such as high chemical and thermal stability, less poisoned by the impurities containing sulfur, chlorine, low cost and easy fabrication have attracted a lot of attention in scientific community.

At low temperature (< 200°C), noble metal catalysts (Pt, Pd, Ru,…) have a much higher catalytic activity than transition metal oxide ones. Therefore, to achieve the economic viability with the application of transition metal oxide catalysts in VOCs effective treatment at low temperature, scientists are looking for technical solutions to impact on the catalyst preparation phase or on operating techniques.

From information on the adsorption method and the oxidation method can be found: (i) adsorption method is not suitable for handling high concentrations of VOCs; regeneration of materials which can be added the next processing stage are used to convert VOCs into non-toxic substances, (ii) oxidation method is suitable for handling high concentrations of VOCs but not suitable for handling VOCs at low concentrations.

To overcome these drawbacks and maximize the advantages of the two methods above, recently the idea of "integrating" the two methods into a new technique - technique adsorption / catalyst has been proposed by the scientist. With this technique, VOCs can be handled efficiently even at low temperatures (< 200°C).

On the basis of those commentaries mentioned, the idea thesis ***"Study on the adsorbent - catalytic properties of bi-functional material on the basis of Co_3O_4 / activated carbon in the meta-xylene treatment"*** has been formed.

Research objectives: Research to establish the most appropriate conditions for successful implementation of adsorption/catalytic technique on the basis of using a bi-functional adsorption/catalytic material. Bi-functional materials are selected cobalt oxide impregnated on Tra Bac activated carbon.

The content of this thesis:

1. Synthesis of cobalt oxide-containing material on activated carbon with three different Co contents of 3.0%, 5.0% and 9.0% in terms of volume (Co/AC). This sample is characterized by chemo-physical methods to choose the most suitable cobalt content with the aim of the thesis research. The selection of activated carbon as a carrier is based on the concept of the material which has the ability to integrate both adsorption properties and catalytic.

2. Research, evaluate the role of activated carbon and cobalt oxide in the *meta*-xylene oxidation. Study on *meta*-xylene adsorption of activated carbon and the effects

of cobalt oxide on the ability and capacity of *meta*-xylene adsorption of activated carbon.

3. Study on the *meta*-xylene treatment by Co/AC material using continuous flow oxidation (one step) and adsorption/catalytic technique (two steps).

4. Kinetic study and propose mechanisms for oxidation of *meta*-xylene with air over Co/AC materials in two techniques used.

Originalities of this thesis:

1. Based on Tra Bac granular activated carbon (AC) (size of 0.65 - 1.00 mm) and cobalt chloride salt, we have prepared successfully the bi-functional adsorption/catalytic material (Co/AC) as a catalyst to effectively oxidize *meta*-xylene using adsorption/catalytic technique.

2. Proposed an adsorption/catalytic technique - a two-stage tehnique: adsorption and then catalytic oxidation. Using Co/AC materials, by means of building breakthrought curve has found the most appropriate conditions to treat successfully *meta*-xylene with performance of 96 - 99% at low temperatures 180 - 200°C, which is adsorption time t_x = 100 minutes, 150 minutes of catalytic oxidation, VHSV = 1936.11 h^{-1} and 0,62g material.

3. Conducted the kinetics of oxidation *meta*-xylene over bi- functional Co/AC material and proposed the mechanisms of *meta*-xylene oxidation in oxygen as follows: *meta*-xylene was adsorbed in priority on adsorption sites of AC which produces adsorption complex $(AC\text{-}X)_{ad}$ while oxygen (air) is adsorbed in priority on Co_3O_4 sites producing $(Co_3O_4\text{-}O_2)_{ad}$ complex. These two complexes interact with each other to generate CO_2 and H_2O products and simultaneously liberate adsorption sites.

Chapter 1. OVERVIEW

This part reviews about origin and influence of VOCs, the VOCs treatment methods, the results in studying on *meta*-xylene treatment in Viet Nam, knowledge about process of adsorption, flow adsorption.

Obtained results from references show that intergating adsortion and catalytic oxidation is effective treatment of VOCs. Moreover, cobalt being transition metal with two oxidation states (Co^{2+}, Co^{3+}) has high catalytic activity for VOCs oxidation. Activated carbon is good adsortion material and is also a suitable catlytic carrier.

Chapter 2. EXPERIMENT PART

2.1. Chemicals: Activated carbon with a size of 0.65 - 1.00 nm produced from coconut hut was purchased at Tra Bac province in Vietnam. $CoCl_2$ salt and *meta*-xylene solution were purchased from China chemical companies.

2.2. 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 3.0 wt%, 5.0 wt.% and 9.0 wt% of Co. The obtained samples were dried at 110°C over night and at 250°C in 3 - 4 hours. These samples were donated by 3Co/AC, 5Co/AC and 9Co/AC.

2.3. Characterization:

2.3.1. Transmission electron microscope (TEM): Microstructure of samples was taken by at 200 kV using TECNHL G2 F20, TEM instrument.

2.3.2. N_2 adsorption isotherms: The structural characterization of the AC and Co/ACwas based on the N_2 adsorption isotherms at 77K using a Micromeritics model TriStar 3000 analyzer.

2.3.3. Temperature programmed reduction of hydrogen (TPR-H_2): was taken by Autochem II 2920 intrument with using H_2/Ar mixture (H_2 = 10%).

2.3.4. X-ray photonelectron spectroscopy (XPS): was performed by ESCA LAB – MkII instrument in condition such as 10^{-10} mbar and Al Kα radiation (hν = 1486,6 eV).

2.3.5. Temperature programmed desorption of oxygen (TPD-O_2): was performed by means of an automated catalyst characterization system (AutoChem II RS232 model, Micromeritics, UAS).

2.4. Conditions

The adsorption-oxidation of *meta*-xylene on catalytic materials was carried out in a quartz tube of a micro-flow system.

Conditions: 0.62 g mass of catalyst, flow rate of input mixture gas W = 2.0 L/hour, pressure of *meta*-xylene at 273 K (P_X = 1.69 mmHg, at 273 K or concentration of *meta*-xylene C_o = 2223 ppm), volume hourly space velocity VHSV = 1936.11 h^{-1} and retention time F = 1.85 sec.

Chapter 3. RESULTS AND DISCUSSION

3.1. *Characterization*

3.1.1. TEM image

Shown in figure 3.1 are TEM images of 3Co/AC, 5Co/AC and 9Co/AC sample.

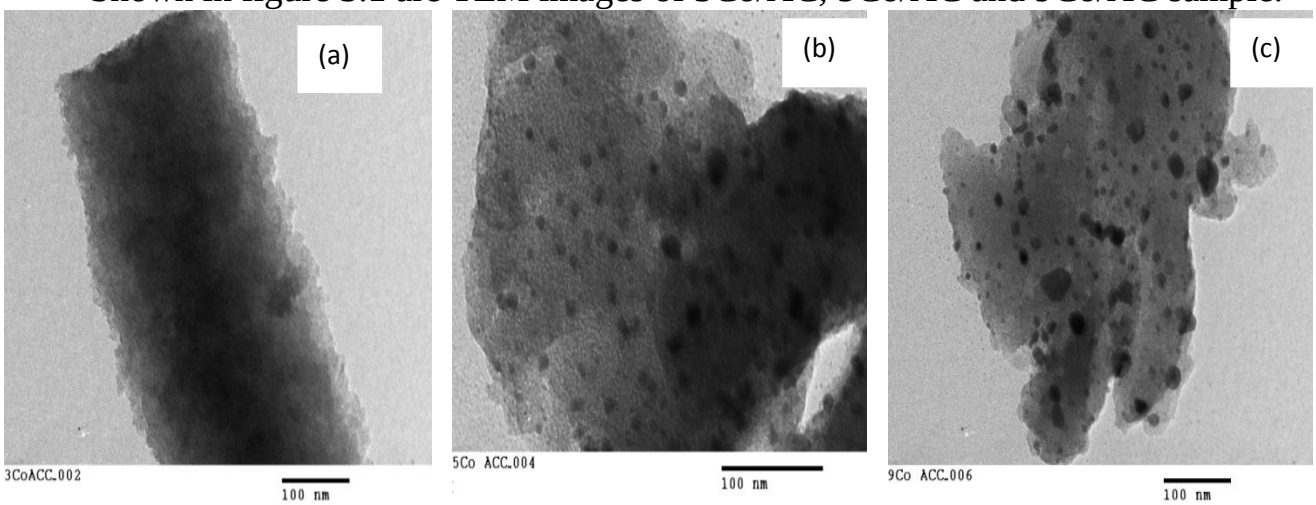
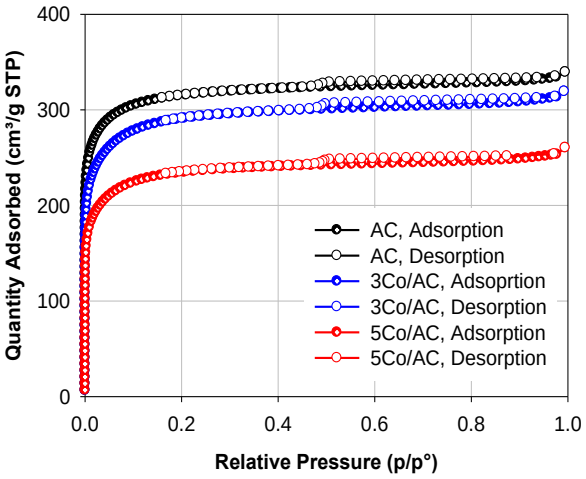


figure 3.1. *TEM* images *of (a)- 3Co/AC, (b) -5Co/AC and (c)-9 Co/AC.*

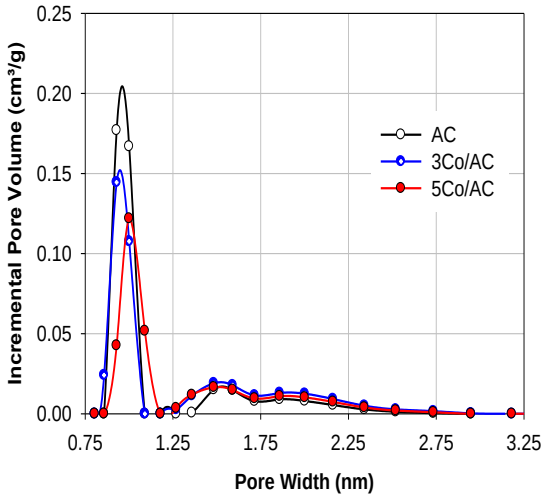
With 3Co/AC material, it is almost difficult to observe "black dots" characterizing CoO_x on AC surface. May be due to low content (3,0%Co), particles containing Co dispersed higly and particle size is very small (< 10 nm). When Co loading increases with 5,0%, its size ranges from 20 to 25 nm and it distributes homogeneously on the AC surface. However, at 9,0%Co loading, homogeneous disperse decreases and its size increases continuely from 27 nm to 35 nm.

