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Catalytic Oxidation of Toluene to Benzaldehyde over Dawson-type Heteropoly Acid Neodymium Salt

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Abstract: A novel Nd salt of Dawson type heteropoly acid ($Nd_3P_2Mo_{15}V_3O_{62} \cdot nH_2O$) was prepared by doping rare-earth Nd in $H_9P_2Mo_{15}V_3O_{62} \cdot nH_2O$, and characterized by infrared spectroscopy (FTIR), X-ray diffraction (XRD). Its catalytic activity was evaluated in the oxidation of toluene to benzaldehyde with H_2O_2 as an oxidant, the catalyst exhibits high activity owing to strong synergistic effect of Neodymium and vanadium. The conversion of toluene and the selectivity for benzaldehyde were up to 90.1%, 51.0%, respectively. The conversion of H_2O_2 and effective utilization ratio of H_2O_2 were 89.0% and 43.1%, respectively. Based on the study of polyoxometalates´structure, a possible reaction mechanism is proposed.

Key words: dawson type; heteropoly acid; neodymium salt; toluene; benzaldehyde
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Benzaldehyde is an important intermediate in the production of perfumery, pharmaceutical, dyestuff and agrochemicals[1]. Traditionally, benzaldehyde is produced by side-chain chlorination of toluene. The product still contains the chlorinated impurities, which can not be used as the raw material for the production of medicines, food and flavors[2-5]. In addition, the process involving Cl_2 causes environmental pollutions and equipment corruptions[6]. Thus, there is an exigent need for "green" technologies in the synthesis of benzaldehyde. Kantham[7] et al. have reported the toluene oxidation on Co-Ni-Cu catalyst by using Co and Cu organic acid salt as cocatalyst. This catalytic system showed maximum toluene conversion of 25%. During this reaction, the concentration of catalyst was low relatively, reduced the corrosivity of equipment, but the conversion rate of toluene was low. At present, toluene has been relatively excessive in the market, so toluene will further development of higher added value of downstream products exhibits the important role.

Heteropoly acids possess unique physicochemical properties, its structural mobility and multifunctionality which are the most important for catalysis[8-11]. They possess, on one hand, a very strong Brønsted acidity and, on the other hand, appropriate redox properties, which can be tuned by varying the chemical composition of HPA. Consequently, acid catalysis and catalytic oxidation are the two major areas of catalysis by HPAs[12]. Heteropoly compounds provide higher activity and selectivity and allowing for cleaner processing compared to conventional catalysts[13]. Doping in rare earth elements in heteropoly acids can change the oxidation ability of heteropoly compounds in great degree, this characteristic can control oxidation and reduction ability of heteropoly compounds. At present, the rare-earth metal dopped heteropoly catalyst was less used for oxidation of toluene system, and the low of toluene conversion was always a problem to solve. In this paper, oxidation of toluene at low temperature was carried on $Nd_3P_2Mo_{15}V_3O_{62}$ catalysts using H_2O_2 as oxidant. The reaction process was simple, it will not cause environment pollution, also can provide certain reference for clean production process.

1 Experimental

1.1 Preparation of catalysts

All chemicals (analytical grade) were purchased and used without further purification, including

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$Na_2HPO_4 \cdot 12H_2O$, $Na_2MoO_4 \cdot 2H_2O$, NH_4VO_3, sulfuric acid, acetonitrile, ether, nitric acid neodymium, acetic acid, acetic acid potassium, toluene and hydrogen peroxide.

$H_9P_2Mo_{15}V_3O_{62} \cdot nH_2O$ was synthesized according to the reference [14-15]. The rare earth metal substituted hydrogen heteropoly compounds $Nd_3P_2Mo_{15}V_3O_{62} \cdot nH_2O$ was prepared by the method described below. About 1 mmol $H_9P_2Mo_{15}V_3O_{62}$ was dissolved in 20 mL deionized water with vigorous stirring and heating up to 343 K, then added few drops of 0.6 mmol/mL $Nd(NO_3)_3$. Sequentially, KAc-HAc buffer solution was slowly added, following the color change from dark red to yellow green, the final pH of the solution was adjusted to 4.5. After stirring for 30 min, the dark suspension solution was filtered, sequentially filtrate was cooled at 273 ~ 277 K until the dark crystal was dissolved out and then dried under vacuum at 333 K for 12 h.

