CHAPTER VII
CATALYSIS OF BIMETALLIC Fe-Ti-MCM-48 FOR PHENOL HYDROXYLATION AND ITS HYDROTHERMAL STABILITY

7.1 Abstract

The phenol hydroxylation was studied in the presence of Fe-MCM-48, Ti-MCM-48, and Fe-Ti-MCM-48 using hydrogen peroxide as oxidant and water as solvent. The influence parameters, viz. reaction time, temperature, phenol to oxidant ratio, catalyst content, and metal loading were investigated. Type of treatment, thermal and photo treatment, was also studied. The optimum conditions observed with the thermal treatment were follows: 30 mg catalyst content, 1:2 phenol:H_2O_2, 323 K reaction temperature, and 2 h reaction time. The photocatalytic system at room temperature resulted in better properties than the thermal system, giving up to 85.6% phenol conversion under optimum condition when using 0.01Fe-MCM-48. As introducing Fe to Ti-MCM-48, the conversion was improved to 58.2% while Ti enhanced the hydrothermal stability of Fe-MCM-48.

7.2 Introduction

Organic pollutants from industrial wastewater affect ecosystems and human health. One of the main water pollutants is phenol which causes harm even at low concentrations.[1] The route for changing this toxic compound to valuable products is to carry out via hydroxylation of phenol. The main product from this oxidation reaction is hydroquinone (HQ) and catechol (CAT) normally used in a wide range of applications, such as pharmaceuticals, antioxidants, polymerization inhibitors, and photographic developer.[2] The strong reductant HQ can be converted to benzoquinone (BQ) by losing two electrons, leading to a bioinspired redox couple of HQ/BQ in dye-sensitized solar cells. [3, 4]

Phenol hydroxylation occurs easily in the presence of a catalyst. However, the homogeneous catalysts are difficult to recover after the reaction. Thus, a heterogeneous catalyst becomes more attractive in this aspect. Unlike microporous materials, mesoporous materials play an important role in term of having larger pores, allowing larger molecules to diffuse through or react in the pores.[5] One of the well-known mesoporous materials, first discovered by Mobil Oil scientists, is the M41S family, having high internal surface areas and narrow pore size distributions.[6] An important mesoporous silicate in this family which was focused in this work is the cubic phase MCM-48, exhibiting three-dimensional channels. These channels prevent pore blockage and allow faster diffusion of reactants than one-dimensional pores.[7] Thus, MCM-48 was applied in many applications, such as catalyst, catalyst support, adsorbent, sensor, and inorganic template.[8] However, pure silica MCM-48 limits the catalytic activity due to lack of active sites. The key to enhance the catalytic ability of the material is to incorporate a heteroatom into MCM-48. Iron (Fe) having high sensitivity in the oxidation-reduction reaction, has been mostly investigated in the oxidation of phenol. Fe incorporated MCM-48 framework performed 43.6% phenol conversion, as reported by Zhao et al.[9] Choi et al.[10] reported that the formation of Fe-O-Si bond in Fe-MCM-41 was an advantage for phenol hydroxylation. Ti substituted mesoporous material, e.g. Ti-MSU, by Song et al.[11] showed phenol conversion ability over Ti-MCM-41 and Ti-HMS due to the three-dimensional pore structure of MSU which reduces the

probability of pore blocking and increases the reactive sites of surface. A good catalytic ability was also observed in Ti-SBA-12 and Ti-SBA-16 because of its three-dimensional pore system as well.[12] However, the phenol conversion percentage using Ti mesoporous silicate catalysts was lower than 25% [11, 12] since Ti is sensitive under UV light.[13]

In this study, bimetallic mesoporous material of Fe-Ti-MCM-48 for the hydroxylation of phenol using 30%w/v H_2O_2 oxidant in water was investigated to expectedly enhance the interaction of the components over a support with new structural and redox properties.[14] Monometallic mesoporous materials of Fe-MCM-48 and Ti-MCM-48 were also studied for comparison. The reaction time, temperature, catalyst content, and amount of oxidant were systemically examined. Leaching, reusability, and hydrothermal stability were observed, as well.

