

Study of heteropolyacids for the hydroxylation of Naphthalene to naphthol

PengjinYe, Wenya Wang&LeiWang*

Shanghai Institution of Technology, Shanghai 201418, China

Abstract. We prepared five heteropolyacid catalyst by one-pot method, the reaction temperature was 65°C, reaction time 8h, hydrogen peroxide 3mL, naphthalene 1000mg, H₄PMo₁₁VO₄₀ 100mg, naphthalene conversion was 30.3%, the selectivity of naphthol was 46.7%. The heteropolyacids have Keggin structure, but also have some hydroxylations catalytic activity in reaction of naphthalene to naphthol. Among which, the H₄PMo₁₁VO₄₀ was best. With the temperature increasing, the conversion of naphthalene and selectivity of naphthol will rise. The conversion of naphthalene and selectivity of naphthol attained optimal value at 65 °C. With the reaction time increasing, the conversion of naphthalene and selectivity of naphthol were increased, and achieved little change at naphthalene conversion after 6h, After 8h, 1-naphthol's selectivity decreased, 2-naphthol's selectivity kept smooth. With the increasing of hydrogen peroxide, the conversion of naphthalene and selectivity of naphthol increased. With the increasing amount of catalyst, the conversion of naphthalene and selectivity of naphthol were significantly increased.

1 Introduction

The formula of monohydric naphthols are C₁₀H₈O, they are two isomers of 1-naphthol and 2-naphthol. The molecular weight is 144.17. Naphthol is an important organic materials, and mainly used in the production of synthetic fibers, synthetic rubber, plastics, pharmaceuticals, pesticides, perfumes, dyes and coatings, the market demand was increasing.

2 Experimental section

2.1 Catalyst preparation

The supported catalysts were prepared by impregnation of metal components. The specific preparation methods as follows: MCM-41 samples were calcined twice in a muffle furnace. Calcined 2 h at 250-350 °C, then kept at 350 °C for 1-2 h more, calcined at 550 °C for another 3-4h. And then Cooling down to room temperature for later use. The sample will changed from white to black, then to white during calcination. Metals (Fe, Cu, Mn) salt was dissolved in 25mL methanol solution, and was stirred until completely dissolved, and then accurate weighing and adding MCM-41, stirring 4h, keeping 4h, rotary evaporation, and then dring overnight at 110 °C. After that, calcination for another 5h at 550 °C, the Fe/MCM-41 catalyst was obtained.

2.2 Characterization of the samples

All catalysts were characterized by Fourier transform infrared spectroscopy (FT-IR).

2.3 Catalytic experiments

V₂O₅(15.8g) and MoO₃(0.91g) were dissolved in deionized water, then stirred and heated to 95°C(±5 °C) with stirring in oil bath. Dripping the phosphoric acid solution(1.15g, 85wt%) in above solution, and kept it under 95 °C ~100 °C for 18~24 h until the orange suspension became clear. Then the solution was filtered, drying under the 60°C. We used liquid chromatography to test the sample. Liquid chromatography to Beijing LabTech Instruments Incorporated (LabTech LC600 HPLC), chromatography conditions: C18 column with a mobile phase of methanol/water = 58/42, the detection wavelength to 220nm, flow rate at 0.8mL / min.