1.2 Physicochemical characterization

The Fourier transform infrared spectroscopy (FT-IR) spectra of the catalysts were measured using a KBr disk on a Digilab FTS3000-FTIR spectrometer. The X-ray diffraction (XRD) patterns were recorded at 2θ = 3°-50° on D/max 2200PC diffractometer instrument operating at 40 kV and 20 mA with Cu target Kα- ray irradiation.

1.3 Catalyst evaluation

The toluene oxidation was carried out in a 100 mL three-neck round bottom flask fitted with a condenser, a thermometer and a magnetic stirrer. In a typical oxidation experiment, 10 mL of acetonitrile solvent, 23.5 mmol of toluene, and a certain amount of catalyst were filled in round bottom flask. When the temperature was raised up to 363 K, hydrogen peroxide was added to the reaction system dropwise within 1 h, and then the resulting mixture was refluxed for 7 h. After reaction, the products were directly analyzed by gas chromatography (SP-3420A) equipped with a FID detector and a capillary column (SE-54 30 m × 0.32 mm × 0.5 μm), an internal standard material ethyl benzene was used to the quantitatively analysis.

2 Results and discussion

2.1 Catalyst characterization

The FTIR spectra of the samples are presented in Fig. 1. The intense IR bands for all the samples observed at 1 060 cm^{-1}, 960 cm^{-1}, 860 cm^{-1} and a broad band at 780 cm^{-1}, attributed to Dawson ion characteristic stretching vibrations of P-Oa, Mo = Od and $V = O_d$, $Mo\text{-}O_b\text{-}Mo$ and $Mo\text{-}O_c\text{-}Mo$, respectively. The band around 1 060 cm^{-1} is due to asymmetric stretching vibrations of $P\text{-}O_d$. A band around 960 cm^{-1} is due to asymmetric stretching vibration of $Mo = O_d$, and absorption at 860 cm^{-1} is due to bending of $Mo\text{-}O_b\text{-}Mo$ vibration. A band around 780 cm^{-1} is due to bending of $Mo\text{-}O_c\text{-}Mo$ vibration [16-17]. Stretching vibrations of water molecules may contribute to -OH peaks (1 600 cm^{-1} and 3 400 cm^{-1}).

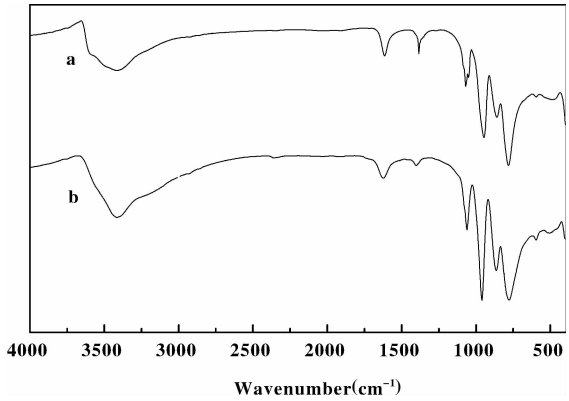


Fig. 1 FT-IR spectra of $Nd_3P_2Mo_{15}V_3O_{62}$ (a) and $H_9P_2Mo_{15}V_3O_{62}$ (b)

By contrast, the FTIR spectra of $Nd_3P_2Mo_{15}V_3O_{62}$ illustrate $Nd_3P_2Mo_{15}V_3O_{62}$ attributed to Dawson type, Rare earth metal Nd did not enter the first level of structure, just occupied the position of the counter ion. Comparing without doping metal Nd of $H_9P_2Mo_{15}V_3O_{62}$, the first and second characteristic absorption peaks of low wave number in the FTIR spectra of $Nd_3P_2Mo_{15}V_3O_{62}$ are not shifted obviously, but the third and fourth characteristic absorption peaks of agobot are shifted to higher wave numbers (red shift)[2]. This shift is due to the coordination influence of Nd which makes Mo = O weakened, finally characteristics peak vibrations frequency is decreased in the Infrared spec-

tra. It showed that the rare-earth metal Nd added have a big influence on electron transition of Mo-O. The key function of the catalyst may be synergistic effect of metal elements V and Nd.

To investigate further the structural stability with the incorporation of vanadium into the primary structure of Dawson ion, the samples were characterized by XRD and the patterns of the samples were shown in Fig. 2. The strong characteristic peaks at 2θ values of 7° ~ 9°, 17° ~ 21°, 26° ~ 29° were assigned to Dawson structure of $H_9P_2Mo_{15}V_3O_{62}$[18]. Comparing with $H_9P_2Mo_{15}V_3O_{62}$, $Nd_3P_2Mo_{15}V_3O_{62}$ had a small change. The strong characteristic peaks at $2\theta = 8° \sim 10°, 14° \sim 19°$, 26° ~ 30°, 33° ~ 35°, were observed in all the samples. The XRD patterns suggested that the Dawson structure was intact even with the incorporation of vanadium into the primary structure and also when hydrogen was substituted by neodymium. Metal Nd did not enter the first level of structure, just occupied the position of the counter ion.

