



Preparation and catalytic activity of P4VP–Cu(II) complex supported on silica gel

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ABSTRACT

Micron-sized silica gel particles were chemically modified on their surfaces with the coupling agent, γ -methacryloxypropyl trimethoxysilane (MPS), double bond was introduced onto the surfaces of silica gel particles, and the modified particles MPS–SiO₂ were obtained. Then, poly(4-vinylpyridine) (P4VP) was grafted from the silica gel surfaces, and grafting particles P4VP/SiO₂ was prepared. Finally, the coordination between grafted P4VP and cupric ions Cu²⁺ was performed, and the supported complex Cu(II)–P4VP/SiO₂ was obtained. The grafting particles P4VP/SiO₂ and the supported complex Cu(II)–P4VP/SiO₂ were characterized with infrared spectra (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Cu(II)–P4VP/SiO₂ was used as a catalyst for the oxidation of ethyl benzene into acetophenone with molecular oxygen under ordinary pressure. The experimental results show that the supported complex Cu(II)–P4VP/SiO₂ can be successfully prepared via grafting polymerization of 4VP and coordination between the grafted P4VP and cupric ions Cu²⁺. In oxidation of ethyl benzene into acetophenone by molecular oxygen under ordinary pressure, the supported complex Cu(II)–P4VP/SiO₂ displayed high catalytic activity and excellent catalytic selectivity up to more than 98% for the transformation of ethyl benzene to acetophenone.

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1. Introduction

4-Vinyl pyridine (4VP) is a functional monomer and the N atom on pyridine ring is a strong donor of electrons. Thus, poly(4-vinyl pyridine) (P4VP) is a functional polymer, it can coordinate with various transition metals ion, and many polymer–metal complexes can be obtained. The complexes between P4VP and many kinds of transition metals have high catalytic activity for organic reactions [1–5]. Especially, the catalytic action of complex P4VP–Cu(II) for some organic reactions has received considerable attentions [6–8]. The chemical structure of complex P4VP–Cu(II) was researched by Jeschke [9] who suggested a geometry model of coordination sphere for the structure of complex P4VP–Cu(II), and this model was supported by a combination of EPR, electron-nuclear double resonance methods (ENDOR) and molecular modelling based on density functional and force-field calculations. Based on the model, he put forward that the coordination number of cupric ion for complex P4VP–Cu(II) is three or fewer, namely there are three or fewer pyridyl groups as ligands around cupric ion. In a previous study, we confirmed Jeschke's viewpoint with experiment results of coordination-conductometric titration and the coordi-

nation number of cupric ion indeed is three for the insoluble and blue complex P4VP–Cu(II) [10], which is a polymer–metal complex formed via coordination crosslinking. Based on studying the chemical structure of complex P4VP–Cu(II), in this work, we grafted complex P4VP–Cu(II) on micron-sized silica gel particles via grafting polymerization of 4VP and coordination of Cu(II), prepared the supported complex Cu(II)–P4VP/SiO₂, and applied it in the catalytic oxidation of ethyl benzene.

Oxidation is one of the most important chemical processes for organic chemical industry because hydrocarbons can be transformed into organics containing oxygen and a great deal of intermediate compounds for organic synthesis can be obtained. If molecular oxygen is effectively activated by catalysts, the oxidation transform of organics can be favorably realized under mild conditions [11,12]. At present, this is one of the most challenging and promising subjects for organic synthesis industry and is also a very active research field in organic synthesis [13,14]. In recent years, heterogeneous oxidation catalysts have been developed for the oxidation of hydrocarbons with molecular oxygen as oxidant, such as supported metalloporphyrin, metalphthalocyanine, metal–Schiff base complex and so on [15–17]. They can effectively activate molecular oxygen and enable hydrocarbons to convert to valuable chemicals with high activity and selectivity. There are several heterogeneous catalytic methods for ethyl benzene oxidation, in which metal complexes were supported on