3 Result and discussion

3.1 FT-IR results

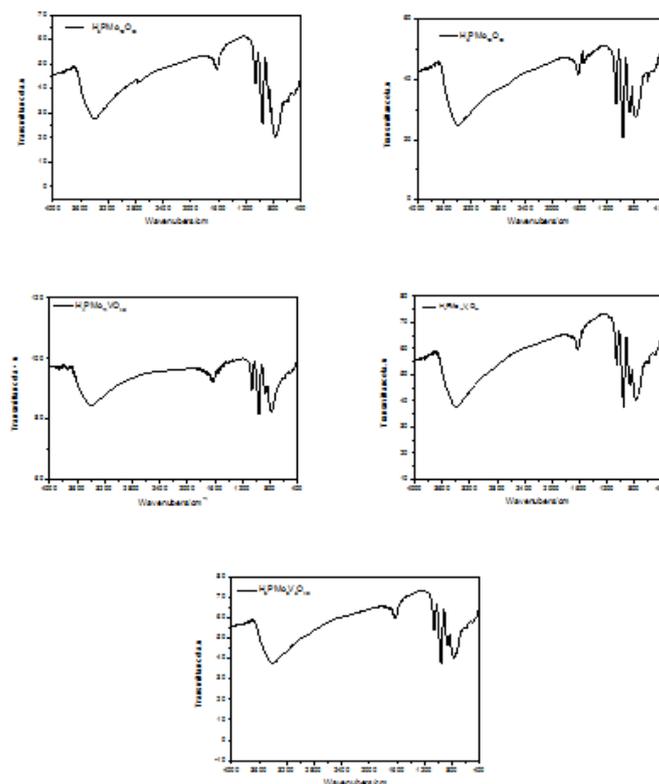


Figure1.FT-IR for Heteropolyacids

Figure 1. shows that it can be seen four Keggin structure peaks, the peak of the five heteropolyacids is between $700 \sim 1100 \text{ cm}^{-1}$. Around 1000 cm^{-1} is PO's stretching vibration peak, around 900 cm^{-1} is Mo-O stretching vibration frequency bonds, 850 cm^{-1} ascribed to Mo-O-Mo bridges, the stretching vibration frequency peak around 750 cm^{-1} attributed to the stretching vibration frequency of Mo-O-Mo bridge bond (oxygen bridge with groups MoO_6 octahedral). Addition, 1620 cm^{-1} is close to the frequency of the bending vibration of water molecules in hydroxy. The analysis chart indicates that the compounds have Keggin structure of heteropoly acid.

3.2 Catalytic activity

Table 1. shows that all the heteropoly acid contain Keggin structure. The catalytic of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ is best, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ have a low yield of naphthol. The catalytic effect of the reaction production were that: $\text{H}_4\text{PMo}_{11}\text{VO}_{40} > \text{H}_5\text{PW}_{10}\text{V}_2\text{O}_{40} > \text{H}_6\text{PMo}_9\text{V}_3\text{O}_{40} > \text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_3\text{PMo}_{12}\text{O}_{40}$. Obviously, the presence of vanadium in heteropolyacids increased the hydroxylation reaction in the conversion of naphthalene to naphthol. However, the $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ property and the selectivity of naphthol was better than $\text{H}_5\text{PW}_{10}\text{V}_2\text{O}_{40}$. Which was consistent with Xu Wenjun's report that the heteropolyacid stability affected catalytic activity, vanadium heteropoly acid catalysis are not as effective as a vanadium-substituted heteropolyacids may because that monoperoxovanadium active intermediate species in oxygen transfer reactions reduced because of its stability.

Table 1. Miscellaneous impact of different types of acid hydroxylation of naphthalene naphthol

Catalyst	Naphthalene Con.(%)	Naphthol Sel. (%)	
		1-nap.	2-nap.
$H_3PMo_{12}O_{40}$	3.8	17.3	6.7
$H_3PW_{12}O_{40}$	4.3	29.2	9.8
$H_4PMo_{11}VO_{40}$	27.15	35.2	10.8
$H_5PMo_{10}V_2O_{40}$	29.47	26.6	9.4
$H_6PMo_9V_3O_{40}$	31.29	22.0	8.1

Reaction conditions: Naphthalene (1000 mg, 7.81 mmol), catalyst(100mg), hydrogen peroxide (30 wt.%, 2 mL, 19.7 mmol), acetonitrile (25 mL), 65°C, 6 h

