

Study on the of MCM-41-supported for the hydroxylation of naphthalene to naphthol

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Abstract. Prepared by impregnation of MCM-41 molecular sieve, zeolite and modified MCM-41; to load 5% of modified Fe/MCM-41 zeolite catalyst, the reaction temperature 60°C, reaction time 8h, hydrogen peroxide 2mL, naphthalene under 1000mg, Fe/MCM-41 catalyst 100mg conditions, naphthalene conversion rate of 5.8% and a selectivity of 45.7%. MCM-41 not only can better maintain the characteristics of the modified hexagonal structure of MCM-41 molecular sieve, and in the hydroxylation reaction of naphthalene-naphthol in the performance of certain catalytic activity in different solvents (acetic acid, acetonitrile, methanol, ethanol, ethyl acetate), hydroxylation of naphthalene tests showed the best solvent was acetonitrile.

1 INTRODUCTION

The formula of monohydric naphthols are $C_{10}H_8O$, there are 1-naphthol and 2-naphthol two isomers, have a molecular weight of 144.17. Naphthol is a very important chemical intermediate raw materials, which is widely used in dyes, medicines, spices, medicine and so on. In recent years, a number of naphthol derivatives developed and widely used, resulting in large demand, market prospects were more optimistic. Transition metal titanium, vanadium, chromium, silver and other metals have variable valency element, and since the redox properties of these elements, the introduction of the zeolite MCM-41 molecular sieves. MCM-41 have a hexagonal structure and a one-dimensional straight channel pore size in the range 2-10nm be adjusted concentrated pore distribution, large surface area and adsorption capacity, within the framework embedded Al, Nb, Zr, B, etc. to adjust the acidic heteroatom. Recently, studies on mesoporous molecular sieve as a carrier of middle distillate aromatics saturation and deep hydrodesulfurization catalysts are of great concern.

1 EXPERIMENTAL SECTION

1.1 Catalyst preparation

Supported catalysts prepared by impregnation of metal components. Specific preparation methods for example as follows: MCM-41 samples were calcined twice and placed in a muffle furnace, a non-hermetic. Calcined at 250 degrees for 1-2 h, warmed to 350 °C, calcined 1-2 h, heated at 550 °C calcined for 3-4h. Description: The sample will be black, black smoke, white to room temperature until re. Remove cooled to ready for use at room temperature. Containing (Fe, Cu, Mn) salt is dissolved in 25mL methanol solution, and stir until completely dissolved solvent preparation, accurate weighing and adding MCM-41, stirred 4h, stewing 4h, rotary evaporation, 110 °C dried overnight, 550 °C calcined 5h, to obtain a catalyst Fe/MCM-41.

1.2 Characterization of the samples

The catalysts were characterized by X-ray diffraction(XRD), Fourier transform infrared spectroscopy (FT-IR) and Transmission Electron Microscope(TEM).

1.3 Catalytic experiments

The reaction is stirred in an oil bath temperature magnetic three-necked flask, and equipped with a thermometer and a condensing unit. Standard addition order is: in solvent was added 25.0 mL of naphthyl 1g, 0.05 ~ 0.15 g catalyst was added all at once at the reaction temperature and the reaction time is counted, 1mL ~ 3 mL of aqueous hydrogen peroxide (30%), by dropping funnel was slowly added dropwise to the reaction system, the hydrogen peroxide was added dropwise, the dropping rate of approximately 0.02mL / min. After the addition was complete, the reaction after 8h, cooled to room temperature and quantitatively analyzed. The reaction temperature is 50 ~ 90 oC, 2h each sample test.

We use liquid chromatography to test sample. Liquid chromatography to Beijing LabTech Instruments Incorporated (LabTech LC600 HPLC), chromatography conditions used: C18 column with a mobile phase of methanol/water = 58/42, the detection wavelength to 220nm, flow rate of 0.8mL / min.

2 RESULT AND DISCUSSION

2.1 XRD results

Figure 1 is a carrier and a catalyst XRD spectra. It is seen from Figure 1, which is typical of the pattern of MCM-41, where $\theta = 2.2$ Role of the diffraction peaks can be attributed to the (100) crystal face diffraction. The crystal face (110), (200) and (210) diffraction peak corresponding to the pattern is not evident, indicating that the catalyst does not appear XRD pattern of sample metal oxide (Fe₂O₃, CuO, MnO₂) characteristic diffraction peaks, i.e. doping MCM-41 may be in the elements of the skeleton, or highly dispersed mesoporous surface.