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polymeric carriers via the ligand action [18,19]. In this work, supported complex Cu(II)-P4VP/SiO₂ is used in oxidation of ethyl benzene into acetophenone with molecular oxygen under ordinary pressure as oxidant and a satisfactory result is obtained. The catalyst of Cu(II)-P4VP/SiO₂ displays excellent catalytic activity and selectivity in the oxidation process of ethyl benzene to acetophenone by O₂ under ordinary pressure. This catalyst combines the catalytic property of complex P4VP-Cu(II) and the characteristics of silica gel, such as high specific area, excellent mechanical property and thermal stability, and has potential in catalytic oxidation synthesis. To our knowledge, a similar study has not been reported.

2. Experimental

2.1. Material and equipment

4-Vinylpyridine (4VP, Aldrich, 98%) was dried with calcium hydroxide over night before used, then was distilled under vacuum (15 mm Hg, 68–69 °C). Silica gel (120–160 mesh, about 125 μm in diameter) was received from Qingdao Ocean Chemical Limited Company (China). 3-Methacryloxypropyl trimethoxysilane (MPS) was supplied by Nanjing Chuangshi Chemical Auxiliary Limited Company (China). Azodiisobutyronitrile (AIBN) was obtained from Fluka without further treatment. Ethyl benzene with A.R. grade was purchased from Beijing Xinjing Chemical plant.

Used instruments were as follows: Shimadzu-8400S FTIR 99 spectrometer (Japanese Shimadzu Company), Unic-2602 UV 100 spectrometer (American Unic Company), LC-10ATvp high performance liquid chromatograph (China), 438VP scanning electron microscope (UK LEO Company), and TGA 71 thermogravimetric analyzer (American PerkinElmer Company).

2.2. Preparation and characterization of supported complex Cu(II)-P4VP/SiO₂

2.2.1. Preparation of grafting particles P4VP/SiO₂

10 g of silica gel particles were activated with the aqueous solution of methane sulfonic acid as described in Ref. [20]. The activated silica gel particles were added into 200 ml of a mixed solvent of ethanol and water in a volume ratio of 1:1, and 15 ml of 3-MPS was also added. The mixture was allowed to react at 50 °C for 24 h and the modified silica gel particles with MPS were obtained designated as MPS-SiO₂.

Monomer 4VP, solvent ethanol and MPS-SiO₂ were added into a four-neck bottle equipped with a mechanical agitator, a reflux condenser, a N₂ inlet and a thermometer. The content was stirred for 1 h under N₂ in order to fully disperse MPS-SiO₂ particles in the system. When the temperature rose to 60 °C, initiator AIBN was added and the graft polymerization was carried out at constant temperature. After finishing the reaction, the product was filtered and extracted with ethanol in a soxhlet to remove the polymer physically absorbed on the surface of the product particles. After washing with ethanol, the product particles were dried under vacuum and the grafting particles P4VP/SiO₂ were obtained. The grafting degree g/100 g was determined with weight method. By varying the polymerization time, two kinds of the grafting particles P4VP/SiO₂ with different grafting degrees (15.4 g/100 g and 20.1 g/100 g, respectively) were prepared and used in the following preparation of the supported catalyst.

2.2.2. Preparation of supported complex Cu(II)-P4VP/SiO₂

A mixed solvent of ethanol and water, grafting particles P4VP/SiO₂ and excess cupric salt CuCl₂·H₂O were added into a four-neck bottle. At the reflux temperature, the coordination reaction was allowed to be carried out for 5 h. After ending the

reaction, the product was filtered, washed repeatedly with water to remove excess cupric salt, and dried under vacuum. By adopting the two kinds of P4VP/SiO₂ with different grafting degrees described above, two kinds of Cu(II)-P4VP/SiO₂ (actually in the form of CuCl₂-P4VP/SiO₂) with different amounts of the supported complex Cu(II)-P4VP (21.2 g/100 g and 28.3 g/100 g, respectively) were gained (the supported amount was determined with weight method).