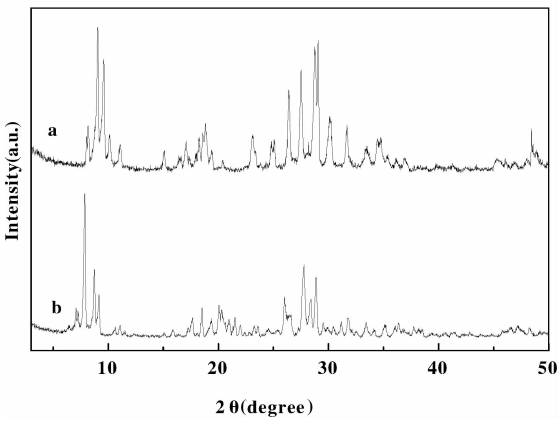


Fig. 2 XRD patterns of $Nd_3P_2Mo_{15}V_3O_{62}$ (a) and $H_9P_2Mo_{15}V_3O_{62}$ (b)

2.2 Effect of experimental conditions on the oxidation of Toluene

The effect of the amount of catalyst $Nd_3P_2Mo_{15}V_3O_{62}$ on the conversion of toluene and the selectivity of benzaldehyde is shown in Fig. 3. Oxidation of toluene gives rise to benzaldehyde, benzyl alcohol, benzoic acid, and other oxidized products. With increased amount of catalyst used, a maximum conversion of toluene of 85.9% at 0.1 mmol catalyst used with a selectivity of benzaldehyde of 50.0% is observed. When the amount of catalyst varies from 0.03 mmol to 0.1 mmol, the conversion of toluene has increased, and the selectivity to benzaldehyde decreases. It is noted that when the amount of catalyst used is greater than 0.1 mmol, the conversion of toluene slight decreased, this may be caused by the faster decompose rate of oxidant. The selectivity of benzaldehyde decreased, this may be due to the unstable characteristics of benzaldehyde capable of being further oxidized to benzoic acid. In order to make the oxidation reaction were completely and improve benzaldehyde selectivity, 0.1 mmol $Nd_3P_2Mo_{15}V_3O_{62}$ is a suitable amount in this reaction.

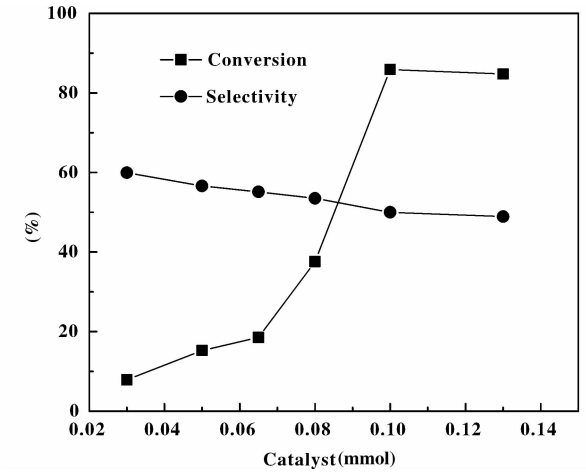


Fig. 3 Effect of the amounts of catalyst on the oxidation reaction

Reaction conditions: 23.5 mmol toluene, w (H_2O_2) = 50% H_2O_2 0.4 mol, using $Nd_3P_2Mo_{15}V_3O_{62}$ as catalyst and acetonitrile (10 mL) as solvent; temperature: 363 K, reaction time: 7 h

The influence of the amount of hydrogen peroxide on the conversion of toluene and the selectivity of benzaldehyde over $Nd_3P_2Mo_{15}V_3O_{62}$ is shown in Fig. 4. The conversion of toluene meets the maximum with 0.4 mol of hydrogen peroxide used. Further increase of H_2O_2 causes further oxidation of benzaldehyde to benzoic acid. When more than 0.4 mol of H_2O_2 addition is applied, both the selectivity of benzaldehyde and the conversion of toluene decreased. This may be due to excessive water bringed into the system with increased the amount of hydrogen peroxide, which reduced the

concentration in the reaction system of the catalyst and the reaction rate. This indicates that the optimum amount of hydrogen peroxide on the conversion of toluene and the selectivity of benzaldehyde over $Nd_3P_2Mo_{15}V_3O_{62}$ is 0.4 mol.