7.3 Experimental

7.3.1 Materials

Fumed silica (99.8%, SiO_2) from Nippon Aerosil, iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), catechol (CAT, 99%), hydroquinone (HQ, 99%), 1,4-benzoquinone (BQ, 98%) from Sigma-Aldrich, USA, titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$) from Acros Organics, cetyltrimethylammonium bromide (CTAB) from Fluka, ethylene glycol (EG) from J.T. Baker, triethanolamine (TEA) from QREC, acetronitrile (CH_3CN, 99.9%), methanol (CH_3OH, 99.9%), and sodium hydroxide (NaOH) from Labscan, phenol detached crystals and hydrogen peroxide (H_2O_2, 30% w/v) from Fisher scientific, UK, were used without purification.

7.3.2 Synthesis of xFe-yTi-MCM-48

Fe-Ti-MCM-48 was synthesized according to Longloilert *et al.*[15] The molar ratio of gel composition was $1.0SiO_2:0.3CTAB:0.5NaOH:62.0H_2O:xFe:yTi$, where $0.01 \leq x,y \leq 0.09$. A desired amount of $FeCl_3 \cdot 6H_2O$ was dissolved in water, followed by addition of 2 M NaOH while the solution was continuously stirred. The solution was slightly heated at 323 K and simultaneously added CTAB. Then silatrane prepared, as reported elsewhere, [16] was added and stirred for 1 h. The mixture was transferred into a teflon-lined stainless steel vessel and autoclaved at 413 K for 16 h. The solid product was filtered and washed with distilled water. The sample was calcined at 823 K for 6 h with a heating rate of 274.5 K/min after drying. MCM-48, Fe-MCM-48 and Ti-MCM-48 were also prepared using the same procedure.

7.3.3 Characterization

The structure of the synthesized sample was characterized according to the study reported elsewhere.[17] X-ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer with CuKα radiation. N_2 adsorption and desorption isotherms were determined by a Quantasorb JR instrument using the Brunauer–Emmett–Teller (BET) method. Diffuse reflectance UV-vis (DRUV) spectra were performed using a Shimadzu UV-2550. The elemental analysis of the different metals was carried out on PANalytical AXIOS PW 4400 model X-ray fluorescence (XRF). Transmission electron micrographs (TEM) were characterized on a JEOL JEM-2010.The product from the reaction was analyzed by high performance chromatography (HPLC, SPD-M20A Shimadzu) with a C-18 reverse-phase column (Inertsil ODS-3) using 10 vol% CH_3CN and 10 vol% methanol in water as a mobile phase at a flow rate of 1.0 ml/min and a UV detector operating at 254 nm.

7.3.4 Phenol hydroxylation

The catalytic experiment was performed in a 50 ml reaction flask equipped with a reflux condenser, a temperature controllable oil-bath, and a magnetic stirrer. Phenol (1.88 g, 20 mmol) and 30% aqueous H_2O_2 (2.28 g, 20 mmol) were introduced to 10 ml of water and the mixture was heated with vigorous stirring.[18] The optimum condition from thermal system was also used for the photocatalytic activity study at room temperature under UV radiation (100 W Hg Sylvania UV lamp). The product was analyzed by HPLC.

7.3.5 Leaching and reusability of catalysts

Leaching of metal ions was investigated at 323 K. The catalyst was filtered from the 30 min reaction time mixture before allowing the filtrate to react further at the same condition. The reaction was continued for 2 h. Before and after separating the catalyst, the solution was collected and identified the product by HPLC.

After the reaction, the used catalyst was filtered and washed with distilled water. The impurities were cleaned by calcination at 773 K for 2 h. The reusability was observed by using the used catalyst for the second and third runs.

7.3.6 Hydrothermal stability

The catalyst was recovered by filtration, washed with distilled water, and calcination at 773 K after finishing the experiment at 323 K for 2 h. The hydrothermal stability of the samples was investigated by XRD and nitrogen adsorption.