3.3 Reaction temperature

Figure2. shows that with the increase of reaction temperature, the conversion of naphthalene and selectivity of naphthol increased at first. When the temperature was raised from 50°C to 65°C, naphthalene conversion rate increased by 8.3% to 27.15%, the naphthol selectivity from 26.5% to 46%; when the reaction temperature is 65°C, the conversion of naphthalene reaches a maximum conversion rate of 27.15%; when the catalyst does not exhibit high catalytic activity, the reaction temperature facilitated the reactive intermediates, accelerated the reaction rate, and improved the selectivity of naphthol. When the temperature rise to 70°C, the selectivity of naphthol fell to 30%, it is probably due to the temperature increasing the depth oxidation of naphthol and hydrogen peroxide decomposition. In addition, according to Arrhenius equation, at reaction temperature, the catalyst should exhibit higher catalytic activity, but V_2O_5 monomers can also be separated from the heteropolyacid skeleton. The generation naphthol have passivation effect of VO^{2+} . With the temperature raised, the enhance activity of the catalyst does not compensate for the reduced activity of the catalyst V_2O_5 monomer removed. Further raising the reaction temperature, the selectivity of 1-naphthol in reducing, and elevated temperatures may be more accessible reduce. The boiling point of the acetonitrile which lead to naphthol concentration increases and in deep oxidation of 1-naphthol, 2-naphthol. 2-naphthol's activity is weaker, the disadvantaged in the competition reaction impact may not obvious affect the selectivity. Therefore, the optimal reaction temperature is 65°C, the catalyst showed higher conversion of naphthalene and selectivity of naphthol has reached 46%.

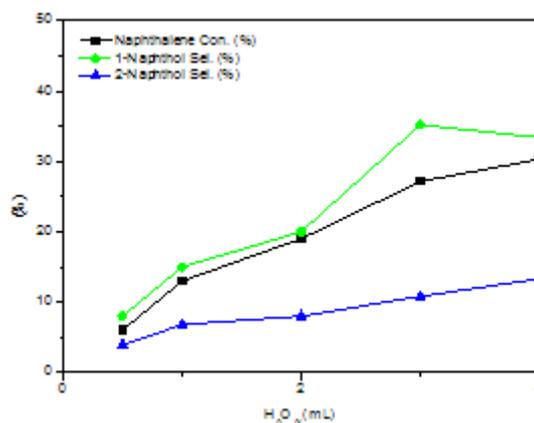


Figure2. Conversion-selectivity-reaction temperature in naphthalene hydroxylation; Reaction conditions: Naphthalene (1000 mg, 7.81 mmol), catalyst(100mg), hydrogen peroxide (30 wt.%, 2 mL, 19.7 mmol), acetonitrile(25 mL), 8 h

3.4 Reaction time

Figure 3. shows that with the time increasing, the conversion of naphthalene and selectivity of naphthol have increasing trend. When the time reach 6h, the conversion trend is slower with the time; when reaction time was more than 6h, the selectivity of 1-naphthol decreased rapidly. Mainly with the high initial concentration of hydrogen peroxide reaction, naphthyl contacted with an oxidizing agent in the catalyst surface. With the reaction proceeds, the concentration of hydrogen peroxide have decreased. The probability of reactant molecules on the catalyst surface in contact have decrease. Resulting in the increasing of selectivity and conversion of naphthalene hydroxylation reaction slow. After more than 6h, naphthol was deep oxidation in the air, so the conversion rate decreased rapidly. Therefore, the best reaction time was 6h.