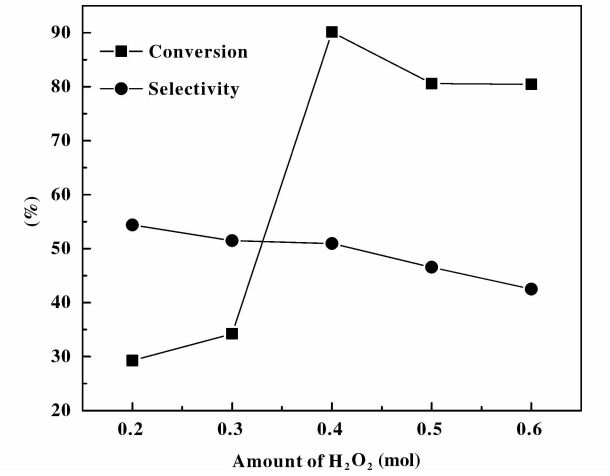


Fig. 4 Effect of the amount of hydrogen peroxide on the oxidation reaction

Reaction conditions: 23.5 mmol toluene, using $Nd_3P_2Mo_{15}V_3O_{62}$ (0.1 mmol) as catalyst and acetonitrile (10 mL) as solvent; temperature: 363 K, reaction time: 7 h

The consumption of hydrogen peroxide is caused competitively by its self-decomposition and the oxidation of toluene. In order to probe the conversion and the effective utilization ratio of hydrogen peroxide in this reaction, we measured the residual H_2O_2 concentration in reaction solution. The hydrogen peroxide concentration is determined by means of iodometric method. The conversion of H_2O_2 and effective utilization ratio of H_2O_2 were 89.0% and 43.1%, respectively.

The effect of reaction temperature on the conversion of toluene and the selectivity of benzaldehyde over $Nd_3P_2Mo_{15}V_3O_{62}$ was also studied and the results are shown in Fig. 5. At low reaction temperature, the reaction had a low rate. Similarly, a low conversion of toluene was less than 10%. As the reaction temperature below 363 K, the conversion of toluene increased first and then decreased with increasing the reaction temperature, the oxidation reaction of toluene reached conversion of 85.9% at the optimum temperature of 363 K. It seems that the decomposition of hydrogen peroxide is important for toluene oxidation. Only a slight changes in the selectivity of benzaldehyde was observed at the reaction temperature ranges from 333 K to 363 K, however, it reduced dramatically when the temperature is high than 363 K, owing to the production of more phenylcarbinol and the further oxydate benzoic acid. An optimal yield of benzaldehyde is obtained at 363 K since further increase in temperature will cause evaporation of the reactant. Based on these results, 363 K was considered as a suitable reaction temperature.

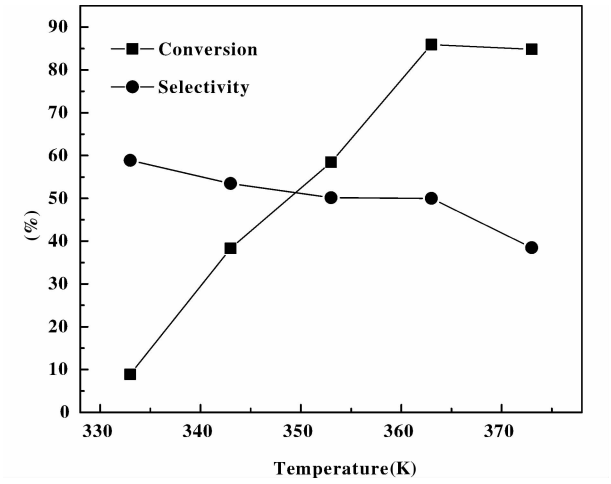


Fig. 5 Effect of the reaction temperature on the oxidation reaction

Reaction conditions: 23.5 mmol Toluene, w (H_2O_2) = 50% H_2O_2 0.4 mol, using $Nd_3P_2Mo_{15}V_3O_{62}$ (0.1 mmol) as catalyst and acetonitrile (10 mL) as solvent; reaction time: 7 h