7.4 Results and Discussion

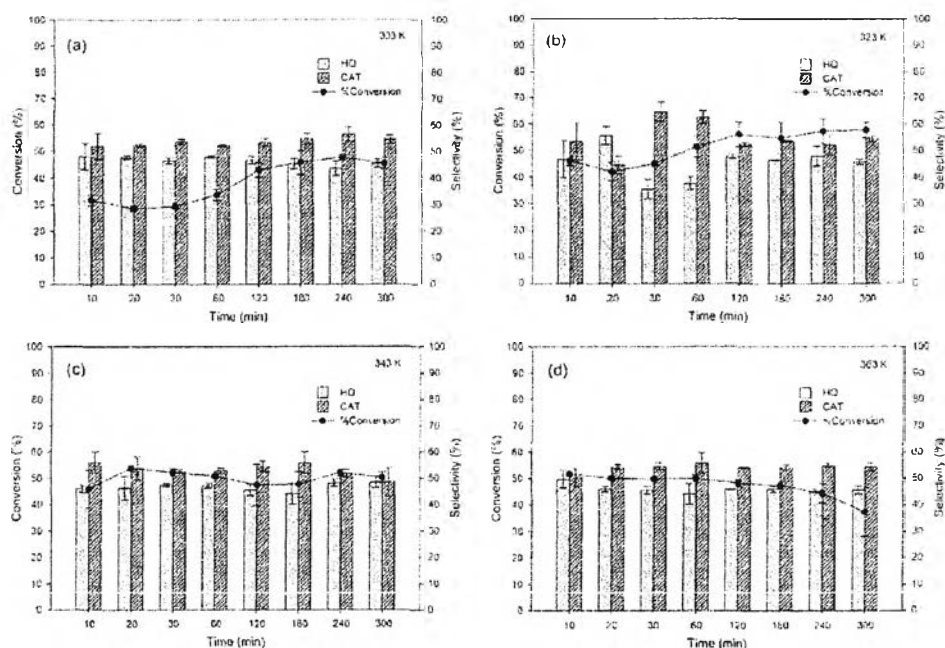### *7.4.1 Effects of the reaction time and temperature*

Figure 7.1 Phenol conversion and product selectivity using 30 mg of 0.01Fe-0.01Ti-MCM-48, 1:1 phenol:H_2O_2, and 5 h reaction time at (a) 303, (b) 323, (c) 343, and (d) 363 K.

Figure 7.1 shows the phenol conversion data over 0.01Fe-0.01Ti-MCM-48 at different times and temperatures. Increase of the reaction temperature from 303 to 323 K tended to increase the phenol conversion. However, the reaction reached a maximum conversion in a short time at 343 and 363 K, giving 53.9 %conversion in 20 min and 51.6 %conversion in 10 min, respectively. The phenol conversion took place immediately to a steady state at a high temperature due to an increase in the reaction rate as increasing the temperature, resulting in the disproportionately large increase in the number of high energy collisions.[19,20] Besides, the conversion obviously dropped after 5 h at 363 K because the thermal decomposition of H_2O_2 occurred at a high temperature, making the oxidant

concentration drastically decrease.[21] Similarly, the phenol conversion decreased as the temperature was higher than 323 K. The high selectivity of CAT over HQ was observed for most of reaction times and temperatures since it was a kinetically favorable product.[20] Based on the results, 323 K reaction temperature for 2 h reaction time was thus the optimal conditions, providing 56.0%conversion with 47.7% HQ and 52.3% CAT selectivity.