2.2.3. Characterization of modified silica materials

The FTIR spectra of modified particle MPS-SiO₂, grafting particle P4VP/SiO₂ and supported complex Cu(II)-P4VP/SiO₂ were determined with KBr pellet method and the chemical structure changes on the surface of silica gel were confirmed. The morphology changes of silica gel before and after grafting were observed by using scanning electron microscope. The thermal stability of complex P4VP-Cu(II) and supported complex Cu(II)-P4VP/SiO₂ were compared with thermogravimetry analysis (TGA). The conditions of the thermal analysis were as follows: under N₂ atmosphere and a heating rate of 10 °C/min.

2.2.4. Oxidation of ethyl benzene catalyzed by Cu(II)-P4VP/SiO₂

40 ml of liquid paraffin, 10 ml of ethyl benzene and catalyst Cu(II)-P4VP/SiO₂ were added in a four-neck bottle of 100 ml equipped with a motor stirrer, a O₂ inlet tube connected to a gauge of oxygen bomb, a reflux condenser (also used as outlet of O₂) and a thermometer. Under ordinary pressure, O₂ was bubbled from gauge at a constant rate. The reaction was performed under stirring at a constant temperature in an oil bath. The samples were taken in a certain time period, diluted with cyclohexane and their UV absorbencies at 279 nm, which is the characteristic absorption of acetophenone, were measured. The yield of acetophenone for different reaction time was calculated using a calibration curve.

In order to examine the selectivity of catalytic oxidation, high performance liquid chromatograph analysis was performed. The chromatograph conditions were as follows: using a mixture of methanol and water (82:18, v/v) as mobile phase, with a flow rate of 1.0 ml/min, 10 μl of sample amount and 254 nm of detecting wavelength. The FTIR spectrum of the product mixture was determined to characterize the chemical structure of the product further.

By varying the conditions of the catalytic oxidation, the effects of various factors on the yield of acetophenone were studied. These conditions included reaction time, temperature, the used amount of catalyst and the amount of P4VP-Cu(II) supported on SiO₂.

3. Results and discussion

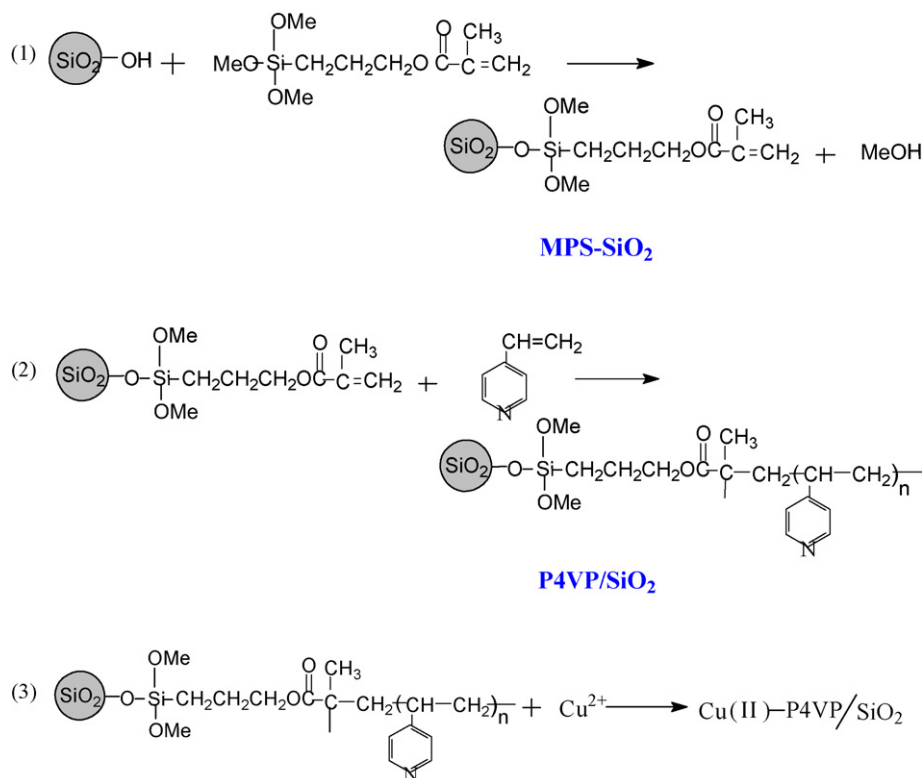
3.1. Reaction process to prepare catalyst Cu(II)-P4VP/SiO₂

