Catalytic Oxidation of Benzaldehyde to Benzoic Acid with Keggin Polyoxometalate [(CH₂)₅NH₂]₃PW₁₂O₄₀

YUANSHENG DING[1], FEI-LU[1,*] and XINBAO- HAN[2]

[1]Department of Chemical and Pharmaceutical Engineering, Jilin Institute of Chemical Technology, Jilin 132022, P.R.China
[2]Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, P.R. China

*Corresponding author: Fax: +86 432 639677171; Tel: +86 150 44667696; E-mail: lufei1893@163.com

The organic-inorganic hybrid catalyst [(CH₂)₅NH₂]₃PW₁₂O₄₀ was prepared by heteropoly acid and piperidine. The heteropoly acid was synthesized by sodium molybdate and sodium silicate and the piperidine was organic ligand. The proposed composition and structure of the catalyst were evidenced by FT-IR, XRD and TG-DTA. The results indicated that the heteropoly anions reserved their Keggin structure in the compound. Its catalytic performance was evaluated in the oxidation of benzaldehyde to benzoic acid. Various reaction parameters were changed to attain the optimal conditions. The optimal reaction conditions were found to be: n(catalyst):n(benzaldehyde) = 3.103 × 10^{-3}:1; n(H₂O₂):n(benzaldehyde) = 4.0:1; reaction temperature 80 ℃; reaction time 4 h. The yield of benzoic acid achieved above 93 %, furthermore and the selectivity was 100 %.

Key Words: [(CH₂)₅NH₂]₃PW₁₂O₄₀, Keggin polyoxometalate, Catalysis, Benzoic acid.

INTRODUCTION

Heteropoly acids (HPAs) and related polyoxometalate compounds (POMs) are a class of poly-oxygen metal complexes. The complexes contain the central atom (such as P, Si, *etc*.) and ligands (such as Mo, W, *etc*.). They combined multi-space oxygen by bridging oxygen atoms. Heteropoly acids and polyoxometalates have a clear size, shape and discrete fragments similar to the structure of metal oxides[1]. They play great roles in catalysis, photochemistry, medicine, materials science and magnetic fields[2-6]. As green catalysts, they contain both acid sites and redox active sites that make them to be potential redox molecular sieves and bifunctional catalysts. Furthermore, they display high catalytic activity, selectivity, rapid response, mild reaction conditions, oxidation and optical, magnetic, stability, micro-light corrosion of equipment. Based on these properties, they can be used for homogeneous and heterogeneous reactions and even can be used for phase transfer catalyst[7-12]. Therefore, synthesis of new efficient polyoxometalates catalysts has become a hot spot.

Keggin type coordination [(CH₂)₅NH₂]₄PW₁₂O₄₀] polyoxometalates catalyst was synthesized and structurally characterized by means of single crystal X-ray diffraction, IR and TG. The composite catalyst was applied to the oxidation of benzoic acid with benzaldehyde. The influence factors of the reaction were also investigated.

EXPERIMENTAL

Na₂WO₄·2H₂O, hexahydropyridine and benzaldehyde obtained from Shanghai Chemical Reagent Co. Ltd., H₂O₂ (30 %) and H₃PO₄ (85 %) were purchased from Beijing Chemical Reagent Co. Ltd. The products were characterized by X-ray powder diffraction (XRD), microscopic meting point meter, Differential Thermal Analysis and Thermo Gravimetric Analysis (TG-DTA).

Materials synthesis: The 20 g Na₂WO₄·2H₂O were dissolved by 40 mL deionized water and kept in boiling water bath for 70 ℃. The 2 mL H₃PO₄ were added in the solutions in the conditions of pH 2, 70 ℃, 120 r/min. After 10 min, the HClO₄ were added into the solutions. Firstly, the yellow deposit emerged. After filtered, the liquid was cooled to ambient temperature. The total reaction times were 2 h. After moved to the separatory funnel, the liquid was extracted with ethyl ether and 6 mol L^{-1} HCl. The below solutions were one more extracted with ethyl ether and HCl. The extracted oil phase with added a small amount of distilled water (10-20 drops) and a few drops of concentrated HNO₃ were evaporated under the 60 ℃ water bath until the films appeared. Then the transparent phosphatotungstic acid was attained after cooled. The purity of crystal was obtained with nearly 100 % after recrystallization.

The precipitate was prepared by mixing the $H_3PW_{12}O_{40} \cdot nH_2O$ and hexahydropyridine with mole ratio 1:3 and reaction at 70 ºC for 2 h. After filteration, the precipitate was cleaned by ethanol, ethyl ether and H_2O in order and dissolved in the mixture of the acetonitrile. After filteration, the filtrates were transferred to the beaker and kept at room temperature for one week. The $[(CH_2)_5NH_2]_4PW_{12}O_{40}$ crystal would crystallize at the bottom of the beaker.