7.4.2 Effect of the phenol and H_2O_2 molar ratio
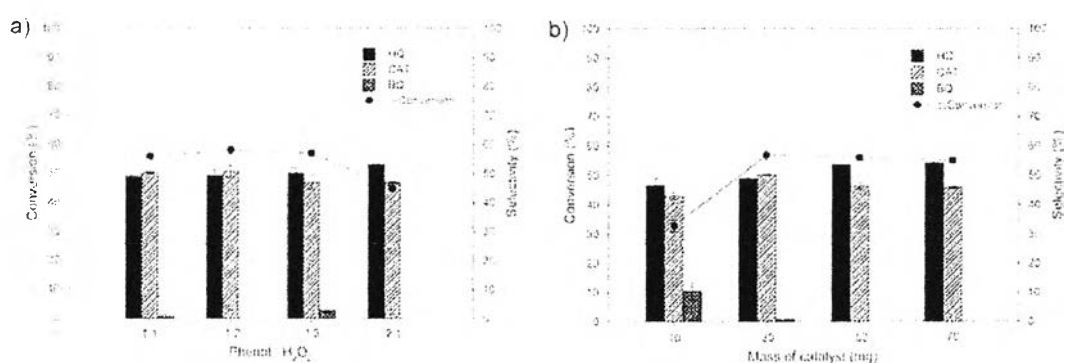

Figure 7.2 Phenol conversion and product selectivity using 0.01Fe-0.01Ti-MCM-48 at 323 K for 2 h reaction time with respect to a) phenol:H_2O_2 molar ratio and b) the amount of catalyst using 1:2phenol:H_2O_2.

The effect of the phenol and H_2O_2 molar ratio using 0.01Fe-0.01Ti-MCM-48 catalyst is presented in Fig. 7.2a. The phenol conversion increased with an increase in H_2O_2 amount. At a low oxidant content (phenol:H_2O_2 = 2:1), the conversion was 45.0% and showed a progressive increase to 55.9, 57.9, and 57.0% as an increase of phenol:H_2O_2 from 1:1 to 1:2 and 1:3, respectively. This could be due to the increase of hydroxyl radicals from H_2O_2 decomposition which enhanced the phenol conversion.[22] However, the selectivity of CAT, HQ, and BQ had no relevant with H_2O_2 concentration since the selective oxidation to produce CAT, HQ and BQ was difficult to control especially at high oxidant concentration.[22]. In this

case, the reactant and oxidant molar ratio of 1:2 gave the best phenol conversion of 57.9%.

7.4.3 Effect of the catalyst content

The effect of different catalyst contents of 0.01Fe-0.01Ti-MCM-48 is shown in Fig. 7.2b. When increasing the amount of catalyst from 10 to 30 mg, the conversion of phenol increased from 32.9 to 56.9%. This could be resulted from more active sites as an increase of catalyst amount.[23] However, the conversion slightly decreased to 56.0 and 55.1% as the catalyst content increased from 50 to 70 mg since high amount of catalyst provided large surface area for H_2O_2 association to form the active intermediate too fast to affect the reaction.[18] Meanwhile, the selectivity of the products did not change significantly with the catalyst content. Thus, 30 mg of the catalyst was considered as the optimal catalyst content, resulting in a good phenol conversion to 48.9% HQ, 50.2%CAT, and 1.3% BQ.

7.4.4 Effect of the metal loading

The catalytic activity for the phenol hydroxylation using various metal contents under thermal and photocatalytic conditions is summarized in Tables 7.1 and 7.2, respectively. Under the thermal condition at 323 K, the conversion was low when the system contained either no any catalyst or pure siliceous MCM-48, giving only 11.4 or 12.7% conversion, respectively. The main reason is no metal active sites for the hydroxyl radical active species to perform efficiently.[24] On the other hand, the system containing 0.01Fe-0.01Ti-MCM-48 catalyst and no H_2O_2 oxidant resulted in no reaction (not shown) due to no active hydroxyl radical generator. Fe-MCM-48 catalyst with 0.01 Fe/Si molar ratio showed the best phenol conversion, yielding 82.4% after 2 h reaction time at 323 K. This result was remarkably improved the catalytic ability of Fe-MCM-48, as compared to that reported by Zhao et al. [9] whose Fe-MCM-48 provided only 43.6% conversion after 4 h reaction time at 333 K.