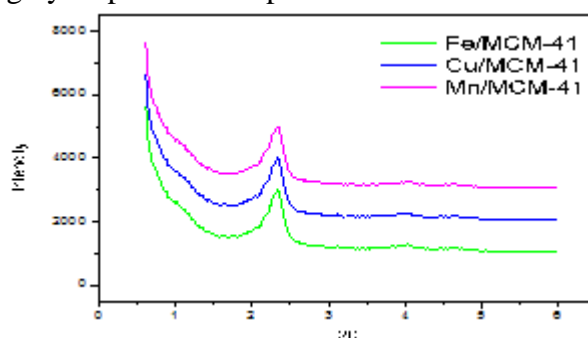


Figure 1. XRD spectra of MCM-41(Fe,Cu,Mn)

2.2 Internal flow field analysis

Static pressure distribution.

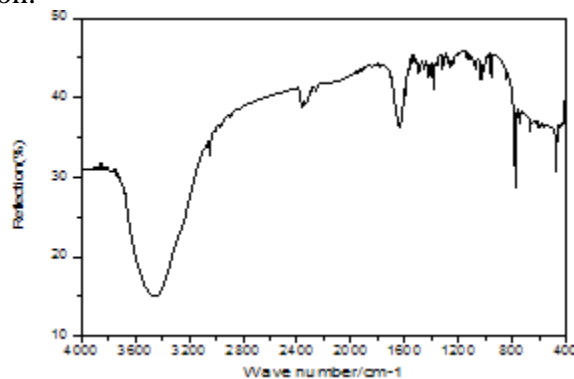


Figure 2. FT-IR for Fe/MCM-41

Figure 2. shows that

FTIR spectra of MCM-41 1000cm⁻¹ absorption peak represents close skeleton Si-O-Si asymmetric stretching vibration between, 810cm⁻¹ absorption peak is close to Si-O-Si stretching vibration, 450 cm⁻¹ belongs to Si-O-Si bending vibration. Figure 3.2 Fe/MCM-41 mesoporous molecular sieves IR spectra, 950 cm⁻¹ attributable to Si-OH vibration, probably due to the adsorption of metal ions of iron, this peak is enhanced, and tiny red shift. At the same time some of the molecular sieve adsorption of metal ions, the calcined at 3400 cm⁻¹ hydroxy-peak has not diminished, indicating that the surface structure of the molecular sieve and not due to the adsorption of metal ions and change.

2.3 Catalytic activity

Table 1. shows that all of the supported MCM-41 catalyst, the catalytic effect of Fe/MCM-41 of the best, naphthol selectivity of 45.7%, followed by the catalytic effect of Fe/MCM-41>Cu/MCM-41>Mn/ MCM-41>MCM-41. Mainly due to the copper surface of the molecular sieve to four ligands and eight-coordinated form, prone to stronger Jahn-eller effect, and acetonitrile, water, hydrogen peroxide molecules coordinated, resulting in greater redox potential. And Mn in theory prone Jahn- Teller effect, but Mn / MCM-41 conversion rate of only 2.2%. Probably due to hydrogen peroxide decomposition catalyst in the MnO₂ faster, it failed to effectively carry out the hydroxylation reaction.

Table 1. impact on naphthalene hydroxylation reaction without catalyst

Catalyst	Naphthalene Con. (%)	1-Naphthol Sel. (%)	2-Naphthol Sel. (%)
MCM-41	0.3	9.2	2.1
Fe/MCM-41	5.8	33.9	11.8
Cu/MCM-41	4.9	27.6	5.7
Mn/MCM-41	2.2	11.4	2.8
No	0.2	6.1	1.2

Reaction conditions: Naphthalene (1000 mg, 7.81 mmol), hydrogen peroxide (30 wt.%, 2 mL, 19.7 mmol), acetonitrile (25 mL), 60 °C, 8 h

2.4 Catalyst amount

With the increase of the amount of catalyst, the conversion and selectivity of naphthalene naphthol significantly increased, and when the amount of the catalyst to reach 100mg, reaction selectivity and conversion rate reaches a maximum, but when the amount of catalyst was more than 100mg, although the conversion and selectivity have increased, but the increase is not that big. Therefore, appropriate amount of catalyst is 100mg.