3.1.2. Adsorption – desorption isotherm of N_2 (BET)

As shown in figure 3.2, at liner plot of P/P^o range, N_2 adsorption-desorption isotherms of AC has I-typed isotherm (UIPAC). It suggests that Tra Bac activated carbon is microporous material ($d_{pore} \leq 2$ nm).



Hình 3.2. N_2 adsorption-desorption isotherms at 77K of AC, 3Co/AC and 5Co/AC.



Hình 3.3. Pore size distributions allowing DFT method.

Table 3.1 lists results related to structural properties of materials such as: total surface area (S_{BET}), micropore area (S_{micro}), micropore volume (V_{micro}), external surface area (S_{ext}), total pore volume (V_{tot}) of AC and Co/AC samples (3,0% Co and 5,0% Co).

Table 3.1. structural properties of materials of AC and Co/ACsamples (3,0% Co and 5,0% Co).

Vật liệu	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_{micro} (cm^3/g)	S_{ext} (m^2/g)	V_{meso} (cm^3/g)	V_{tot} (cm^3/g)
AC	1090	1038	0.4601	52	0.0552	0.5153
3Co/AC	1024	974	0.4258	50	0.0537	0.4795
5Co/AC	836	805	0.3493	31	0.0391	0.3884

As can be seen from table 3.1, total surface area (S_{BET}) decreased from 1090 m^2/g to 1024 m^2/g and 836 m^2/g and total pore volume (V_{tot}) also reduced from 0.5153 cm^3/g to 0.4795 cm^3/g and 0.3884 cm^3/g when AC were added 3,0% Co and 5,0%Co, respectively. These changes were due to the decrease in the amount of micropores.

Figure 3.3 shows pore size distributions allowing DFT method of AC, and AC samples containing 3,0% và 5,0% Co. It is observed that adding 3,0% Co on AC do not appear pores, but reduce slightly the amount of micropores. The results indicated that cobalt clusters distribute into pores of AC and may exist as ultranano CoO_x. It is the reason why CoO_x clusters were not observed on TEM image of 3Co/AC sample. These ultranano CoO_x clusters are considered as effective sites for *meta*-xylene oxidation.

Similarly, for 5Co/AC sample: the part of cobalt clusters diperses into pores of AC and the other part of cobalt clusters exits as ultranano CoO_x particles. The cobalt clusters having higher size than pore diameter of AC would ditribute on the exteral surface causing external surface area of AC (reducing from 52 m^2/g to 31 m^2/g) and would cover the part of micropores. This effect results in the decrease in total surface area from 1024 m^2/g (for 3Co/ACsample) to 836 m^2/g (for 5Co/ACsample) as well as micropore volume from 0.4258 cm^3/g (for 3Co/ACsam ple) to 0.3493 cm^3/g (for 5Co/ACsample).

3.1.3. X-ray photoelectron spectroscopy

Figure 3.4 and figure 3.5 describe the peak separation in the 2p XPS of Co of 5Co/AC.

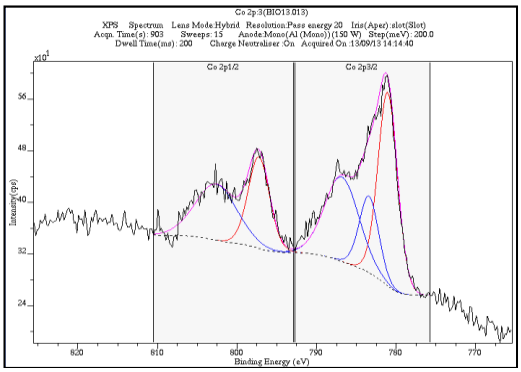


Figure 3.4.*The peak separation in the XPS of 5Co/AC*

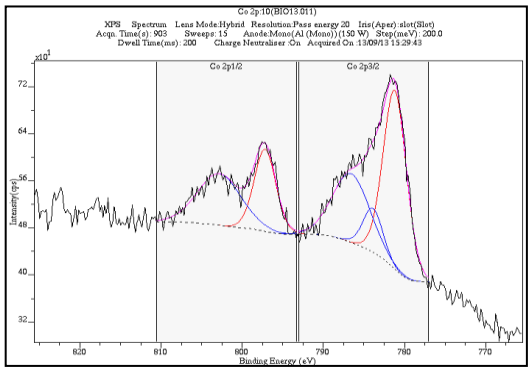


Figure 3.5.*The peak separation in the XPS of 9Co/AC*

From the figure 3.4 it can be seen that

- The $2p_{3/2}$ XPS of Co is separated into 2 peaks corresponding to the bond energy of 781.1 eV and 786.9eV.

- The $2p_{1/2}$ XPS of Co is also separated into 2 peaks corresponding to the bond energy of 797.3 eV and 802.7 eV.

Therefore, cobalt exists in two oxidation states: Co^{3+} and Co^{2+}.

To confirm the stability of the material synthesis process, samples containing 9.0% (denoted 9Co/AC) is selected to analyze because the content of 9.0%Co is large enough to easily compare reviews.

From the figure 3.5 it can also be seen for 9Co/AC that:

- The $2p_{3/2}$ XPS of Co is separated into 2 peaks corresponding to the bond energy of 781.2 eV and 786.6 eV.

- The $2p_{1/2}$ XPS of Co is also separated into 2 peaks corresponding to the bond energy of 797.3 eV and 802.8 eV.

Therefore, cobalt also exists in two oxidation states: $Co^{3+}$and Co^{2+}.

3.1.4. H_2-TPR

Figure 3.6 and figure 3.7 depict the H_2-TPR of AC, 5Co/AC and 9Co/AC sample.

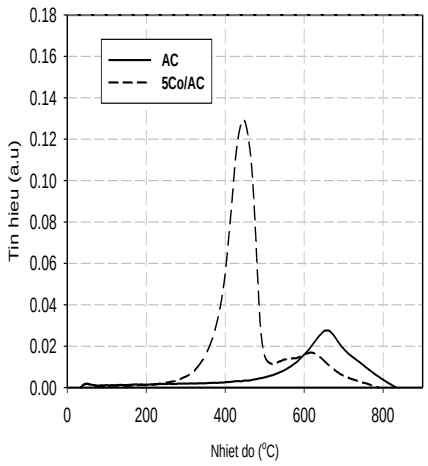


Figure 3.6. H_2-TPR profile of AC and 5Co/AC

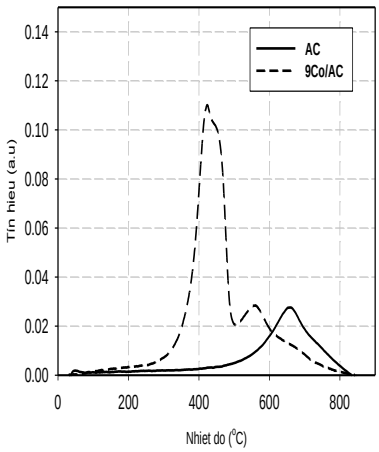


Figure 3.7.H_2-TPR profile of AC and 9Co/AC

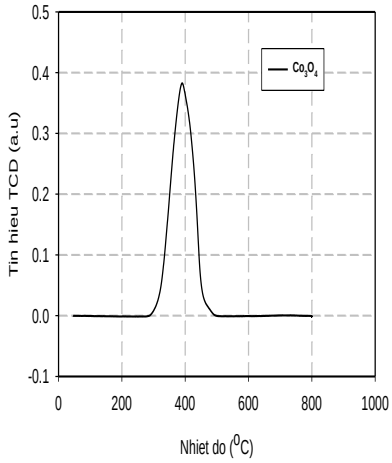


Figure 3.8. H_2-TPR profile of Co_3O_4.

From the figure 3.6 and figure 3.7, it can be seen that:

- In the H_2-TPR profile of AC there is the unique reduction peak at about 656°C. This peak may be related to the reduction of functional groups and aromatic ring on AC surface. , It also corresponds to the methanation of carbon: $C + H_2 \rightarrow CH_4$

- In the H_2-TPR profile of 5Co/AC sample the reduction peak at 656°C moves on lower temperature (≈ 584°C) with low intensity. This may be due to the inhibition of the methanation on the surface of AC by cobalt oxide.

Moreover, in the H_2-TPR profile of 5Co/AC one reduction peak with rather strong intensity is observed at 300 - 500°C (peak at ~ 440°C) with the shoulder at 584°C. Reduction peak at ~ 440^{0}C is attributed to the reduction of Co_3O_4 to CoO and Co metal by H_2 reducing agent.

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O \text{ and } CoO + H_2 \rightarrow Co + H_2O$$

- When the content of Co increases to 9,0%Co (figure 3.7) the reduction peak at 300 - 500°C can be also observed (peak at ~ 431°C). Therefore, the oxidation state of CoO_x on AC still retain when increasing the Co content to 9%.

Moreover, figure 3.8 decribes the H_2-TPR profile of Co_3O_4. One reduction peak with rather strong intensity is observed at 384,7 - 426°C. Reduction peak is aslo attributed to the reduction of Co_3O_4 to CoO and Co metal by H_2 reducing agent.

Therefore, from the H_2-TPR, it can be concluded that cobalt oxide on AC exists mostly in the form of Co_3O_4.

3.1.5. TPD-O_2 measurement

Figure 3.9 shows TPD-O_2 profiles of AC, 5Co/AC and 9Co/AC samples in the temperature range from 120°C to 300°C. As shown in figure 3.7 (a), 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. Whereas, 5Co/AC and 9Co/AC samples exhibit a peak at about 198°C. The appearance of the peak proves that these samples are able to adsorb oxygen gas in the form of O^-_{2ad} in the temperature range of 150 - 250°C.