After surface modification of silica gel, coupling agent MPS in whose molecule polymerizable double bond is contained was bound on the surface of silica gel particles chemically. By initiating of AIBN, 4VP was grafted on the surface of silica gel in the manner of "grafting from" [21], further, the coordination between the grafted P4VP and cupric ion was carried out, and finally the supported complex Cu(II)-P4VP/SiO₂ was obtained. the procedure to prepare Cu(II)-P4VP/SiO₂ is given in Scheme 1.

3.2. Characterization of chemical structure and physical chemistry property for Cu(II)-P4VP/SiO₂

3.2.1. FTIR spectra

Fig. 1 gives the FTIR spectra of modified particle MPS-SiO₂, grafted particle P4VP/SiO₂ and supported complex Cu(II)-P4VP/SiO₂ as well as SiO₂. In comparison with the spectrum of



Scheme 1. Process to prepare the supported complex Cu(II)-P4VP/SiO₂.

SiO₂, in the spectrum of MPS-SiO₂, the asymmetry stretching vibration absorption of C-H bond, the stretching vibration absorption of C=O bond of carbonyl group at 1730 cm⁻¹ and the stretching vibration absorption of C-O-C bond of ester group at 1297 cm⁻¹ appear, respectively. The appearance of these bands suggests that the reaction between MPS and silanol groups on silica gel particles has occurred and modified particles MPS-SiO₂ have been formed. In the spectrum of P4VP/SiO₂, the new bands at 1596, 1558, 1496 and 1415 cm⁻¹ are the characteristic absorptions of pyridine ring, and among them the band at 1596 cm⁻¹ is the stretching vibration absorption of C-N bond and the bands at 1558, 1496 and 1415 cm⁻¹ are attributed to the stretching vibration absorption of C-C bond. The appearance of the above bands show that P4VP has grafted onto the surface of silica gel and the grafting particles P4VP/SiO₂

have obtained. In the spectrum of Cu(II)-P4VP/SiO₂, a new shoulder peak appears at 1616 cm⁻¹, which is ascribed to the pyridine ring-Cu²⁺ bond absorption [22], and the bands of the characteristic absorption of pyridine ring exhibit slight blue shifts (for example, the band at 1415 cm⁻¹ has shifted to 1425 cm⁻¹) because of the strengthening of C-N and C-C bonds as Cu²⁺ ions are incorporated [22]. The above observations reveal that the coordination between N atoms on pyridine ring and ions Cu²⁺ ions has occurred, and the supported complex Cu(II)-P4VP/SiO₂ has been obtained.

3.2.2. Thermogravimetric analysis (TGA)

Fig. 2 displays the TGA curves of unsupported complex P4VP-Cu(II) and supported complex Cu(II)-P4VP/SiO₂ under N₂ atmosphere. The weight loss for P4VP-Cu(II) begins at 268 °C because of thermo-degradation of P4VP polymer chains and the degradation ends at 425 °C; whereas for Cu(II)-P4VP/SiO₂, the

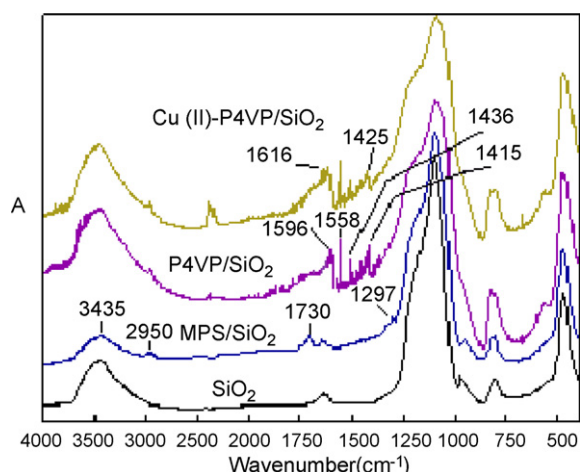


Fig. 1. FTIR spectra of modified silica materials.