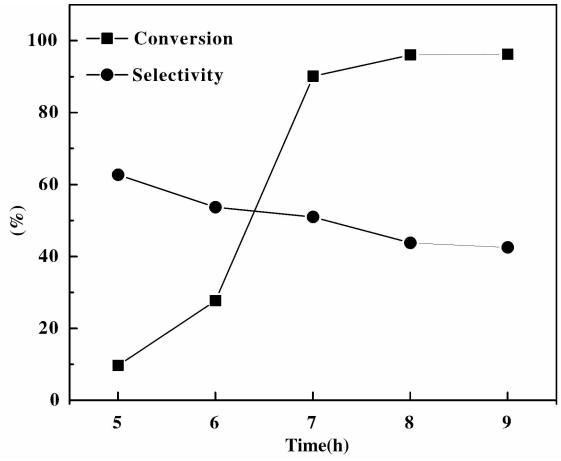


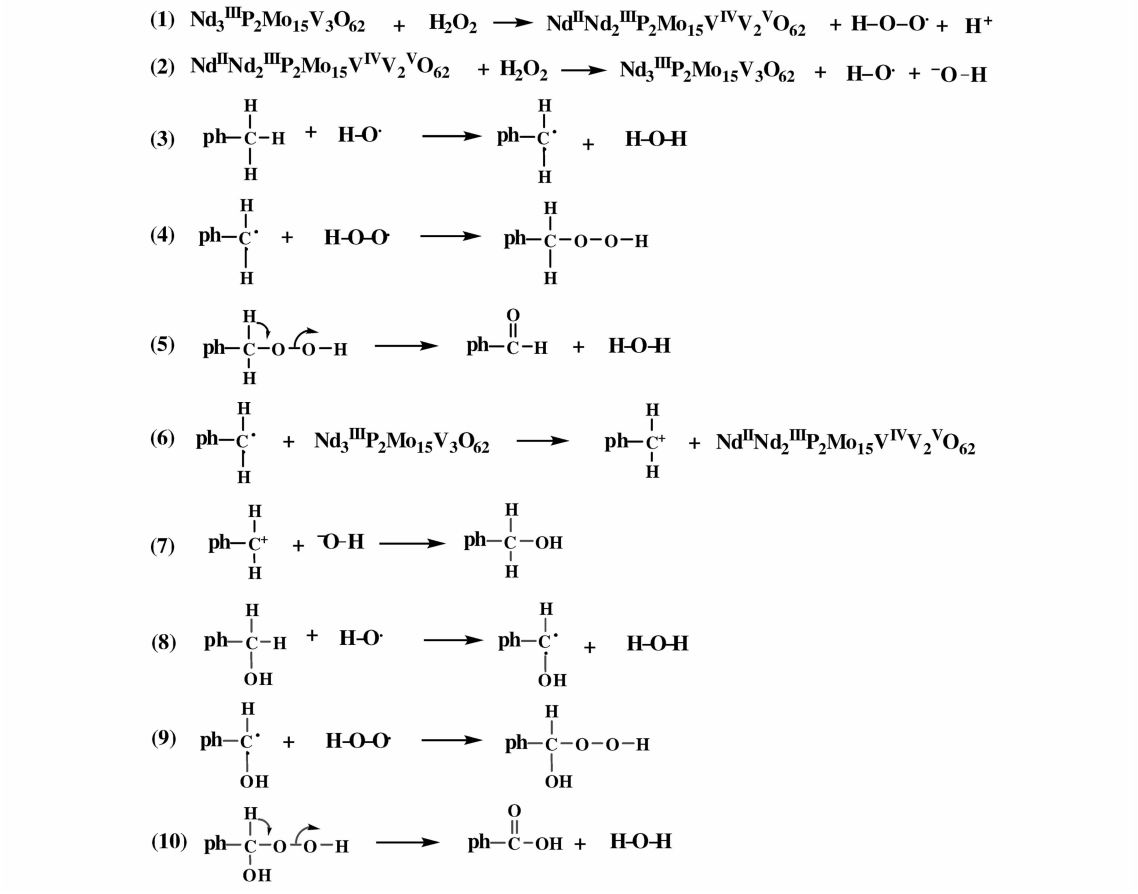
Fig. 6 Effect of the reaction time on the oxidation reaction

Reaction conditions: 23.5 mmol Toluene, w (H_2O_2) = 50% H_2O_2 0.4 mol, using $Nd_3P_2Mo_{15}V_3O_{62}$ (0.1 mmol) as catalyst and acetonitrile (10 mL) as solvent; temperature: 363 K

Fig. 6 shows the result for the oxidation reaction of toluene as a function of reaction time over $Nd_3P_2Mo_{15}V_3O_{62}$ catalyst at a reaction temperature of 363 K. It can be observed that the conversion of toluene increased with the reaction time up to 9 h. The selectivity of benzaldehyde decreased with the reaction time, because of further oxidation of benzaldehyde. So, it is concluded that the optimum reaction time is 7 h.