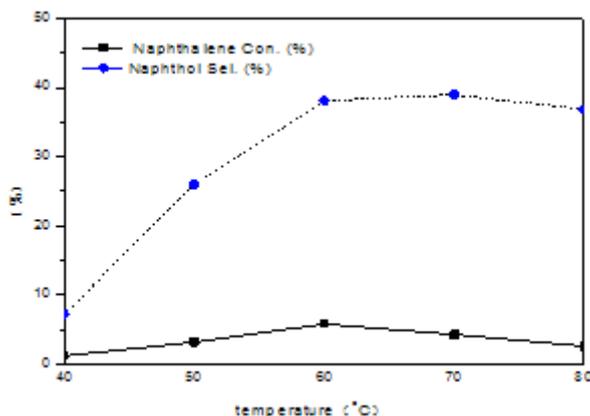


Figure 3. Conversion-selectivity-reaction temperature in naphthalene hydroxylation; Reaction conditions: Naphthalene (1000 mg, 7.81 mmol), catalyst(100mg), hydrogen peroxide (30 wt.%, 2 mL, 19.7 mmol), acetonitrile(25 mL), 65°C.

3.5 Reaction H2O2

Figure 3. shows that with the increase of hydrogen peroxide, the conversion of naphthalene and selectivity of naphthol were increased. When the amount of hydrogen peroxide increased from 0.5mL to 3.0mL, the conversion decreased from 6% to 27.15%, the selectivity increased to 46% from 11.9%. Mainly due to lower initial hydrogen peroxide concentration produced hydroxyl radicals and peroxide free a very small group, there is a certain induction period; with the increasing of hydrogen peroxide content, the free radicals generated can be efficiently and naphthalene molecules, accelerate the reaction of naphthol. However, with increasing hydrogen peroxide content 3.0 mL to 4.0mL, naphthalene conversion rate changed little. And 1-naphthol and 2-naphthol selectivity decreased slightly. Therefore, the appropriate amount of oxidant is 3.0mL.

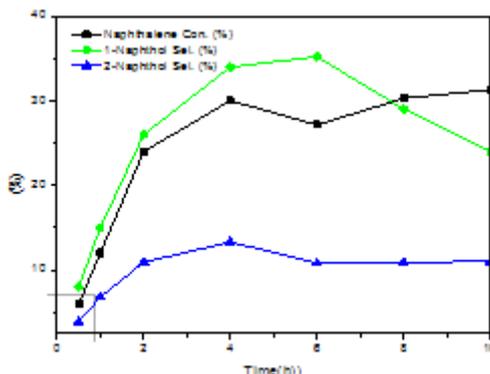


Figure 3. Conversion-selectivity-volume of H₂O₂ in naphthalene hydroxylation; Reaction conditions: Naphthalene (1000 mg, 7.81 mmol), catalyst(100mg), hydrogen peroxide (30 wt.%), acetonitrile(25 mL), 65°C.

4 Conclusion

1. Prepared five heteropolyacid catalyst, the best reaction conditions: Naphthalene (1000 mg, 7.81 mmol), catalyst(100mg), hydrogen peroxide (30 wt.%), acetonitrile(25mL), at 65°C, under $H_4PMo_{11}VO_{40}$ catalyst, the conversion of naphthalene was 30.3%, selectivity of naphthol was 46.7% .

2. Heteropolyacid catalysts have Keggin structure. The catalytic effect of $H_4PMo_{11}VO_{40}$ is best, the selectivity of naphthol was 46.7%, the catalytic effect as follows:
 $H_4PMo_{11}VO_{40} > H_5PW_{10}V_2O_{40} >$

$H_6PMo_9V_3O_{40} > H_3PW_{12}O_{40} > H_3PMo_{12}O_{40}$.

3. With the temperature increases, the conversion of naphthalene and selectivity of naphthol will be increased. In close to 65°C, naphthalene conversion rate was 27.15%, reached the maximum, the naphthol selectivity was 46%. With the increasing of reaction time, the conversion of naphthalene and selectivity of naphthol increased, and the naphthalene conversion had achieve little change after 6h. 1-naphthol selectivity decreased after 8h, and 2-naphthol selective retention kept smooth. With the increase of the content of hydrogen peroxide, the conversion of naphthalene and selectivity of naphthol increased. With the increasing of the amount of catalyst, the conversion of naphthalene and the selectivity of naphthol were significantly increased.

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