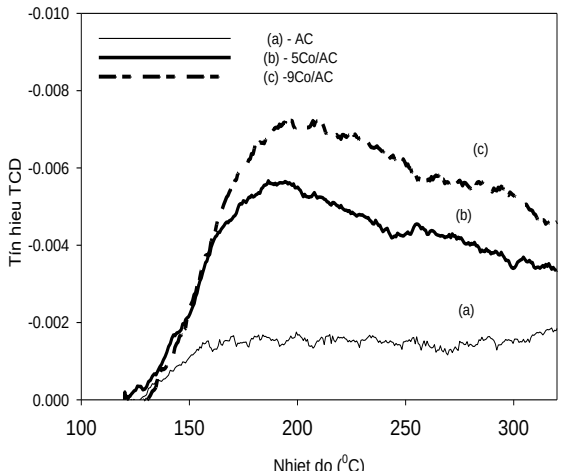


Figure 3.9. *TPD-O_2 profiles of (a)-AC, (b)-5Co/AC and (c)-9Co/AC*

3.2. Characteristics of *meta*-xylene Adsorption

Dynamic *meta*-xylene adsorption of AC and 5Co/AC sample was performed in a quartz tube of a micro-flow system, where nitrogen was used as carrier gas with the *meta*-xylene concentration of 2223 ppm, catalyst mass of 0.62 g and flow rate of 2.0 L/hour. Figure 3.10 shows the breakthrough curves of *meta*-xylene adsorption of AC at different temperatures (100°C, 150°C, 180°C, 200°C và 220°C).

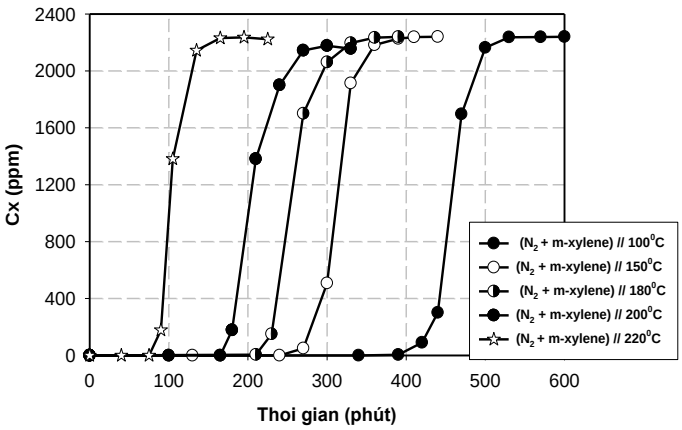


Figure 3.10. *Breakthrough curves of dynamic meta-xylene adsorption of AC at the range of temperature of 100 - 220°C (0,62 g AC, W = 2,0 L/h)*

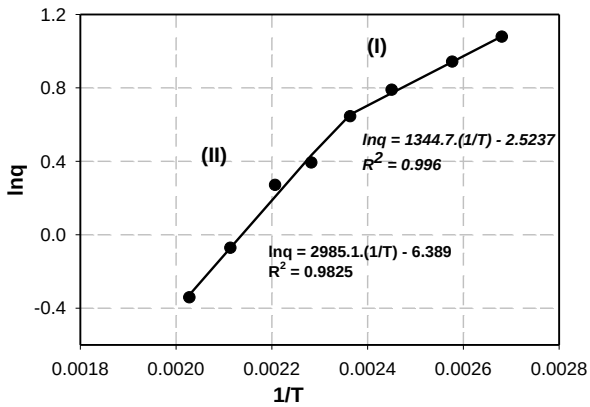


Figure 3.11. *Linear relationship between lnq and 1/T of meta-xylene adsorption over AC*

From these curves, adsorption capacities AC at different temperatures can be determined and are listed in table 3.2.

Table 3.2. *Adsorption capacity (q) of AC at different temperatures (T)*

t ***(^{o}C)***	***q*** ***(mmol.g^{-1})***	***t*** ***(^{o}C)***	***q*** ***(mol.g^{-1})***
100	2.94	165	1.48
115	2.56	180	1.31
135	2.23	200	0.93
150	1.91	220	0.71

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

$$q = q_0.e^{-\frac{\Delta H}{RT}} \quad (3.1) \qquad \text{or} \quad \ln q = -\frac{\Delta H}{RT} + \ln q_0' \quad (3.2)$$

Where: q (mol.g^{-1}) is adsorption capacity of catalyst material, ΔH (kJ.mol^{-1}) is adsorption heat at temperature T, R is universal gas constant.

By fitting data listed in table 3.2 to equation (3.2), the linear relationship between lnq and 1/T can be depicted as shown in figure 3.11.

As shown in figure 3.11, the curve contains 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) of sample can be calculated.

- At range of temperature: 100 - 150°C:

$$\Delta H = -1344.7 \times 8.314 = -11180 \text{ J/mol} \sim -11.18 \text{ kJ/mol}$$

- At range of temperature: 165 - 220°C:

$$\Delta H = - 2985.1 \times 8.314 = - 24818 \text{ J/mol} \sim - 24.82 \text{ kJ/mol}.$$

As the obtained results, it is concluded that at range of temperature 100 - 200°C AC sample possesses two types of adsorption area with different adsortion heat values, (I) adsorption area corresponding to low value of adsorption heat (-11.18 kJ mol^{-1}) and (II) adsorption area corresponding to higher value of adsorption heat (- 24.82 kJ mol^{-1}).

Therefore, the *meta*-xylene adsortion on AC can be demonstrated that because *meta*-xylene molecules are nonpolar, they are not adsorbed on the functional groups of AC. So that, it is suggested that the mechanism of the adsorption of *meta*-xylene is obeyed by π-π interaction between aromatic ring of *meta*-xylene and π - exchanged electrons of AC.

(I) adsorption area can be assigned to the *meta*-xylene adsorption (X) on external surface of AC. It does not facilitate *meta*-xylene adsorption due to the inhibition of functional surface groups. The π-π interaction can be reduced and there only exits molecular interaction (Van der waals interaction) between *meta*-xylene and external surface of AC. So that, adsorption heat of this area is low.

(II) adsorption area can be responsible for the *meta*-xylene adsorption (X) into micropores of AC material, the diffusion of *meta*-xylene into micropores results in the strong formation of the bond of π-π interaction. Moreover, Van der waals interaction in micropores is increased strongly. Therefore, in the case of (II) adsorption area, the adsorption of *meta*-xylene is facilitated and adsorption heat value is more negative. And only the adsorption of *meta*-xylene in this area can result in the chemical reaction in the presence of suitable catalysts and O_{2ad} oxygen adsorbed species:

$$(AC\text{-}X)_{ad} + O_{2,\,ad} \rightarrow CO_2 + H_2O \qquad (3.3)$$

Figure 3.12 shows the breakthrough curves of *meta*-xylene adsorption of 5Co/AC sample at different temperatures (100°C, 150°C, 180°C, 200°C và 220°C).

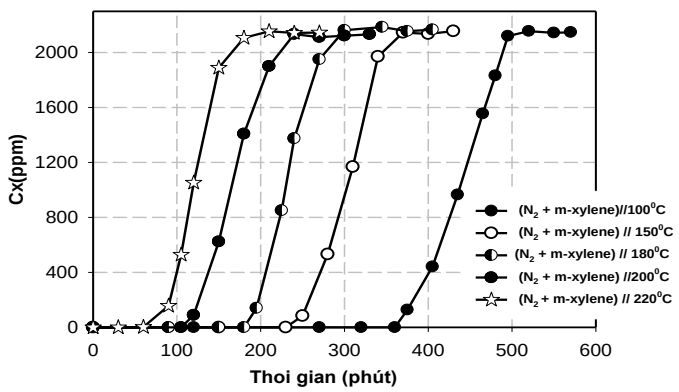


Figure 3.12. *Breakthrough curves of dynamic meta-xylene adsorption of 5Co/AC at the range of temperature of 100 - 220°C*

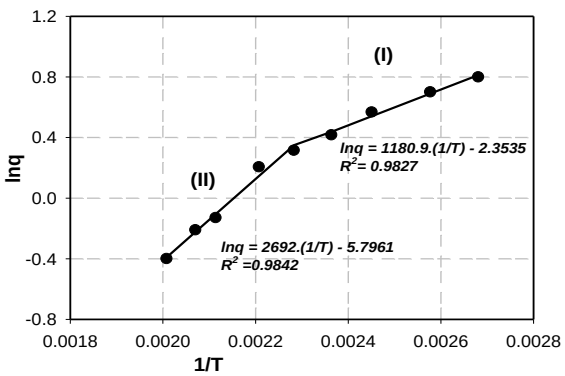


Figure 3.13: *Linear relationship between lnq and 1/T of meta-xylene adsorption 5Co/AC.*

From these curves, adsorption capacities of 5Co/AC at different temperatures can be determined. The obtained capacities are listed in table 3.3.

Table 3.3. *Adsorption capacity (q) of 5Co/AC at different temperatures (T)*

t ***(^oC)***	***q*** ***($mol.g^{-1}$)***	***t*** ***(^oC)***	***q*** ***($mol.g^{-1}$)***
100	2.11	165	1.37
115	1.94	180	1.23
135	1.78	200	0.87
150	1.51	220	0.69

By fitting data listed in table 3.3 to equation (3.2), the linear relationship between lnq and 1/T can be depicted as shown in figure 3.13.

From the slopes of linear curves, the adsorption heat (ΔH) of samples can be calculated.

- At temperature: 100 - 150°C: the adsorption area (I): $\Delta H = -9.82$ kJ.mol^{-1}
- At temperature: 165 - 220°C: the adsorption area (II): $\Delta H = -22.38$ kJ.mol^{-1}

The presence of some Co sites (in form of Co_3O_4) on Tra Bac AC does not affect to the property of AC in the *meta*-xylene adsorption. The explanation is that the adsorption of *meta*-xylene on AC or 5Co/AC occurs mainly in micropores at two site types as mentioned above.

Abstract:

- There are two adsorption areas on AC material corresponding to different values of adsorption heat such as: (I) adsorption area with $\Delta H = -9,82 \div -11,18$ kJ.mol^{-1} and (II) adsorption area with higher value of adsorption heat $\Delta H = -22,38 \div -24,82$ kJ.mol^{-1}.

- At the range of temperature of 100 - 220°C, the adsorption of meta-xylene takes place on two adsorption area which can be represented as below:

+ On (I) adsorption area, the asdorption takes place by weak interaction between organic compound (meta-xylene) and the external surface of AC due to Van der waals force.