For Ti-MCM-48, the catalytic activity increased from 16.2 to 31.6% conversion as increasing the amount of Ti to 0.09Ti-MCM-48 again due to an increase of metal center active sites.[21] This conversion result was considerably improved when comparing to the activity of Ti-MSU[11], Ti-SBA-12 or Ti-SBA-16[12]. One of the reasons could be a larger surface area of Ti-MCM-48 to provide more available active sites.[18, 21]

Table 7.1 Effect of metal loading onto MCM-48 on the phenol hydroxylation under thermal condition

Catalyst	Conversion (%)	Selectivity (%)			CAT/HQ
		HQ	CAT	BQ	
No catalyst	11.4	0	19.9	80.1	-
MCM-48	12.7	0	16.3	83.8	-
0.01Fe-MCM-48	82.4	49.0	50.0	1.1	1.20
0.01Ti-MCM-48	16.2	79.8	20.2	0	0.25
0.03Ti- MCM-48	20.5	60.2	39.8	0	0.66
0.05Ti- MCM-48	28.0	48.7	24.1	27.1	0.49
0.07Ti- MCM-48	25.8	50.1	23.3	26.5	0.47
0.09Ti- MCM-48	31.6	32.7	22.9	44.4	0.70
0.01Fe-0.01Ti- MCM-48	56.9	49.3	50.7	0	1.03
0.01Fe-0.03Ti- MCM-48	35.4	39.6	47.1	13.3	1.19
0.01Fe-0.05Ti- MCM-48	30.5	37.7	41.6	20.8	1.10
0.01Fe-0.07Ti- MCM-48	17.0	25.8	40.1	34.1	1.55

Reaction conditions: Phenol: H_2O_2 = 1:2, catalyst = 30 mg, T = 323 K, reaction time = 2 h.

When comparing between Ti-MCM-48, Fe-MCM-48, and bimetallic Fe-Ti-MCM-48, Fe had much higher sensitivity than Ti for the phenol hydroxylation whereas bimetallic Fe-Ti-MCM-48 gave a higher phenol conversion than Ti-MCM-48, but a lower phenol conversion than Fe-MCM-48. Moreover, the phenol conversion using the bimetallic catalyst decreased with an increase Ti content in the catalyst. As explained by Adam *et al.*, [18] the high metal content caused the metal clusters, giving less active species for the phenol hydroxylation. The presence of Fe in Ti-MCM-48 improved the ability of Ti from 16.2 to 56.9% conversion and provided more than 1 CAT:HQ ratio at 0.01Ti/Si molar ratio. Large amount of BQ was observed in the low phenol conversion, as a result of the over-oxidation of HQ in the high concentration of H_2O_2.[25]

Under the UV radiation at room temperature, no conversion was observed in the system with no oxidant (not shown) owing to lack of active radical generator. The phenol hydroxylation results in Table 7.2 indicated that the conversion of the systems with only pure MCM-48 or no catalyst was 30.9 or 23.4%, respectively, which was higher than those under the thermal condition. This is probably due to the fact that the UV light induces the decomposition of H_2O_2 better than the heat. Fe-MCM-48 gave the conversion under the irradiation, 85.6%, slightly better than that under the heat, 82.4%. As expected for Ti-MCM-48, the phenol conversion increased with an increase of Ti content because Ti induces more metal center active sites under the irradiation.[21] However, the activity dropped as the concentration of Ti was over than 0.05 Ti/Si molar ratio due to the aggregation of TiO_2 which reduced the number of active sites for the light penetration.[26] Comparison between the best conversions of Ti-MCM-48 under the thermal and the photo conditions, 0.05Ti-MCM-48 under UV radiation showed better activity (34.4% conversion) than 0.09Ti-MCM-48 under applied heat (31.6% conversion). Therefore, it can be concluded that Ti substituted MCM-48 was rather sensitive with the light than the heat. For bimetallic Fe-Ti-MCM-48, the conversion decreased with increasing Ti amount owing to the metal cluster formation which shielded the light and active sites.[26] Incorporation of Fe enhanced the conversion of Ti-MCM-48. The amount of BQ product under the UV light was significantly larger than that

under the heat. This could be from the fact that the light intensity (100 W) used was not sufficient to convert BQ to a higher energy HQ.[27] Most samples had CAT/HQ ratio more than 1 because CAT was the kinetically product. Ortho position was close to the electron donor group, thus, CAT formed rapidly during the reaction.[20]