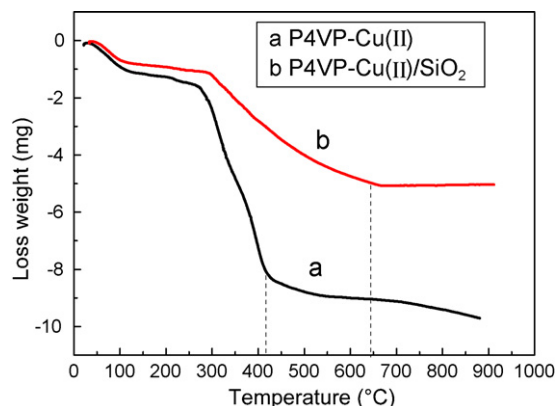


Fig. 2. TGA curves of P4VP-Cu(II) and Cu(II)-P4VP/SiO₂.

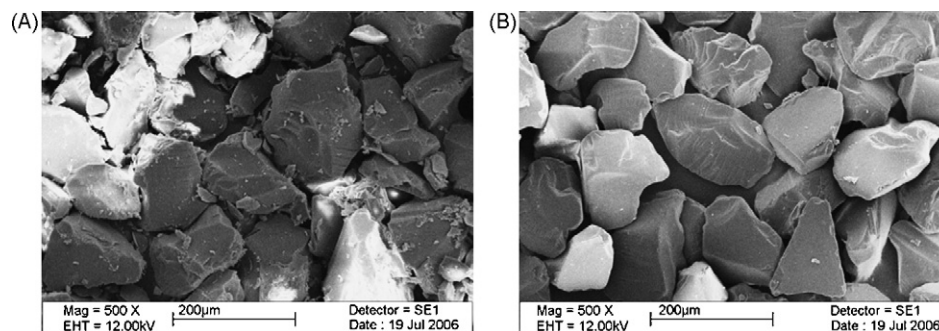


Fig. 3. TEM photographs of SiO₂ and P4VP/SiO₂.

weight loss appears only at 300 °C and the degradation ends until at 665 °C. Obviously, the supported complex Cu(II)–P4VP/SiO₂ has higher thermal stability and slower degradation rate than unsupported complex P4VP–Cu(II). Therefore, after complex P4VP–Cu(II) is supported on silica gel, the thermal stability is enhanced greatly, and this is very important for the catalyst application.

3.2.3. Morphology of grafting particles P4VP/SiO₂

Fig. 3 gives the scanning electron microscopy (SEM) photographs of bare silica gel and the grafting particle P4VP/SiO₂. It is obvious that before grafting the surface of bare silica gel is somewhat coarse and irregular, whereas after grafting, the surface of silica gel becomes smooth. This results from the covering and filling of grafted polymer P4VP.

3.3. Catalysis action of Cu(II)–P4VP/SiO₂ in oxidation of ethyl benzene by O₂

3.3.1. Adsorption spectrum of product mixture

Fig. 4 shows the FTIR spectra of the product mixture and ethyl benzene. In the spectrum of the product mixture, except the characteristic absorptions of unreacted ethyl benzene, a new band appears at 1712 cm⁻¹ and it is the characteristic absorption of carbonyl C=O. This reveals that alpha (α) C atoms on the side chains of ethyl benzene have been oxidized and the product is mainly acetophenone.