+ On (II) adsorption area, the asdorption occurs in micropores of AC which is the result of the π-π interaction between aromatic ring of meta-xylene and π- electron system of AC. Only this adsorption may be result in the chemical reaction and can be called "active" adsorption.

- The presence of some Co sites (in form of Co_3O_4) on Tra Bac AC does not affect to the property of AC in the meta-xylene adsorption on AC.

3.3. Study on meta-xylene treatment by catalytic method over 5Co/AC sample

3.3.1. The catalytic properties

The *meta*-xylene oxidation of 5Co/AC sample was performed in a quartz tube of a micro-flow system, where the air was used as carrier gas with the *meta*-xylene concentration of 2223 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 3.14.

In order to investigate the role of oxygen in the oxidation of *meta*-xylene, the similar experiment was carried out using nitrogen as the carrier gas.

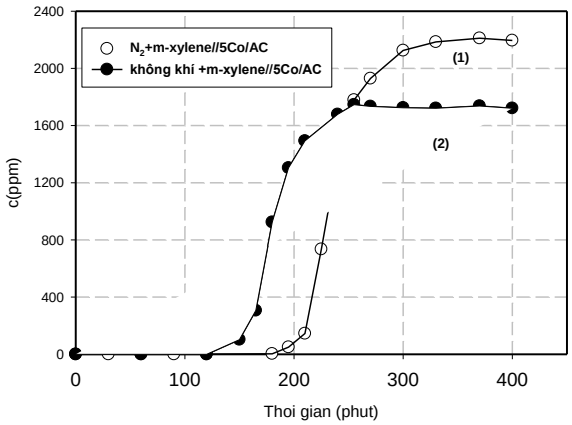


Figure 3.14. Breakthrough curves of oxidation of meta-xylene at 180°C over Co/AC line (1): carrier gas is N_2 and line (2): carrier gas is air

As shown in figure 3.14, *meta*-xylene was almost not oxidized when nitrogen is used as a carrier. In contrast, *meta*-xylene was oxidized when the air is used as a carrier. The concentration of *meta*-xylene in the output flow reduces 23.12% in comparison to the concentration of *meta*-xylene in input flow. The decrease of concentration of *meta*-xylene means that 23.12% of it was oxidized.

$$\alpha(\%) = \frac{C_0 - C_f}{C_0} x100(\%) = \frac{2223 - 1709}{2223}.100\% = 23{,}12\% \qquad (3.4)$$

From the experimental data, it can conclude that catalytic sites for oxidation reaction between *meta*-xylene and oxygen (in the air) are cobalt particles (in form of ***Co_3O_4***) distributed on Tra Bac AC.

3.3.2. Effect of Co loading (%Co)

Figure 3.15 (a, b) show breakthrough curves of oxidation of *meta*-xylene of 3Co/AC và 9Co/AC.

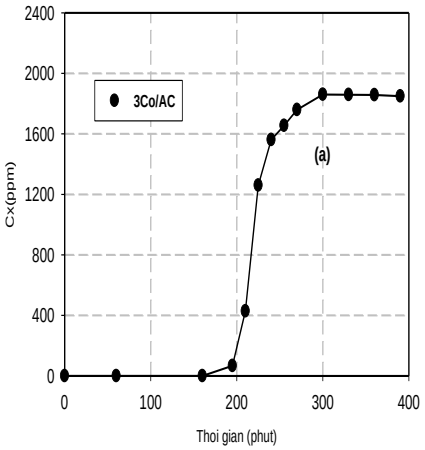


Figure 3.15 a. *Breakthrough curves of oxidation of meta-xylene (air + meta-xylene) of 3Co/AC sample*

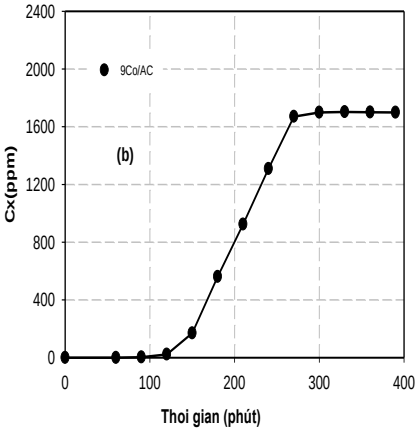


Figure 3.15 b. *Breakthrough curves of oxidation of meta-xylene (air + meta-xylene) of 9Co/AC sample*

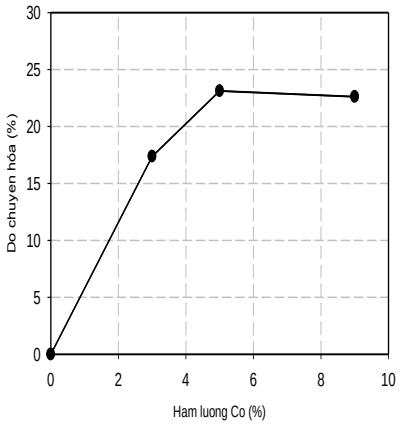


Figure 3.16. *Effect of conversion of meta-xylene α (%) depending on the Co loading*

As shown in figure 3.14, the concentration of *meta*-xylene in the output flow reduces 17.36% (for *3*Co/AC) and 22.62% (*9*Co/AC*)* in comparison to the concentration of *meta*-xylene in input flow. The decrease of concentration of *meta*-xylene means that 17.36% (for *3*Co/AC) and 22.62% (*9*Co/AC of it was oxidized.

$$\alpha(\%)_{3Co/AC} = \frac{C_0 - C_f^{3Co/AC}}{C_0}.100\% = \frac{2223-1837}{2223}.100\% = 17,36\%$$

$$\alpha(\%)_{9Co/AC} = \frac{C_0 - C_f^{9Co/AC}}{C_0}.100\% = \frac{2223-1720}{2223}.100\% = 22,62\%$$

Figure 3.16 displays effect of conversion of *meta*-xylene α (%) depending on the Co loading of Co/AC sample.

As observed in figure 3.16, at 3.0% Co and 5.0% Co, the conversion of *meta*-xylene increased with increasing of Co - loading, the conversions were observed to be 17.36% and 23.13%, respectively. However, conversion decreased slightly with further increase in Co-loading beyond 9.0% Co. This was attributed to the the fact that beyond 9.0%, the formation of relatively larger metal crystalllites ocurred causing the blockage of micropores.

3.3.3. Effect of temperature

Figure 3.17 describes breakthrough curves of oxidation of *meta*-xylene at temperature of 180°C, 200°C, 220°C và 250°C.

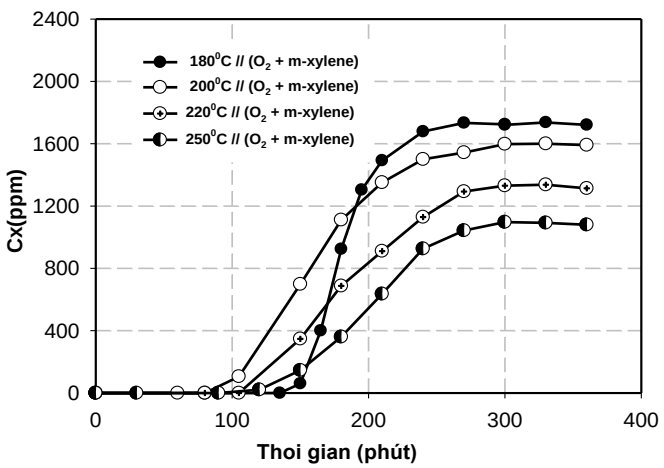


Figure 3.17. *Breakthrough curves of oxidation of meta-xylene over 5Co/AC at different temperature.*

t (^{o}C)	α (%)	r (mmol.g^{-1}.h^{-1})
180°C	23,12	4,426
200°C	28,69	5,260
220°C	42,10	7,461
250°C	55,02	9,153

Table 3.4. *meta*-xylene conversion at different temperatures

From these curves, *meta*-xylene conversion at different temperatures can be determined and are listed in table 3.4. From data listed in table 3.4 and equation (3.5), the reaction rate can be determined and the results are listed in table 3.4.

$$r = \frac{W}{22,4}.\frac{273}{t+273}.\frac{P_X}{P_{kq}}.\frac{\alpha}{m}.10^3 (mmol.g^{-1}.h^{-1}) \qquad (3.5)$$

Therefore, *meta*-xylene conversion and reaction rate of oxidation of *meta*-xylene over Co/AC catalyst increase with the increase of temperature.

Abstract:

(i) Co/AC material is capable to catalyze the oxidation of meta-xylene with air oxygen even at temperatures below 200°C. This transformation temperature is only published with the noble metal catalysts and never particularly been announced for the catalysts based on other metals. Outstanding results of studied Co/AC materials is assigned to its special nature: bi-functional adsorbent/catalyst properties. In this material, AC material plays the role of an adsorbent of meta-xylene in the micropores by strong interaction between aromatic rings of meta-xylene and π-π bond of AC (to create active complex (AC - X)$_{ad}$). The cobalt oxide clusters play the role of catalytic sites and oxygen adsorbent. In particular, the existence of the nano Co_3O_4 cluster in the pores of the activated carbon as the active sites plays a major role in catalytic conversion of meta-xylene

(ii). With experimental conditions: VHSV = 1936.11 h^{-1}, t = 180°C and concentration of meta-xylene Co = 2223 ppm, meta-xylene conversion achieved 23.12%.

3.4. Proposal of mechanism and equation for reaction rate

3.4.1. Determination the kinetic domain

Kinetic domain of a chemical reaction is determined by the relationship of the reaction rate with the retention time (F) of the reactant gas through the catalyst. In particular, the retention time can be calculated based on the the speed of space volume (VHSV) (F = 1/VHSV). Without the prevent of diffusion, the reaction rate will be linear with retention time in the domain kinetics. The determination of kinematic domain was conducted at three temperatures 180°C, 200°C and 235°C. The results obtained are presented in Table 3.5.

Table 3.5. The effect of retention time F(s) on reaction rate r at different temperature

W (L/h)	***VHSV (h^{-1})***	***F (s)***	***r (mmol.g^{-1}.h^{-1})***		
			180°C	***200°C***	***235°C***
1.5	1451.61	2.48	4.67	5.97	10.65
2.0	1936.11	1.86	4.12	5.08	8.66
2.5	2419.35	1.49	3.88	4.38	7.07
3.0	2903.22	1.24	3.69	4.09	6.38

From data listed in table 3.5, the relationship between (r) and F(s) can be depicted as shown in from figure 3.18 to figure 3.20.