Catalytic activity: The crystal $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ were used as the catalyst in the process of the oxidation benzoic acid with benzaldehyde. The effects of catalyst, reactants, temperature and reaction time were investigated.

RESULTS AND DISCUSSION

The FTIR spectrum of charge transfer polyoxometalates $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ (Fig. 1) exhibited four bands located at 1078, 978, 892 and 799 cm^{-1} corresponding to P-Oa, W-Od, W-Ob-W and W-Oc-W vibrations, respectively. These absorption peaks closed to those reported[13,14] for heteropolyanions $[PW_{12}O_{40}]^{3-}$. The result showed the syntheses transfer POMs exhibit Keggin structure. However, relative to the starting heteropoly acids, the absorption peak of P-Oa and W-Od showed an obvious blue shift, while that of W-Ob-W and W-Oc-W showed a blue shift. This may be due to the charge transfer from protoned piperdine to the heteropolyanions. The absorption bands at 1581 and 1439 cm^{-1} are assigned to the stretching vibrations for piperdine ring. FTIR 2863 cm^{-1} peak and 2939 cm^{-1} peak were assigned to the CH_2 symmetric stretch and asymmetric stretch (CH_2-as) of the γ-methylene and β-methylene groups. The bands corresponding to the axial amine N-H stretching vibrations appear in the 3174 cm^{-1} region. The FTIR spectrum showed that the stronger charge transfer between polyanions and its counterions that result in forming the charge transfer polyoxometalates.
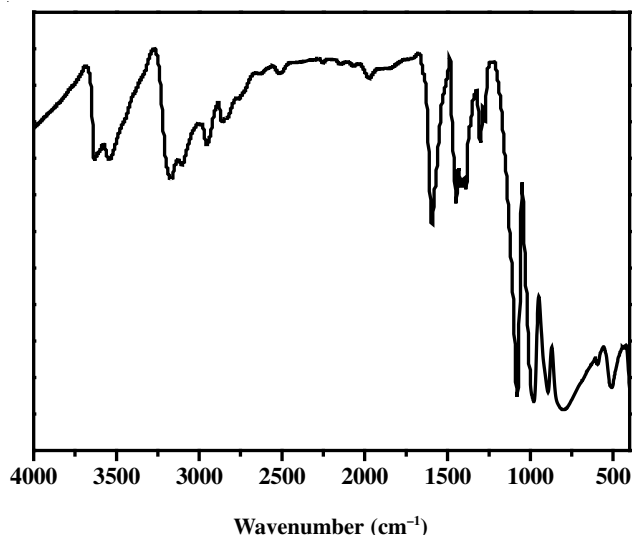

Fig. 1. FTIR spectrum of charge transfer POMs $[(CH_2)_5NH_2]_3PW_{12}O_{40}$

XRD result of the prepared catalyst before reduction was presented in Fig. 2. Four peaks at around 8.56, 4.58, 9.78 and 8.76º were observed for catalyst. These four peaks were similar to the Keggin-type $H_3PW_{12}O_{40}$ phase[3].

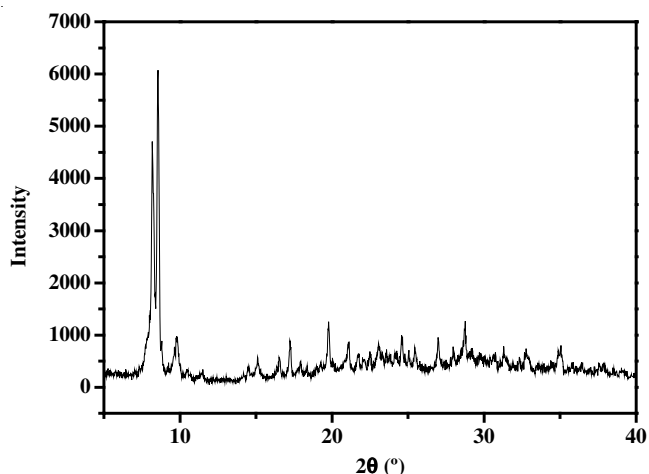Fig. 2. X-Ray powder diffraction patterns of charge transfer POMs $[(CH_2)_5NH_2]_3PW_{12}O_{40}$

The TG curve indicated hat their thermal decomposition processes of $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ can be divided into four mass loss steps. According to TG curve, the degradation in the temperature range of 50-800 ºC consisted of four mass loss steps.