Fig. 5 gives the UV spectra of ethyl benzene, acetophenone and the product mixture in a range of 270–300 nm. It is observed from Fig. 5 that the spectrum of the product mixture is the result of overlying of the spectra of acetophenone and ethyl benzene; there is a characteristic absorption at 279 nm for acetophenone; but there

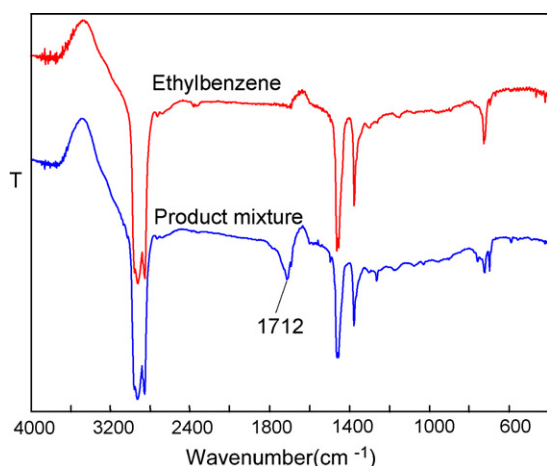


Fig. 4. FTIR spectrum of the product mixture.

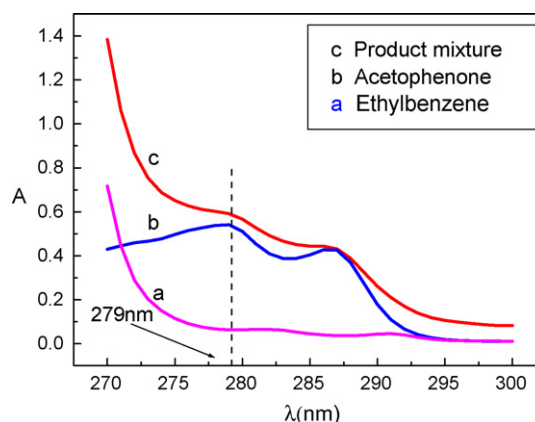


Fig. 5. UV spectra of the reactant, product and product mixture.

is not any absorption at 279 nm for ethyl benzene. Therefore, in this work the yield of acetophenone was determined spectrophotographically by utilizing the absorbency at 279 nm.

3.3.2. Catalytic activity

The oxidation reaction of ethyl benzene was conducted with liquid paraffin as solvent and Cu(II)–P4VP/SiO₂ as catalyst, gas O₂ at ordinary pressure was let in the reaction system, and the oxidation reaction was allowed to be carried out at 100 °C. Catalyst Cu(II)–P4VP/SiO₂ was added and was not added into the reaction system, respectively. The acetophenone yield as a function of reaction time is shown in Fig. 6. It is displayed that the reaction nearly

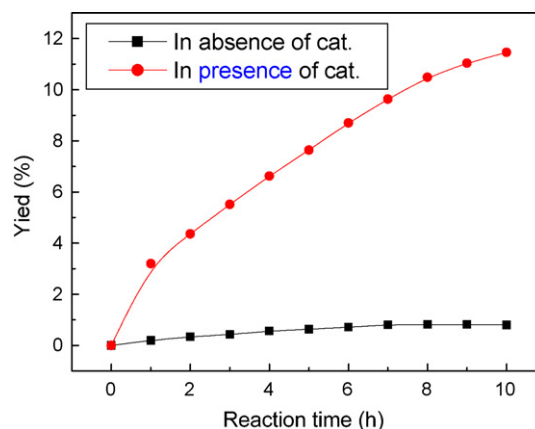


Fig. 6. Variation of acetophenone yield with time. Supported amount of Cu(II)–P4VP of catalyst Cu(II)–P4VP/SiO₂: 28.3 g/100g; used amount of catalyst: 0.25 g; temperature: 100 °C.