2.5 Solvent effects

Table 2. shows that a greater impact on the type of solvent naphthalene naphthol hydroxylation reaction, wherein acetonitrile as solvent, the yield of naphthalene naphthol hydroxylation reaction selectivity higher, 1-naphthol and 2-naphthol selectivity respectively, 33.9% and 11.8%.

In Fe/MCM-41 catalyst, respectively, acetonitrile, acetic acid, ethyl acetate, methanol, ethanol larger solvent conversion difference naphthol naphthyl hydroxylation reaction, mainly due to the inner surface of the oxygen-containing solvent with the molecular sieve hydroxyl groups readily form hydrogen bonds formed catalytic decomposition of hydrogen peroxide resistance, solvent and oxygen atoms may also be involved in metal ion zeolite surface reaction with hydrogen peroxide, naphthalene competitive adsorption on the surface of MCM-41 molecular sieve, especially acetic acid and ethyl alcohol, which with hydrogen peroxide, the catalyst is formed liquid-solid three-phase, in-

creasing the mass transfer resistance. The acetonitrile is a weakly basic aprotic solvent, is the most widely used aromatic hydroxylated solvents, conducive to decomposition of hydrogen peroxide into hydroxyl radicals and peroxy radicals. While not inert solvent acetonitrile, and hydrogen peroxide can form oligomers, change over time, to form an intermediate. The formula shown, this process may be transferred to the hydroxyl radicals naphthyl, final forming naphthol. In addition, the acetonitrile cyano nitrogen and iron and copper may also effect, weakening the decomposition of hydrogen peroxide to produce hydroxyl radicals, inhibiting the rapid decomposition of hydrogen peroxide. Therefore, the hydroxylation of naphthalene naphthol more suitable solvent is acetonitrile.

Table 2. catalysis different solvents hydroxylation reaction results

Solvent	Co n. (%)	1- Naphthol Sel. (%)	2- Naphthol Sel. (%)
acetonitrile	5.8	33.9	11.8
acetone	3.3	18	3.2
acetic acid	3.2	19.8	5.6
ethyl acetate	2.2	11.4	1.9
methyl alcohol	1.9	7.1	3.2
ethyl alcohol	1.5	6.1	3.1

Reaction conditions: Naphthalene (1000 mg, 7.81 mmol), hydrogen peroxide (30 wt.%, 2 mL, 19.7 mmol), Solvent (25 mL), 60 °C, 8 h

2.6 Reaction temperature

Figure 3. shows that with the reaction temperature, the conversion and selectivity of naphthalene increased first decrease. When the reaction temperature was raised from 40 oC to 60 oC, the conversion rate from 1.2 percent to 5.8 percent increase in selectivity by a 8.7% increase to 45.7%; When the reaction temperature is 60 oC, the maximum conversion rate of naphthalene was 5.8 percent; when the reaction temperature is 70 oC, the maximum naphthol selectivity is 46.8%. Mainly due to a temperature above 60 oC, accelerates the decomposition of hydrogen peroxide, resulting in reduced utilization of hydrogen peroxide, the conversion rate decreases but the selectivity at 70 oC naphthol has reached the maximum value, after the catalytic naphthalene to generate naphthol, naphthol increase and the solubility of the reaction system, and as the reaction proceeds, hydrogen peroxide decomposition rate accelerates, there is not enough time for the deep oxidation of hydrogen peroxide continue naphthol. However, the temperature reached 70 oC, naphthalene conversion rate sharply dropped, is not conducive to the reaction proceeds. Therefore, the more appropriate reaction temperature is 60 oC.

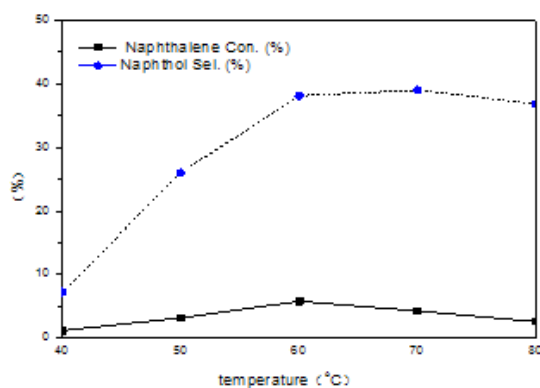


Figure 3. Conversion-selectivity-reaction temperature in naphthalene hydroxylation; Reaction conditions: Naphthalene (1000 mg, 7.81 mmol), hydrogen peroxide (30 wt.%, 2 mL, 19.7 mmol), acetonitrile (25 mL), 8 h