The first mass loss step was in the temperature range of 50-468.11 ºC with similar mass losses of *ca.* 0.295 %. In the process, six crystallization waters that connected with acidic proton *via* H-bond were lost. The second decomposition step in the temperature range of 468.11-481.19 ºC. The polyanions began to decompose in this process. The third decomposition step started at 481.19 ºC and continued up to 542.39. The third step can be assigned to the oxidative decomposition of protoned piperdine with a strong exothermic peak marking the collapse of Keggin structure. The mass losses in the third step were 6.957 %. The four decomposition step in the temperature range of 542.39-800 ºC. In the four step, the polyanions were total decomposed into WO_3. According to DTA, the decomposition temperature of $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ was at 481.19 ºC that lower than decomposition temperature (465 ºC) of the starting heteropoly acid[15]. It can be seen the charge transfer POMs have more hermodynamically stable structures compare to starting heteropoly acid.

Effects of reaction conditions: The effect of catalyst dosage on the yields of products was shown in Fig. 3. The molar ratio of $[(CH_2)_5NH_2]_3PW_{12}O_{40}$/benzaldehyde was varied from 1.9×10^{-3}-3.7×10^{-3}. As can be seen, catalyst dosage significantly affected the reaction. The yield of the benic acid was promoted with the increase of molar ratio. The most beneficial molar ratio of $[(CH_2)_5NH_2]_3PW_{12}O_{40}$/benzaldehyde was chosen to be 3.1×10^{-3}.

The effect of H_2O_2 on reaction was also studied (Fig. 4). The conversion of benzoic acid was promoted with the molar ratio of H_2O_2/benzaldehyde when the molar ratio was less than 4.0:1. While above the molar ratio 4.0:1, the yield of benzoic acid was decreased with the molar ratio of H_2O_2/benzaldehyde.

The effect of reaction temperature on the reaction was investigated and the experiments were conducted at 60, 70, 80 and 90 ºC, respectively. Fig. 5 showed the effect of the temperature on the yields of product. It can be observed that temperature have a significant effect on the reactions. When
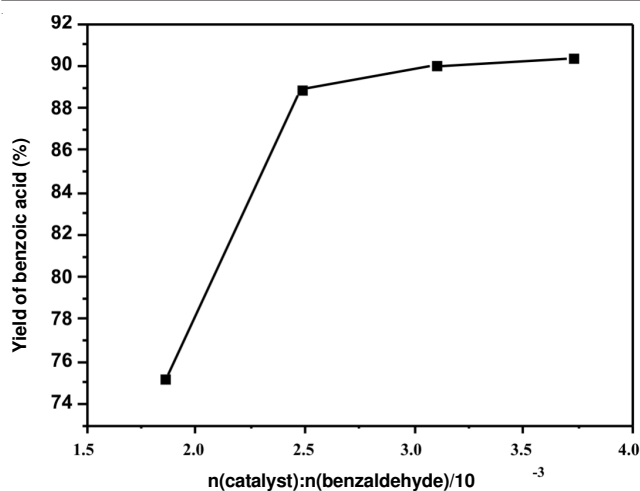
Fig. 3. Catalytic effect of $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ dosage on the conversion of benzoic acid (reaction conditions: nH_2O_2:benzaldehyde = 4.0:1, temperature 80 ºC, time 4 h)

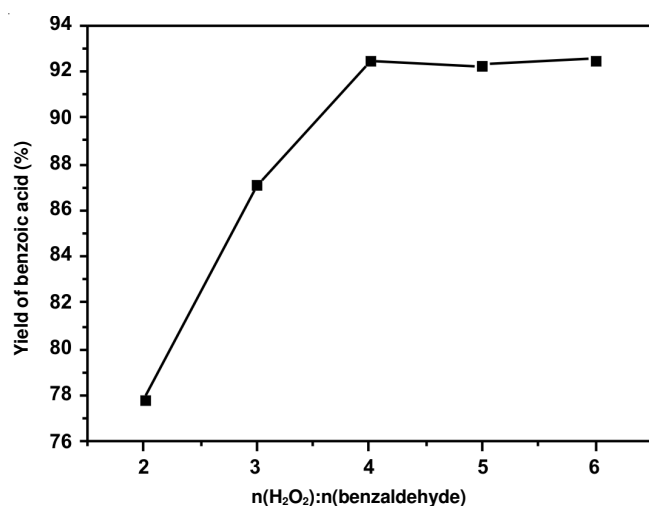Fig. 4. Effect of H_2O_2 dosage on the conversion of benzoic acid (reaction conditions: $n[(CH_2)_5NH_2]_3PW_{12}O_{40}$:$n$-benzaldehyde = 3.1×10^{-3}, temperature 80 ºC, time 4 h)
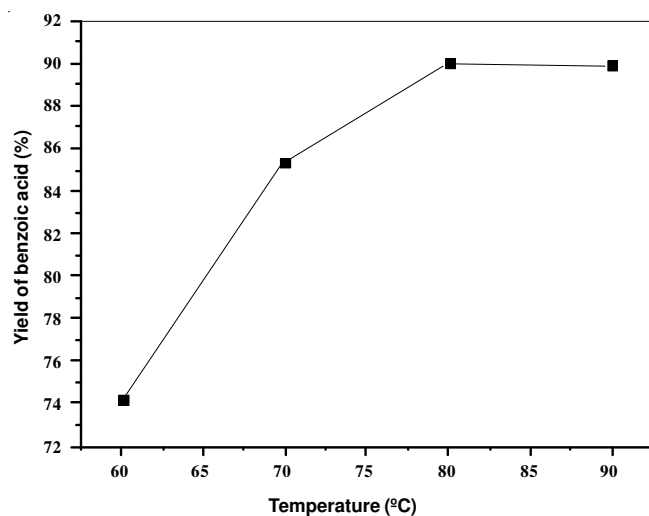