These figures showed that the relationship between reaction rate and retention time is the linear relationship at experimental conditions (0.62g mass, flow rate W = 1.5 L/h - 3.0 L/h). The results propsed that the oxidation of *meta*-xylene in air is taken placed in kinematic domain.

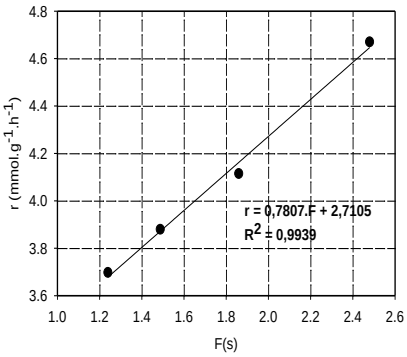


Figure 3.18: *Linear relationship between r and F (S) at 180°C*

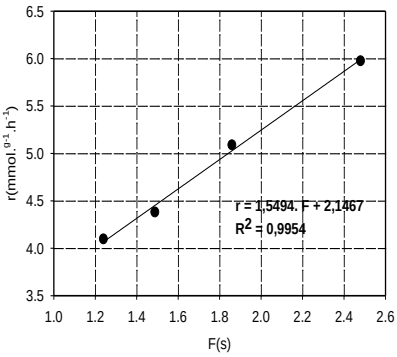


Figure 3.19: *Linear relationship between r and F (S) at 200°C*

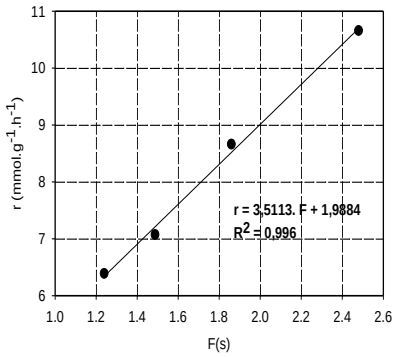


Figure 3.20: *Linear relationship between r and F (S)* at 235°C

3.4.2. Proposal of mechanism

Analytic results show that: *meta*-xylene and oxygen were adsorbed on two different sites of 5Co/AC material (*meta*-xylene is more favored to adsorb on AC and O_2 is more favored to adsorb on Co_3O_4).

Mechanism of the oxidation of *meta*-xylene can be proposed as follows:

$$X_{(g)} + AC_{(r)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (AC\text{-}X)_{ad} \qquad (3.6)$$

$$O_{2(g)} + Co_3O_4 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (Co_3O_4\text{-}O_2)_{ad} \qquad (3.7)$$

$$(AC\text{-}X)_{ad} + (Co_3O_4\text{-}O_2)_{hp} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (Co_3O_4\text{-}O\text{-}O\text{-}X) + \bullet \qquad (3.8)$$

$$(Co_3O_4\text{-}O\text{-}O\text{-}X) \xrightarrow{k_4} a\,CO_2 + bH_2O + Co_3O_4 \qquad (3.9)$$

Where, X: meta-xylene

AC: Adsorption sites on AC; ●*: adsorption sites*

$(AC\text{-}X)_{ad}$, $(Co_3O_4\text{-}O_2)_{hp}$ *and* $(Co_3O_4\text{-}O\text{-}O\text{-}X)$*: adsorption types of meta-xylene and oxygen on Co/AC material.*

Suppose that the (3.9) stage is surface reaction which is taking place slower than (3.6), (3.7) and (3.8) stages. Therefore, the rate of the reaction:

$$\textit{meta}\text{-xylene} + O_2 \rightarrow aCO_2 + bH_2O \qquad (3.10)$$

can be determined by (3.9) stage and the rate law can be expressed as:

$$r = k_4.\theta_{phuc} \qquad (3.11)$$

Where, θ_{phuc}*: 5Co/AC surface occupied by* $(Co_3O_4\text{-}O\text{-}O\text{-}X)$ *complex.*

Knowing that, in the (3.7) stage, P_{O2} is large and k_{-2} is small, so that θ_{O2} = const (θ_{O2}*: 5Co/AC surface occupied by oxygen*)

From (3.8), it can be written as: $\theta_{phuc} = K_3.\theta_{O2}.\theta_X$ (3.12)

(where θ_X is 5Co/AC surface occupied by *meta*-xylene và $K_3 = \dfrac{k_3}{k_{-3}}$)

Moreover, according to kinetic of heterogenous catalysis:

$$\theta_X = q_0 \frac{K_X.P_X}{1 + K_X.P_X} \qquad (3.13) \qquad \left(K_X = \frac{k_1}{k_{-1}} \right)$$

Therefore, $$r = k_4.K_3.\theta_{O2}.q_0 \frac{K_X.P_X}{1+K_X.P_X} \quad (3.14)$$

Or $$r = \frac{A.P_X}{1+K_X.P_X} \quad (3.15)$$

Where, $A = k_4.K_3.\theta_{O2}.q_0.K_X$.

If vapor pressure of *meta*-xylene is small then ($K_X.P_X << 1$), and

$$r = A.P_X \quad (3.16)$$

The reaction has the first order with respect to *meta*-xylene and zero order with respect to O_2.

If vapor pressure of *meta*-xylene is high enough then $K_X.P_X >> 1$ and:

$$r = \frac{A}{K_X} = k_{bk} \quad (3.17)$$

(Where k_{bk} is apparent constant)

The reaction has the first zero order with respect to both *meta*-xylene and oxygen

3.4.3. Experimental determination of order of oxidation reaction of meta-xylene by oxygen over 5Co/AC material.

The reaction rate is calculated according to Langmuir-Hinshelwood model:

$$r = \frac{A.P_X}{1+K_X.P_X} \quad (3.18)$$

Value of reaction order varies from 0 to 1 depending on the equilibrium pressure. Therefore, equation (3.21) can be written as: $r = k_{bk}.P_X^n$ (3.19)

Where n is order of reaction, n = 0 ÷ 1

The order of reaction can be determined experimentally by using (3.22) equation as following: $\ln r = \ln k_{bk} + n \ln P_X$ (3.20)

Order of reaction, n, is the slope of the linear line which can be plotted from (3.20).

The values of rate r which depends on pressure of *meta*-xylene (P_x) at 180°C, 200°C, 220°C và 235°C are listed on Table 3.6.

Table 3.6. The relationship between r and P_x at 180°C, 200°C, 220°C và 235°C

P_X (mmHg)	Reaction rate r ($mmol.g^{-1}.h^{-1}$)			
	180°C	**200°C**	**215°C**	**235°C**
0.845	3.788	4.290	6.032	7.272
1.267	4.148	4.893	6.667	8.128
1.695	4.422	5.240	7.149	8.639
2.512	4.919	5.695	7.812	9.635
3.330	5.281	6.100	8.423	10.260

From the results listed on table 3.6, the relationship of "lnr-lnP_X" is built and displayed from figure 3.21 to figure 3.24.

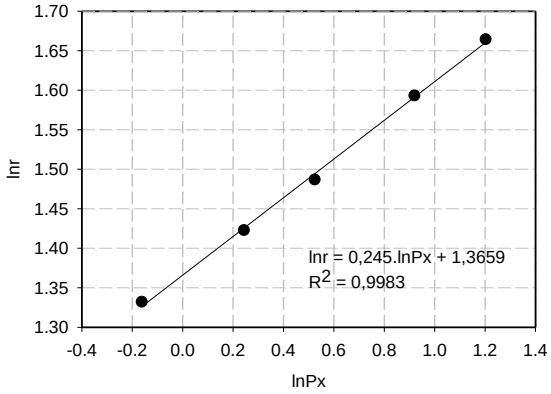


Figure 3.21. Linear relationship between lnr and lnP_X at 180°C.

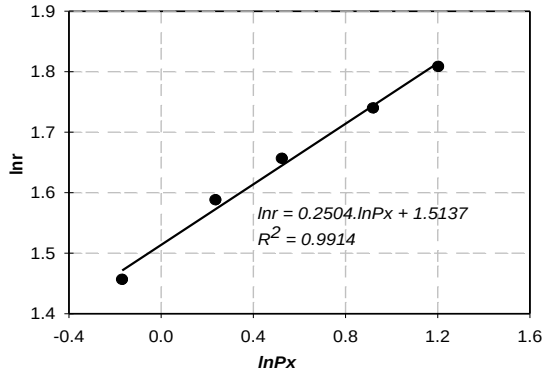


Figure 3.22. Linear relationship between lnr and lnP_X at 200°C.

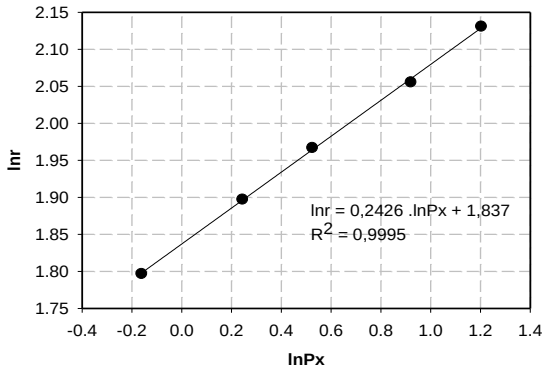


Figure 3.23. Linear relationship between lnr and lnP_X at 220°C

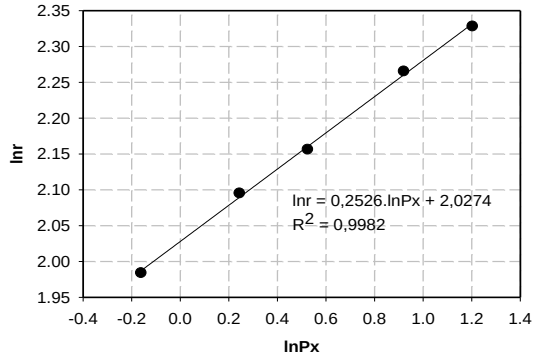


Figure 3.24. Linear relationship between lnr and lnP_X at 235°C

These figures show that the relationship between lnr and lnP_x is the linear relationship at experimental conditions. Order of reaction can be determined from the slope of the "lnr-lnP_X" plot, has value of 0.25 with $R^2 \geq 0{,}99$. The apparent constant values also were determined and displayed on table 3.7.