Table 7.2 Effect of metal loading onto MCM-48 on the phenol hydroxylation under UV light

Catalyst	Conversion (%)	Selectivity (%)			CAT/HQ
		HQ	CAT	BQ	
No catalyst	23.4	21.0	24.9	54.2	1.19
MCM-48	30.9	27.9	36.7	35.5	1.32
0.01Fe-MCM-48	85.6	48.9	51.1	0	1.04
0.01Ti-MCM-48	10.7	46.8	19.9	33.3	0.43
0.03Ti- MCM-48	12.2	31.8	27.6	40.6	0.87
0.05Ti- MCM-48	34.4	20.7	33.5	45.7	1.62
0.07Ti- MCM-48	23.2	19.9	31.3	48.7	1.57
0.09Ti- MCM-48	27.6	12.0	26.5	61.5	2.21
0.01Fe-0.01Ti- MCM-48	58.2	31.6	49.8	18.6	1.58
0.01Fe-0.03Ti- MCM-48	40.3	24.1	36.5	39.4	1.51
0.01Fe-0.05Ti- MCM-48	38.1	18.6	34.3	47.2	1.84
0.01Fe-0.07Ti- MCM-48	17.1	3.8	21.3	74.9	5.61

Reaction conditions: Phenol: H_2O_2 = 1:2, catalyst = 30 mg, T = room temperature, reaction time = 2 h.

Under both thermal and light conditions, Fe-MCM-48 performed the best catalytic activity while Ti-MCM-48 was more effective under the light. Among bimetallic MCM-48 catalysts, 0.01Fe-0.01Ti-MCM-48 showed the optimum

conversion. Under UV radiation, the overall phenol conversion was improved since the light induced H_2O_2 decomposition efficiently. However, the selectivity was much impressive since the pore diameter of the synthesized catalysts was in a range of 2-3 nm while the molecular sizes of HQ and CAT were about 0.5 nm [28], thus there was no product selectivity since both HQ and CAT can easily pass through the pore of catalyst. The light intensity and the oxidant concentration influenced only on the BQ formation.

Table 7.3 Leaching test of 0.01Fe-0.01Ti-MCM-48 for the phenol hydroxylation

Time (min)	Conversion (%)	Selectivity (%)			CAT/HQ
		HQ	CAT	BQ	
30	30.0	19.8	36.0	44.2	1.82
40	26.1	15.0	31.2	53.8	2.08
50	26.4	15.7	31.5	52.8	2.01
60	27.4	15.0	32.9	52.1	2.20
120	28.8	19.8	37.7	42.5	1.90

Reaction conditions: Phenol: H_2O_2 = 1:2, catalyst = 30 mg, T = 323 K, reaction time = 2 h.

7.4.5 Leaching and reusability of catalysts

The leaching test for 0.01Fe-0.01Ti-MCM-48 is shown in Table 7.3. The catalyst was removed after 30 min stirring and the solution was allowed to continue further reaction. After the removal of catalyst, the phenol conversion slightly decreased from 30.0% (30 min) to 28.8% (120 min) which had insignificant change in both the conversion and the CAT/HQ ratio (about 2). Therefore, it can be stated that the leaching of metal ions is neglect.

0.01Fe-0.01Ti-MCM-48 was also used to study the reusability. After first run, the used catalyst was washed with distilled water and calcined at 500 °C. It was found that the second run showed a dramatically drop of phenol conversion from 60.2 to 8.2%, implying the collapse of catalyst which blocked the active sites.