Fig. 5. Effect of temperature on the catalytic activity (reaction conditions: $n[(CH_2)_5NH_2]_3PW_{12}O_{40}$:$n$-benzaldehyde = 3.1×10^{-3}, nH_2O_2:benzaldehyde = 4.0:1, time 4 h)

the reaction temperature was increased from 60-80 ºC, there was a significant increase in the yield of benzoic acid. When the reaction temperature rose above 80 ºC, the yield of benzoic acid began to fall and higher temperatures thus could accelerate the rate of chemical reactions, but unwanted side reactions also appeared at the same time. For example, H_2O_2 could decompose, thus the reaction temperature was set to 80 ºC in this experiment.

Time course of oxidation was shown in Fig. 6. The amount of benzoic acid grew very fast for the first 2 h. Then it was observed slightly to decrease after 4 h. It was found that 4 h were sufficient for completion of the oxidation reaction.
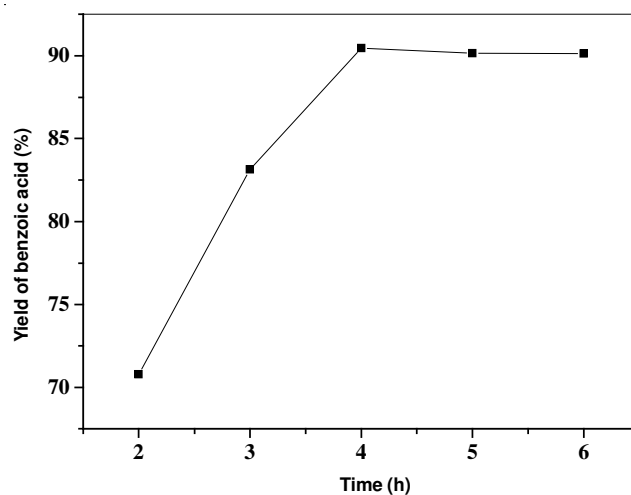

Fig. 6. Effect of reaction time on the catalytic activity (reaction conditions: $n[(CH_2)_5NH_2]_3PW_{12}O_{40}$:$n$-benzaldehyde = 3.1×10^{-3}, nH_2O_2:benzaldehyde = 4.0:1, temperature 80 ºC)

To estimate the potential $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ contribution in the reaction, benzaldehyde oxidation was also carried out at mole ratio (H_2O_2/benzaldehyde) of 4:1 at 80 ºC without $[(CH_2)_5NH_2]_3PW_{12}O_{40}$, the product yield was only 27.5 % that lower than the product conversion of reaction with $[(CH_2)_5NH_2]_3PW_{12}O_{40}$. While H_2O_2 was not added into the system, no product was formed. It can conclude that the $[(CH_2)_5NH_2]_3PW_{12}O_{40}$ was not an oxidizing agent, however it played great role in promoting the benzaldehyde oxidation reaction as catalyst.

Above the about analysis, the optimal reaction conditions were drawn. For verification three parallel experiments were carried out, the results were shown in the Table-1.

Conclusion

The proton-transfer reactions between hexahydropyridine and Keggin-type heteropolyacid produced solid charge transfer hybrid materials $[(CH_2)_5NH_2]_3PW_{12}O_{40}$. The charge transfer interactions are strong enough to cause evident changes in FTIR spectrum from heteropolyacids to hybrid materials. The optimal reaction conditions were as follows: $n[(CH_2)_5NH_2]_3PW_{12}O_{40}$: n-benzaldehyde = 3.1×10^{-3}, nH_2O_2: benzaldehyde = 4.0:1, 80 ºC, 4 h. Under the optimum conditions, the yield of the product is 93.1 %.

TABLE-1					
REACTION CONDITIONS (VERIFICATION)					
Number	nH_2O_2:n-benzaldehyde	Reaction temperature (ºC)	$n[(CH_2)_5NH_2]_3PW_{12}O_{40}$:$n$-benzaldehyde $\times 10^{-3}$	Time (h)	Yeild (%)
1	4.0:1	80	3.1	4	93.03
2	4.0:1	80	3.1	4	93.15
3	4.0:1	80	3.1	4	93.87

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