Table 3.7. The apparent constant values at different temperatures (180°C, 200°C, 220°C and 235°C).

t^{o}C	**180°C**	**200°C**	**220°C**	**235°C**
lnk	1,366	1,514	1,837	2,028
k (mmol.g^{-1}.h^{-1}.(mmHg)$^{-0.25}$	3,919	4,5435	6,277	7,598

Since, rate law of oxidation reaction of *meta*-xylene by oxygen in the air over 5Co/AC material can be expressed as follows:

$$r = k_{bk}.P_X^{0,25} \qquad (3.\ 21)$$

From the study on adsorption activity of 5Co/AC the *meta*-xylene oxidation reaction using oxygen in the air, it can be concluded that:

(i) Oxidation *meta*-xylene on materials Co/AC takes place in the kinetic domain.

(ii) Meta-xylene adsorption and oxygen do not compete. The reaction between 2 surface adsorption complexes $(AC\text{-}X)_{hp}$ and $(Co_3O_4\text{-}O_2)_{hp}$ follows Langmuir-Hinshelwood mechanism. Order of oxidation reaction varies from 0 - 1 depending on the meta-xylene ủa pressure in the reaction gas mixture

(iii) Experimental kinetic equation of oxidation of the form: $r = k_{bk}.P_X^{0,25}$ with the order respect to *meta*-xylene of 0.25.

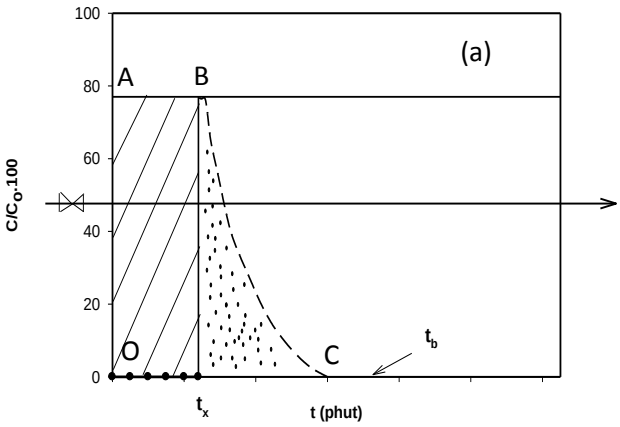
3.5. Treatment of *meta*-xylene using the technique of "adsorption/catalytic" over Co/AC material

The results described in section 3.3.1 show that 5Co/AC material converted 23.12 ÷ 28.69% *meta*-xylene at the temperature range from 180 to 200°C in a very short period of time (1.85 sec.) and the volume hourly space velocity of 1936.11h^{-1}. The unconverted *meta*-xylene will be adsorbed on sites of AC. This means that the 5Co/AC can be considered as a bi-functional material. If there is no further study on this material, there is no reliable application due to its low conversion degree. Therefore, to increase the conversion of *meta*-xylene to 100% at low temperature (180 - 200°C), operation technique must be modified. One of the modified method is the use of adsorption-catalyst technique (first stage is adsorption, the later stage is oxidation).

Figure 3.25a is a model described the adsorption of *meta*-xylene at the temperature from 180 - 200°C under a mixture of (air and *meta*-xylene) during a period of time t_x (t_x is less than t_b - the time at which *meta*-xylene is observed and can be calculated from breakthrough curve). Then, the flow is stopped. An adsorbed column (ABCO) of *meta*-xylene was obtained (areas which are denoted by slash lines and dots) and conversion degree of *meta*-xylene is of 23.12 - 28.69% (after contacting time of 1.85 sec.).

Figure 3.25b is a model described the efficiency of catalytic oxidation of the *meta*-xylene adsorbed on AC surface by replacing (air + *meta*-xylene) flow with air flow for complete oxidation of *meta*-xylene adsorbed.

The problem needed to solve is how to find the adsorption time t_x to get the efficiency of 100% at the oxidation stage. The basis for determining the adsorption time t_x is t_b which can be determined from breakthrough curve.



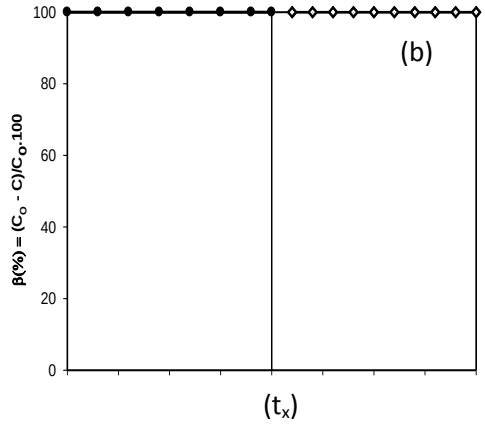


Figure 3.25 (a). Model describes the adsorption of *meta*-xylene under (air + *meta*-xylene) flow during time t_x.

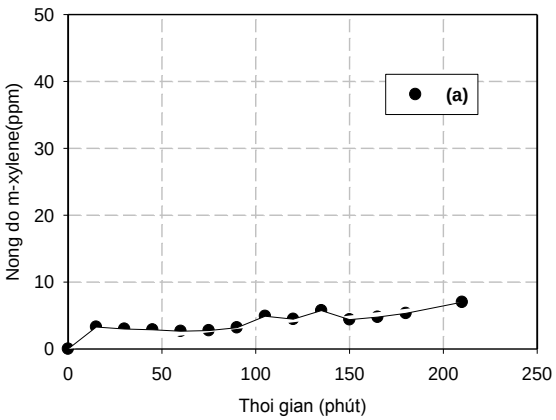
Figure 3.25 (b). Model describes the efficiency of catalytic oxidation of adsorbed *meta*-xylene on AC.

3.5.1. Experimental results on the study of adsorption time (t_x) at 180°C.

From a result the construction of the *meta*-xylene breakthrough curve over 5Co/AC sample, the time t_b equals to 150 minutes so that adsorption time t_x should be selected is 100 minutes and 120 minutes.

- Step 1 – Adsorption stage: Blowing the gas flow (air + *meta*-xylene) through the material column in 100 minutes (or 120 minutes).

- Step 2 – Oxidation stage: Oxygen was used to blow directly into the *meta*-xylene adsorbed layer of the material in the step 1 with the air flow of 2.0 L/h. To determine the amount of *meta*-xylene remaining after the oxidation, we also determined from the relationship between *meta*-xylene concentration escaping over time (Figure 3.26).



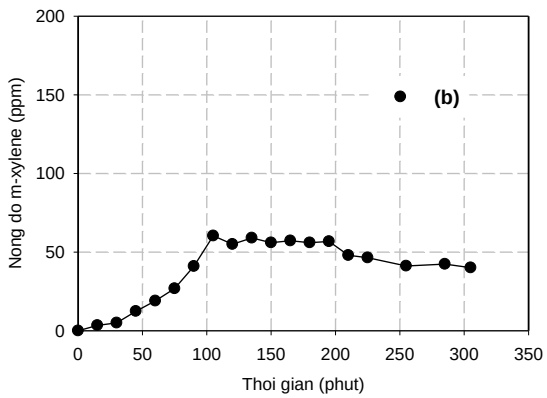


Figure 3.26. The concentration of *meta*-xylene escaping from the reactor over time at 180°C after (a) - 100 minute adsorption *(b) - 120* minute adsorption

In the Figure 3.26, it can be easily found that after being oxidized by oxygen of air, the *meta*-xylene concentration escaping from the reactor is very low, less than 100 ppm, below the maximum contaminant level for *meta*-xylene gas < 200 ppm. This proves that the oxygen atmosphere has almost completely oxidized *meta*-xylene adsorbed on the surface layer.

Likewise, from the figure 3.26 and combining with the following formula (3.22)

$$[X]_{ad} = \frac{W(L/h).\ S(ppm.min^{-1}).10^{-6}}{60(min.h^{-1}).\ 22.4(L.mmol^{-1}).10^{-3}.m(g)}[mmol/g] \qquad (3.22)$$

where, W: N_2 flow used for desorbing ($L.h^{-1}$)

S: area which is formed by the curve and horizontal axis.

m: the mass of adsorbent/catalyst material.

the amounts of *meta*-xylene remaining after the oxidation reaction when the adsorption time are 100 minutes and 120 minutes are 0.0076 mmol/g and 0.0303 mmol/g, respectively.

To calculate the effeciency of the conversion of *meta*-xylene in the adsorbed surface layer, adsorbed *meta*-xylene was determined. Repeat step 1, N_2 was used to desorb the adsorbed *meta*-xylene.

Figure 3.27 and 3.28 shows the *meta*-xylene concentration reduced versus time

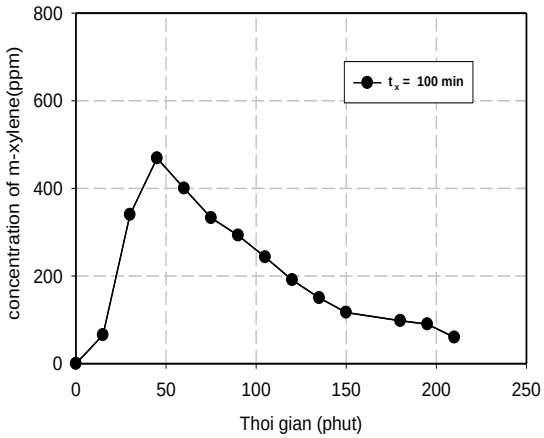


Figure 3.27. *meta*-xylene reduced versus time at 180°C when t_x = 100 minutes

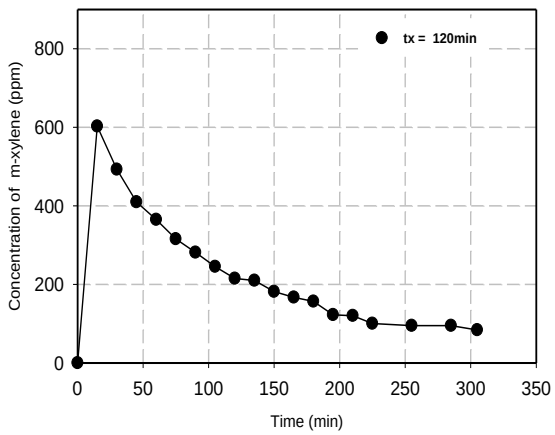


Figure 3.28. *meta*-xylene reduced versus time at 180°C when t_x = 120 minutes

Similarly, using figure 3. 27 and 3.28 and equation (3.22):

The amount of *meta*-xylene adsorbed is 0.223 mmol/g with t_x = 100 minutes and 0.321 mmol/g with t_x = 120 minutes.