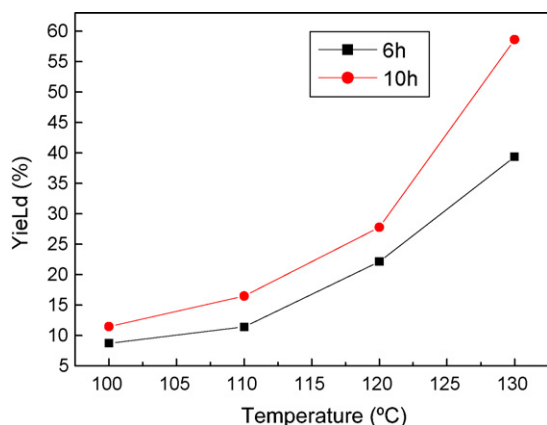


Fig. 7. Variation of acetophenone yield with temperature at different temperatures. Supported amount of Cu(II)-P4VP of catalyst Cu(II)-P4VP/SiO₂: 28.3 g/100 g; used amount of catalyst: 0.25 g.

does not occur in the system without catalyst Cu(II)-P4VP/SiO₂, whereas in the system into which Cu(II)-P4VP/SiO₂ was added, acetophenone is produced at 100 °C and the yield is increased with time. The catalytic oxidation was carried out at different temperatures, and Fig. 7 gives the relationship between the yield of acetophenone and reaction temperature. It is clearly shown that the oxidation rate is very sensitive to the reaction temperature. At 100 °C, only a yield of 10% was obtained in 10 h, whereas as the reaction was carried out for 10 h at 130 °C, the yield of acetophenone nearly reached 60%. The above experimental results show obviously that the complex P4VP-Cu(II) supported on SiO₂ can effectively activate molecular oxygen and it has obvious catalysis action in oxidation of ethyl benzene to acetophenone with molecular oxygen.

3.3.3. Catalytic selectivity

The product mixture taken from the reaction system at 120 °C for 10 h was diluted, analyzed on a high performance liquid chromatograph, and the result is given in Fig. 8. It was estimated according to the molecular structure of ethyl benzene that α -methyl benzyl alcohol was a possible oxidation product of ethyl benzene. It is obvious that in the chromatogram of product mixture the main peak is the peak of acetophenone, whereas the peak of α -methyl benzyl alcohol is very small. Liquid chromatograph analysis shows that catalyst Cu(II)-P4VP/SiO₂ has excellent selectivity in the oxidation of ethyl benzene to acetophenone by molecular oxygen and more than 98% of the product mixture is acetophenone. This is in agreement with the results of Bennur [23], who used N-containing macro-ring complex of Cu(II) as catalyst for oxidation of ethyl benzene into acetophenone.

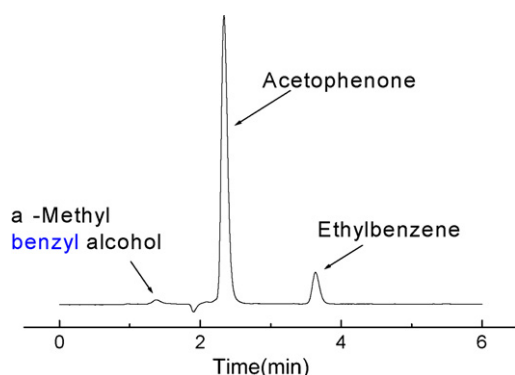


Fig. 8. Liquid chromatogram of the product mixture.

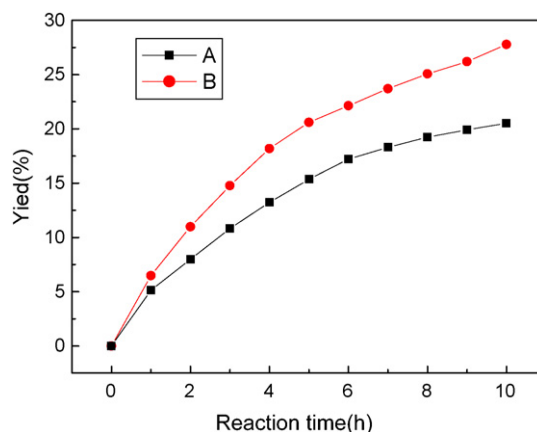


Fig. 9. Effect of supported amount of supported Cu(II)-P4VP on the catalytic oxidation. (A) 19.2 g/100 g and (B) 28.3 g/100 g. Used amount of catalyst: 0.25 g; reaction temperature: 120 °C