7.4.6 Hydrothermal stability

Figure 7.3 illustrates the XRD patterns of 0.01Fe-MCM-48, 0.01Ti-MCM-48 and 0.01Fe-0.01Ti-MCM-48 after hydrothermal stability test at 323 K for 2 h. The peak of Fe-MCM-48 was less order while Ti-MCM-48 still remained its well-order structure, as mentioned by Galacho et al., who reported that the hydrothermal stability of mesoporous titanosilicate materials was improved through the presence of Ti extra-framework which shielded the water molecule to attack the siloxane bonds.[29] As Ti was introduced into Fe-MCM-48, the hydrothermal stability slightly improved.
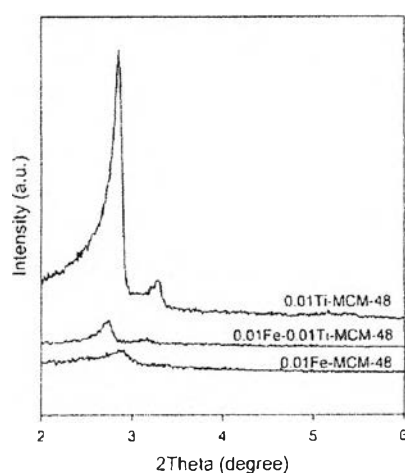

Figure 7.3 XRD patterns of 0.01Fe-MCM-48, 0.01Ti-MCM-48, and 0.01Fe-0.01Ti-MCM-48 after hydrothermal stability test at 323 K for 2 h.

Figure 7.4 presents isotherms and pore size distribution of 0.01Ti-MCM-48, 0.01Fe-MCM-48 and 0.01Fe-0.01Ti-MCM-48 after hydrothermal stability test at 323 K for 2 h. The capillary condensation of 0.01Fe-MCM-48 was less steep

and the broad pore size distribution was obtained due to the destruction of the structure from the reaction. While 0.01Ti-MCM-48 and 0.01Fe-0.01Ti-MCM-48 still showed the sharp capillary condensation step with narrow pore size distribution, meaning that the presence of Ti slightly improved the hydrothermal stability in the bimetallic MCM-48.
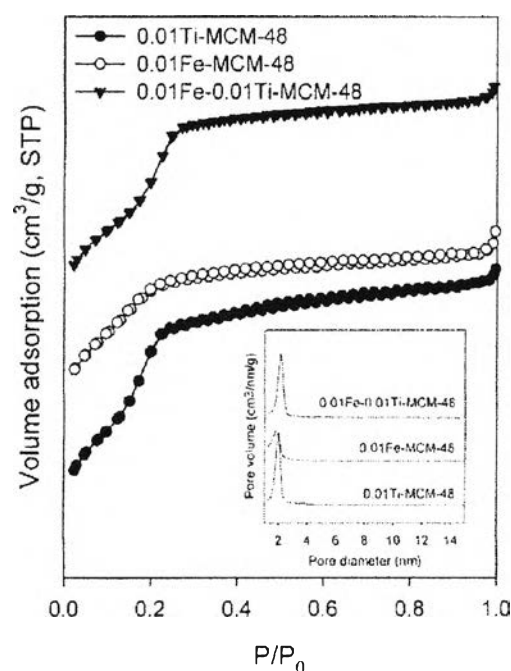

Figure 7.4 N$_2$ adsorption/desorption isotherms and pore size distribution of 0.01Ti-MCM-48, 0.01Fe-MCM-48, and 0.01Fe-0.01Ti-MCM-48 after hydrothermal stability test at 323 K for 2 h.

7.5 Conclusions

The phenol hydroxylation was carried out using Fe-MCM-48, Ti-MCM-48 and Fe-Ti-MCM-48 as the catalyst. The best activity was belonging to 0.01Fe-MCM-48. However, Fe-MCM-48 lacked the hydrothermal stability. The advantage of bimetallic materials was proved that both Ti and Fe were supplementing each other. Ti slightly improved the hydrothermal stability of Fe-MCM-48 and Fe obviously

enhanced the catalytic activity of Ti-MCM-48. No leaching of metal ions was observed, but the reusability was not successful.

7.6 Acknowledgements

7.7 References

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