2.3 Catalysis mechanism

The selective formation of benzaldehyde over these vanadium containing polyoxometallate catalysts is might be due to the plausible mechanism as shown in Scheme 1. The $Nd_3P_2Mo_{15}V_3O_{62}$ reacts with H_2O_2 invariably proceed with initial formation of HOO· and HO·[19]. The HO· reacts with toluene to form the benzyl radical. The benzyl radical combines with HOO· to yield benzaldehyde. The formation of benzyl alcohol proceeds via the formation of benzyl cation by the transfer of electron from benzyl radical to the catalyst. The benzyl cation reacts with hydroxyl anion to yield benzyl alcohol[2]. The reduced catalyst is reoxidized by H_2O_2. It was possible that the formation of suitable strong synergistic effect of Neodymium and vanadium to decrease the surface acidity and meanwhile to enhance the redox ability seemed to be a way to improve the catalytic behavior for the selective oxidation of toluene. One cannot rule out the formation of benzaldehyde from the benzyl alcohol over these catalysts. It is reported that the $Nd_3P_2Mo_{15}V_3O_{62}$ catalyst through transfer of two electrons and two protons from the benzyl alcohol to the catalyst to yield benzaldehyde[20].



Scheme 1 Plausible reaction mechanism for the formation of benzyl alcohol, benzaldehyde and benzoic acid

2.4 Comparison of toluene oxidation by different catalysts

The present catalyst is compared with some of the heterogeneous catalysts reported in the literature for the low temperature oxidation of toluene and the details are shown in Table 1.

Table 1 A comparison of toluene oxidation activity of the $Nd_3P_2Mo_{15}V_3O_{62}$ catalyst with other reported catalysts

Catalysts	Oxidant	Conversion of toluene (%)	Selectivity of benzaldehyde (%)
$VO(acac)_2$ [1]	H_2O_2	18.7	62.0
$K_{15}[La(PMo_9V_2O_{39})_2]\ 6H_2O$ [21]	H_2O_2	93.6	15.5
$Co_3H_2PV_2Mo_{10}O_{40}$ [22]	TBHP	28.5	55.5
V-Ag/OMS-2 [23]	O_2	1.9	61.0
γ-MnO_2 [24]	O_2	47.8	15.0
$H_9P_2Mo_{15}V_3O_{62}$	H_2O_2	14.8	82.7
$Nd_3P_2Mo_{15}V_3O_{62}$	H_2O_2	90.1	51.0

3 Conclusion

In summary, the present study reveals a convenient method for selective oxidation of toluene to yield benzaldehyde at low temperature. The $Nd_3P_2Mo_{15}V_3O_{62}$ catalyst is an efficient solid catalyst for selective oxidation of toluene using H_2O_2 as an oxidant. The present catalytic system is environmentally benign, non-corrosive and active at low temperature. The results illustrate that rare-earth metal Nd does not enter the first level of structure, just occupies the position of the counter ion. Metal Nd also ameliorats acidity, oxidability and reducibility of catalyst. Toluene oxidation with $Nd_3P_2Mo_{15}V_3O_{62}$ catalysts using H_2O_2 as oxidant offers about 90.1% conversion, 51.0% selectivity of benzaldehyde, 24.5% selectivity of benzyl alcohol, 24.1% selectivity towards benzoic acid and 0.4% selectivity of other oxidized products at 363 K. The disclosed catalyst offers considerably high activity than most of reported the catalysts.

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Dawson 型杂多酸钕盐催化氧化甲苯制备苯甲醛

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摘 要: 合成了 Dawson 型磷钼钒杂多酸稀土(钕)盐, 并用红外光谱分析(IR)、X 射线衍射(XRD)方法对催化剂进行了表征; 以H_2O_2为氧化剂, 进行了甲苯氧化制备苯甲醛的反应研究. 由于钕和钒的协同作用, 催化剂表现出高的活性. 实验结果表明, 甲苯的转化率 90.1%, 苯甲醛的选择性达 51.0%, 双氧水的转化率 89.0%, 双氧水的有效利用率 43.1%. 基于对杂多酸盐结构的研究, 对反应机理进行了初步的探讨.

关键词: Dawson 型; 杂多酸; 钕盐; 甲苯; 苯甲醛