Hence, (i) when adsorption time t_x is 100 minutes, the effeciency of the conversion of *meta*-xylene in the adsorbed surface layer is 96.55%, and (ii) when adsorption time t_x is 120 minutes, the effeciency of the conversion of *meta*-xylene in the adsorbed surface layer is 90.55%. The optimum adsorption time is 100 minutes.

3.5.2. Experimental results on the study of adsorption time (t_x) at 200°C.

This experiment was conducted similarly to the experiment at 180°C. At 200°C, adsorption time t_x was selected as 80 and 100 min, respectively (t_b =120 min). The amount of *meta*-xylene adsorbed in adsorption time t_x = 80 min and t_x = 100 min at 200°C are also be determined by using the curve of the amount of *meta*-xylene desorbted vs time (Fig. 3.29 and 3.30). The obtained results as followed:

(i) Adsorption time t_x = 80 min: $[X]^0_{HP}$ = 0.218 mmol/g

(ii) Adsorption time t_x = 100 min: $[X]^0_{HP}$ = 0.331 mmol/g.

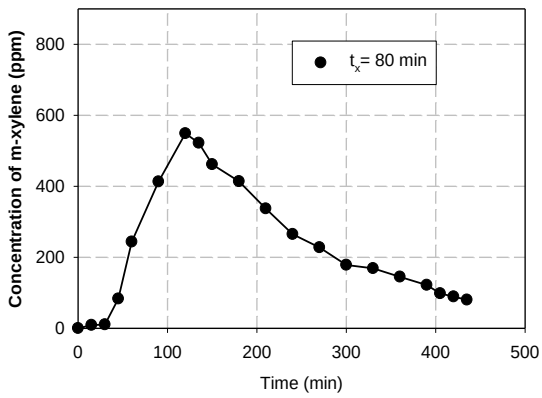


Figure. ***3.29.*** Desorpted *meta*-xylene concentration over time (t_x = 80 min)

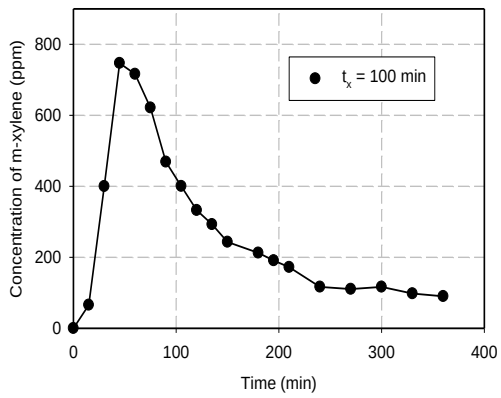
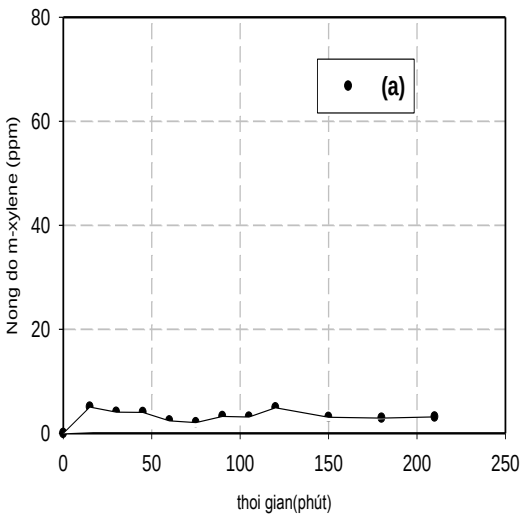


Fig. 3.30. Desorpted *meta*-xylene concentration over time (t_x = 100 min)

The *meta*-xylene remained after oxidation reaction is:

(i) Adsorption time t_x = 80 min: [X] = 0.0016 mmol/g

(ii) Adsorption time t_x = 100 min: [X] = 0.0019 mmol/g (Fig. 3.31).



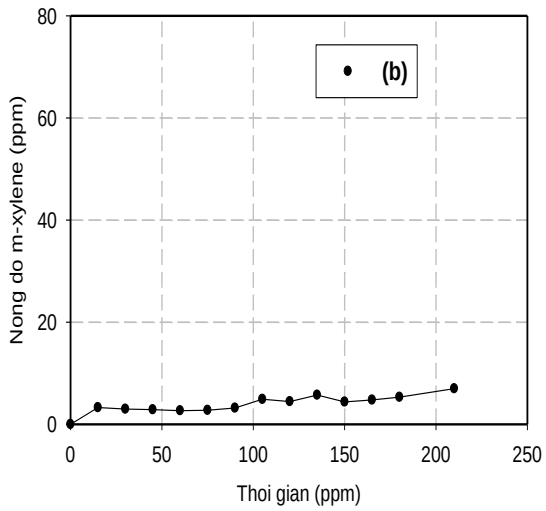


***Fig.* 3.11.** The concentration of *meta*-xylene escaping from the reactor over time at 200°C: (a) - 80 minute adsorption *(b) - 100* minute adsorption

Therefore, *meta*-xylene conversion efficiency at the surface-adsorbed layer is:

(i). H = 99.22% with t_x = 80 min.

(ii). H = 99.32% with t_x = 100 min.

Thus, for the removal of *meta*-xylene over Co/AC, the adsorption/catalytic technique can achieve much higher efficiency (96 - 99%) compared to the catalytic oxidation technique in *meta*-xylene contimuous flows (23.12 - 28.69% at 180 - 200°C). The optimum adsorption time is (i) t_x = 100 min at 180°C and (ii) t_x = 80 min at 200°C.

3.5.3. Kinetic of the oxidation reaction of meta-xylene at the surface-adsorbed layer

After adsorbing *meta*-xylene on 5Co/AC sample to reach a certain adsorption capacity (at condition: t_x = 100 min at 180°C, t_x = 80 min at 200°C), *meta*-xylene

adsorption is stopped blowing. Then *meta*-xylene oxidation is begun. The oxidation reaction at the surface-adsorbed layer will be as followed:

$$(\textit{meta}\text{-xylene})_{ad} + (O_2)_{ad} \rightarrow CO_2 + H_2O \qquad (3.23)$$

The rate of reaction (3.23) can be represented as followed:

$$r = \frac{d[X]_{ad}}{dt} = k_{bk}[X]_{ad}^{m}.[O_2]_{ad}^{n} \qquad (3.24)$$

O_2 concentration is extremely high compared to *meta*-xylene concentration, $[O_2]_{ad} >> [X]_{ad}$, therefore, the concentration of oxygen may be assumed to have remained unchanged throughout the reaction, $[O_2]_{ad}$ = const and $k.[O_2]_{ad}^{n} = const = k_{bk}$ (k_{bk}: rate constant of surface reactions):

$$r = k_{bk}.[X]_{ad}^{m} \qquad (3.25)$$

$[X]_{ad}$ at different reaction time can be estimated as followed:

- Step 1: Perform the adsorption of *meta*-xylene through the reactor containing 0.62g 5Co/AC at 180^0C, at a flow rate of 2.0 L/h (*meta*-xylene + air) in adsorption time t_x = 100 min.

- Step 2: Stop the gas flow (*meta*-xylene + air).

- Step 3: Allow the compressed air to flow over the reactor in 10 min for the oxidation of adsorbed *meta*-xylene. There after, using the inert gas N_2 (100%) to remove adsorbed *meta*-xylene molecules for identifiying the *meta*-xylene remaining after the oxidation reaction took place.

- Follow the same procedure and change the oxidation time to 20, 30 and 40 min.

The desorbed *meta*-xylene concentration versus time is illustrated in Fig. 3.32.

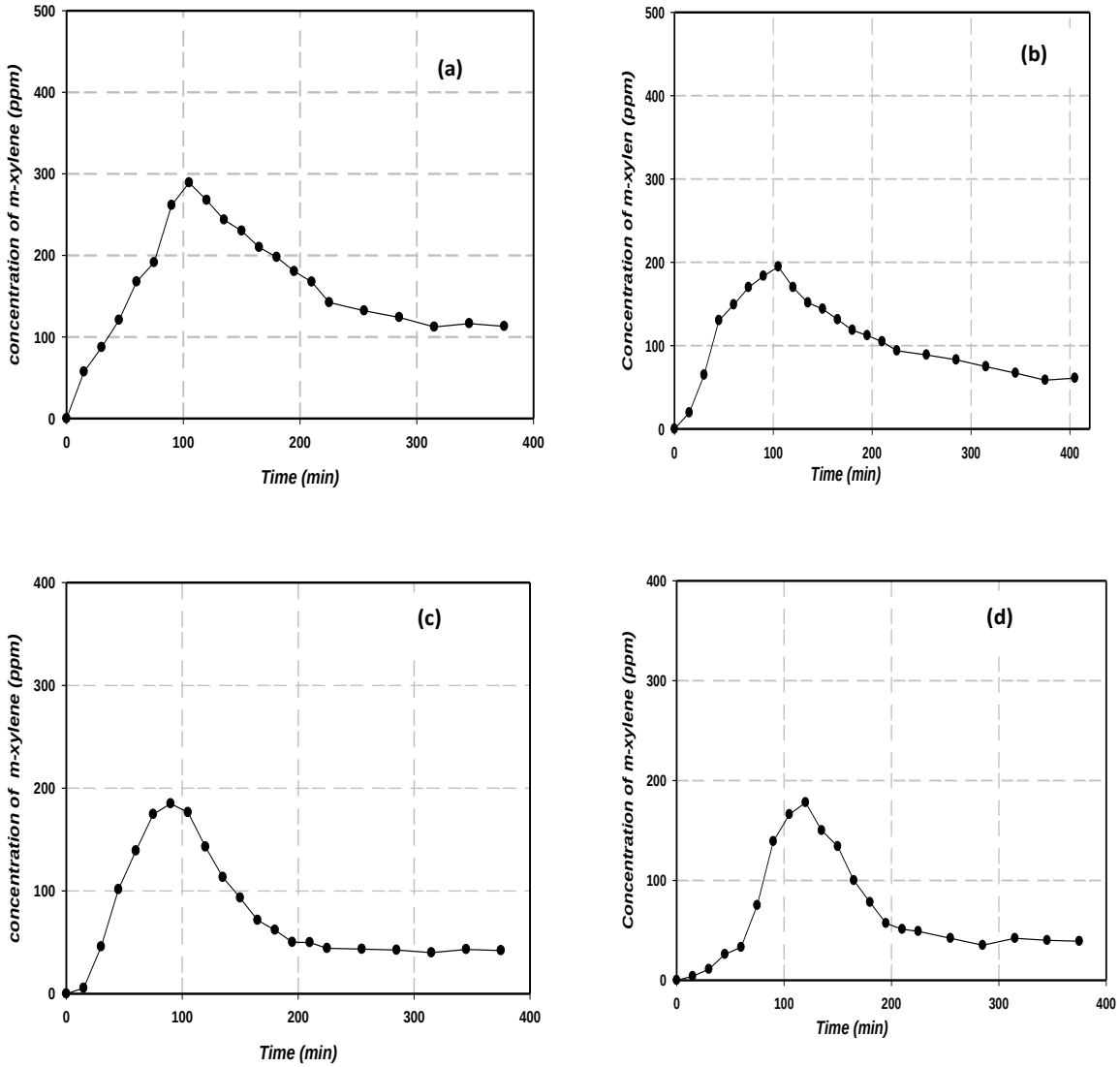


Fig. 3.32.