2.7 Reaction temperature

Figure 4. shows that with increasing reaction time, the conversion of naphthalene and selectivity of naphthol increased, when the reaction time reach 8h, the conversion trend with the reaction time is slower; when the reaction time exceeds 10h, naphthol choice decreased rapidly. Mainly due to the initial reaction, higher concentrations of hydrogen peroxide, naphthalene opportunities for contact with an oxidizing agent in the catalyst surface more rapidly reacted with naphthalene, but as the reaction proceeds, the concentration of hydrogen peroxide continues to decrease, the reactant molecules on the catalyst surface in contact chance to continue to decrease, resulting in a naphthyl hydroxylation reaction selectivity and conversion rates are slowing growth. After more than 10h, naphthol is deep oxidation in the air, so the conversion rate decreased. Therefore, the best reaction time was 8h.

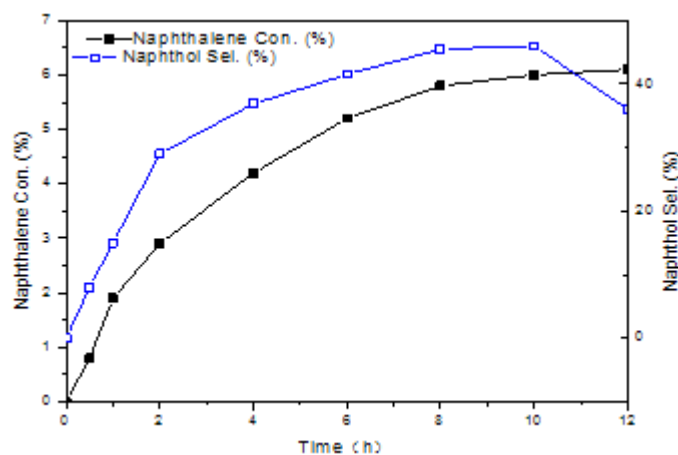


Figure 4. Conversion-selectivity-reaction temperature in naphthalene hydroxylation; Reaction conditions: Naphthalene (1000 mg, 7.81 mmol), hydrogen peroxide (30 wt.%, 2 mL, 19.7 mmol), acetonitrile (25 mL) h

3 CONCLUSION

1, MCM-41 zeolite prepared by impregnation method, and MCM-41 zeolite was modified; to load 5% of modified Fe/MCM-41 zeolite catalyst, the reaction temperature 60°C, reaction time 8h, hydrogen peroxide 2mL, naphthalene 1000mg, lower Fe/MCM-41 catalyst 100mg of conditions, the conversion of naphthalene was 5.8% and the selectivity was 45.7%.

2, After the modified MCM-41 not only to better maintain the hexagonal structure of MCM-41 zeolite characteristics, but also in the hydroxylation reaction of naphthalene-naphthol in the performance of some catalytic activity. Wherein the catalytic effect of Fe / MCM-41 is preferably, naphthol selectivity of 45.7%, followed by the catalytic effect of Fe/MCM-41 > Cu/MCM-41 > Mn/MCM-41 > MCM-41.

3, In different solvents (acetic acid, acetonitrile, methanol, ethanol, ethyl acetate), naphthalene hydroxylation reaction test showed the best acetonitrile as solvent. Acetonitrile as a solvent, naphthalene hydroxylation reaction naphthol yield, high selectivity, the selectivity of 1-naphthol and 2-naphthol, respectively, 33.9% and 11.8%.

4, With the temperature increases, the conversion and selectivity naphthalene naphthol will increase, at the temperature close to 60 °C, naphthalene conversion reached a maximum of 5.8%, 45.7% selectivity naphthol. With increasing reaction time, the conversion and selectivity of naphthalene naphthol were increased, and achieve little change naphthalene conversion after 8h, 10h after naphthol selectivity decreased. With the increase of the content of hydrogen peroxide, the conversion of naphthalene and selectivity of naphthol selectivity increases. With the increase of the amount of catalyst, the conversion and selectivity of naphthalene naphthol significantly increased.

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