3.3.4. Effect of the supported amount of complex P4VP-Cu(II) on silica gel on the catalytic oxidation

Two kinds of catalyst Cu(II)-P4VP/SiO₂, on which the amount of the supported complex Cu(II)-P4VP are 21.2 g/100 g and 28.3 g/100 g, respectively, were used in the oxidation of ethyl benzene with molecular oxygen and Fig. 9 displays the experimental result. Obviously, the greater the supported amount of complex P4VP-Cu(II) on silica gel, the higher the catalytic activity of the catalyst Cu(II)-P4VP/SiO₂.

3.3.5. Effect of the used amount of catalyst Cu(II)-P4VP/SiO₂ on the catalytic oxidation

In the reaction system consisting of 10 ml of ethyl benzene and 40 ml of liquid paraffin, the catalytic oxidations were carried out at 120 °C with different added amounts of the catalyst. In fixed periods of time (6 and 10 h), the samples were taken and analyzed. Fig. 10 gives the yield of acetophenone as a function of the used amounts of catalyst Cu(II)-P4VP/SiO₂. It is shown in Fig. 10 that the yield of acetophenone is rapidly enhanced with the increase of the used amount of catalyst Cu(II)-P4VP/SiO₂ as the amount of the catalyst is less, whereas after the used amount of the catalyst reaches about 0.7 g, the yield tends to plateau. It can be considered that 0.7 g is a suitable amount of used catalyst Cu(II)-P4VP/SiO₂ probably for the above described reaction system.

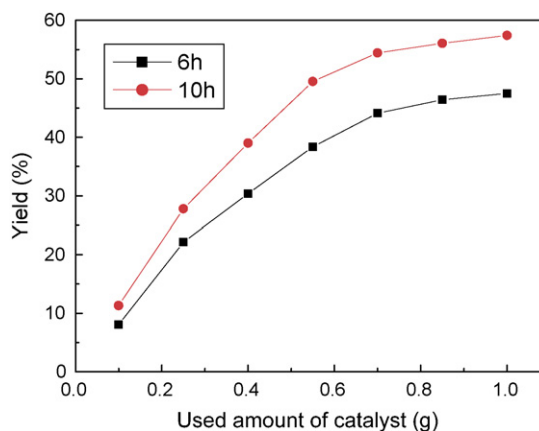


Fig. 10. Effect of the used amount of catalyst Cu(II)-P4VP/SiO₂ on the catalytic oxidation. Reaction temperature: 120 °C

4. Conclusions

In this work, functional polymer P4VP was grafted on the surfaces of micron-sized silica gel particles with “grafting from” manner, and grafting particles P4VP/SiO₂ were prepared. Then, the coordination between the grafted P4VP and cupric ions Cu²⁺ was allowed to be carried out and the supported complex Cu(II)–P4VP/SiO₂ was obtained. Cu(II)–P4VP/SiO₂ was used in the oxidation of ethyl benzene into acetophenone with molecular oxygen. The supported complex Cu(II)–P4VP/SiO₂ behaved with fine catalytic activity and selectivity. Furthermore, the catalyst combines well the catalytic property of the complex Cu(II)–P4VP with the characteristics of silica gel particles, such as high specific area, fine mechanical property, thermal stability and chemical stability. Such catalyst has potential application prospect in the catalytic oxidation field. This method to prepare supported metal complex catalyst is convenient and is a new route to obtain heterogeneous catalysts. About the stability and reuse performance of the heterogeneous catalyst Cu(II)–P4VP/SiO₂, further study needs to be carried out.

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