(*a):* The *meta*-xylene concentration desorbed by N_2 *after 10 min oxidation*
(b): The *meta*-xylene concentration desorbed by N_2 *after 20 min oxidation*
(c): The *meta*-xylene concentration desorbed by N_2 *after 30 min oxidation*
(d): The *meta*-xylene concentration desorbed by N_2 *after 40 min oxidation*

From Fig. 3.32, it can be calculated to determine the *meta*-xylene remained after oxidation using equation (3.22). The obtained results are sumarized in Table 3.8.

Table 3.8. *The kinetic parameters of (meta-xylene +air) oxidation reaction over 5Co/AC sample at 180°C*

Time (min)	**Temperature, 180^{0}C**			
	$[X]_{hp}.10^{-2}$	$r_{pu}.10^{-3}$	$\ln[X]_{hp}.10^{-2}$	$\ln r_{pu}.10^{-2}$
0	32.14	7.69	-113.50	- 489.29
10	24.80	5.12	-139.43	- 527.30
20	20.03	3.33	-160.78	- 570.39
30	18.09	2.38	-170.93	- 604.03
40	16.90	2.00	-177.78	- 621.46

From the data of table 3.8, plot the remained *meta*-xylene concentration $[X]_{ad}$ versus oxidation time 10, 20, 30 and 40 min and it is illustrated in Fig. 3.33.

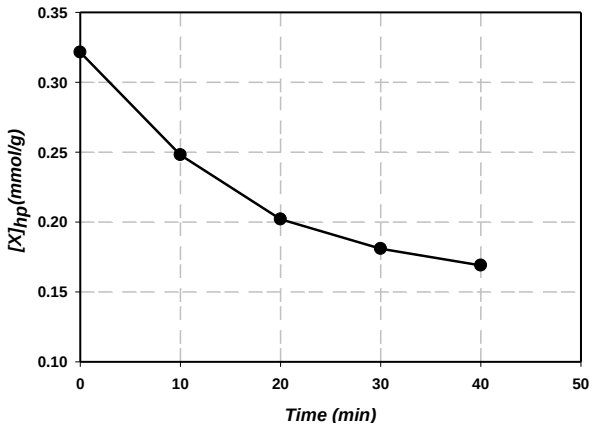


Fig. 3.33. *Plot of remained meta-xylene concentration versus oxidation times*

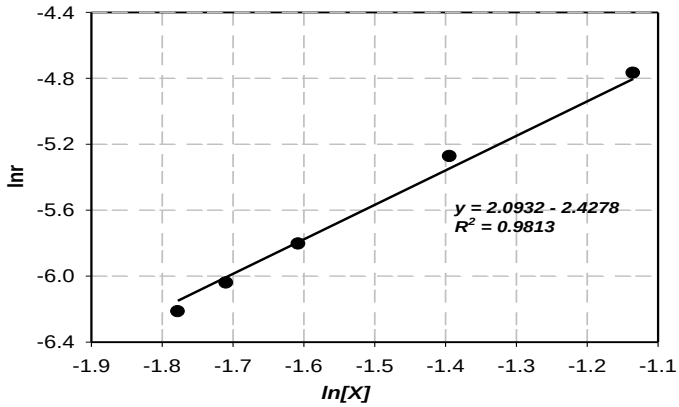


Fig. 3.34. *Plot "lnr-ln[X]$_{ad}$"*

The instantaneous reaction rate (r) can be determined using linear method and summarized in table 3.8.

From equation (3.25), it can be obtained: $\ln r = \ln k_{bk} + m \ln[X]_{ad}$ (3.26)

Plot the linear relationship (3.26) from the data in table 3.8 and presented in Fig. 3.34.

Calculated from data obtained from Fig.3.34 showed that the rate constant k_{bk} = 0.089 ($mol^{-1}.g^{1}.h^{-1}$) and the order with respect to *meta*-xylene m ≈ 2.

From the experiment data, it can be concluded that the oxidation reaction of *meta*-xylene by air occured in surface-adsorption layer is zero order with respect to oxygen and second order with respect to *meta*-xylene:

$$r = k_{bk}.[X]_{ad}^{2} \qquad (3.27)$$

From (3.27), it is easy to determine the required time to convert the initial adsorted *meta*-xylene $[X]_{ad}^{0}$ to required concentration $[X]_{ad}$ (to ensure environmental safety).

3.4.4. meta-xylene oxidation mechanism

The adsorption - oxidation of *meta*-xylene is proposed as followed:

(i) The adsorpted complex $(X\text{-}AC)_{ad}$ move to the active sites $(Co_3O_4\text{-}O_2)_{ad}$:

$$2(X-AC)_{hp} + (Co_3O_4 - O_2)_{hp} \underset{(-1)}{\overset{(1)}{\rightleftharpoons}} (X_2 - Co_3O_4 - O_2)_{hp} + 2AC \qquad (3.28)$$

(ii) X_2 and O_2 within the complex $(X_2\text{-}Co_3O_4\text{-}O_2)_{ad}$ interact to form CO_2 and H_2O:

$$(X_2 - Co_3O_4 - O_2)_{hp} \xrightarrow{(2)} a\ CO_2 + b\ H_2O + Co_3O_4 \qquad (3.29)$$

Assuming that the step (3.29) is the slowest stage and is the rate determining step:

$$(X_2)_{hp} + (O_2)_{hp} \xrightarrow{Co/AC} CO_2 + H_2O \qquad (3.30)$$

Therefore:

$$r_{pubm} = \frac{d\theta}{dt} = k_2.\theta_{phuc} \quad (3.31)$$

Because: $$\frac{\theta_{phuc}}{\theta_{O2}.\theta_X^{\ 2}} = \frac{k_1}{k_{-1}} = K_1 \quad (3.32)$$

(Where, θ_{phuc}: 5Co/AC surface occupied by (Co_3O_4-O-O-X) complex).

Therefore $$\theta_{phuc} = K_1.\theta_{O2}.\theta_X^{\ 2} \quad (3.33)$$

(Where: θ_{O2}: 5Co/AC surface occupied by oxygen and θ_X: 5Co/AC surface occupied by meta-xylene and $K_1.\theta_{O2} = \text{const}$.

Moreover, according to kinetic of heterogenous catalysis:

$$\theta_X = q_0 \frac{K_X.P_X}{1 + K_X.P_X}$$

Then, $$r = k_2.K_1.\theta_{O2}.\left(q_0.\frac{K_X.P_X}{1 + K_X.P_X}\right)^2 \quad (3.34)$$

If assumed $K_X.[X]_{hp} << 1$, and $k_{surface} = k_2.K_1.\theta_{O2}.q_0^{\ 2}.K_X^2$

Then rate equation as followwed: $$r_{pubm} = k_{suface}.(P_X)^2 \quad (3.35)$$

The equation (3.35) coincides with the empirical equation (3.27). Thus, the reaction mechanism of *meta*-xylene adsoption on 5Co/AC is based on two ideas:

(i) Oxygen adsorbed on active center Co_3O_4 as O_2 molecule $(Co_3O_4\text{-}O_2)_{ad}$

(ii) *meta*-xylene adsorbed on AC active center, two adsorption complexes $(X\text{-}AC)_{ad}$ move to the same active center $(Co_3O_4\text{-}O_2)_{ad}$ to create new surface complex $(X_2\text{-}Co_3O_4\text{-}O_2)_{ad}$, the reaction between X and O occurs within the adsorption complex.

CONCLUSION

Based on the results presented in the thesis, we can draw the following conclusions:

1. Successfully synthesized bi-functional adsorption/catalytic materials (Co/AC) based cobalt oxide and activated carbon Tra Bac. Materials characterization was assessed by the chemo-physical methods such as TEM, BET, H_2-TPR, XPS, O_2-TPD. Results showed that the cobalt oxide dispersed in the form of Co_3O_4 on AC. The tiny nano Co_3O_4 clusters scattered in the micropore is considered as active sites for oxidation *meta*-xylene. Cobalt oxide clusters of particles ~ (20 - 5 nm) distributed fairly regularly on the outer surface of the AC.

2. Studied the *meta*-xylene adsorbent on activated carbon and the results showed that activated carbon adsorption has two separate areas depending temperature range.

The meta-xylene adsorbed on the activated carbon is assumed to be due to interactions π-π interaction and no competition by air oxygen. The presence of Co_3O_4 reduces negligibly adsorption capacity of activated carbon.

3. Studied *meta*-xylene oxidation in air over dual functional Co/AC by continuous flow oxidation (one step). *Meta*-xylene conversion reaches 23 - 55% at 180 - 250°C in conditions VHSV = 1936.11 h^{-1}, flow rate W = 2.0 L / h.

4. Proposed adsorption/catalyst technique (two stages oxidation technique) using bi-functional material Co/AC. *meta*-xylene conversion efficiency is 99% at temperature 180 - 200°C and VHSV = 1936.11 h^{-1}.

5. Suggested *meta*-xylene catalytic oxidation by air following Langmuir-Hinshelwood mechanism: *meta*-xylene is prioritized on activated carbon and Co_3O_4 act as the active site which adsorbed oxygen priority air.

6. Kinetics of catalytic oxidation of *meta*-xylene is different when different techniques are used. With continuous flow technique, kinematic equation is the form of $r = k_{bk}.P_X^{0,25}$. With adsorption/catalyst technique, kinematic equation is the form of $r = k_{bk}.[X]_{ad}^2$

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