



Catalytic Synthesis of 2-(1-Cyclohexenyl)cyclohexanone by Mixed Heteropoly Acids Catalyst (PW₁₂ + PMo₁₂/SBA-15)

YING-YING WANG¹, BO WU¹, CHUN-LI LIU², FU-XIANG LI¹, ZHI-PING LV¹ and JIAN-WEI XUE^{1*}

¹Research Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, Shanxi Province, P.R. China

²Shandong Hualu Hengsheng Chemical Industrial Stock Co., Ltd., Dezhou, Shandong Province, P.R. China

*Corresponding author: Fax: +86 351 6111178; Tel: +86 13099072796; E-mail: xuejianwei@yeah.net

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Mixed heteropoly acids (phosphotungstic acid and phosphomolybdic acid) supported on SBA-15 (PW₁₂+PMo₁₂/SBA-15) by impregnation method was used as catalysts of self-condensation reaction of cyclohexanone to synthesize the 2-(1-cyclohexenyl)cyclohexanone. The experimental results indicated that the mixed heteropoly acids supported on SBA-15 had effective catalytic performance, which catalytic synthesis of 2-(1-cyclohexenyl)cyclohexanone. The effects of various parameters on the conversion ratio such as the amount of catalyst, loading amount, reaction time and reaction temperature were investigated. The optimum reaction conditions were as follows: The loading of the PW₁₂+PMo₁₂/SBA-15 was 29 %, the percentage of catalyst in reactants was 3 %, the reaction time was 2.5 h and the reaction temperature was 150 °C. The conversion rate could reach 86.5 %.

Keywords: Catalytic, 2-(1-Cyclohexenyl)cyclohexanone, Impregnation method, Mixed heteropoly acids, SBA-15.

INTRODUCTION

O-Phenylphenol (OPP) is one of the most important fine chemical industrial products derived from cyclohexanone and is widely used as fungicide, antiseptic, assistant agent in dyeing, surface activator and thermal stabilizer *etc.*^{1,2}. The synthesis of O-phenylphenol primarily was based on cyclohexanone as raw material and was obtained by a two-step chemical reaction process *via* condensation and dehydrogenation. And the target product of self-condensation of cyclohexanone³ is 2-(1-cyclohexenyl)cyclohexanone which can generate O-phenylphenol by further dehydrogenation. Therefore, it is very important for the preparation of 2-(1-cyclohexenyl)cyclohexanone. Self-condensation reaction of cyclohexanone belongs to nucleophilic substitution reaction on α -carbon atom, which can not only be acid-catalyzed⁴, but can also be alkali catalyzed⁵.

Heteropoly acid (HPA) catalysts have received considerable attentions, because of their moderate reaction conditions, less dosage, high activity and selectivity, fast regeneration speed, non-toxic, non-corrosiveness, operational simplicity which are all in favor of the design of catalysts. The most popular heteropoly acids are those with the Keggin structure⁶, *e.g.*, H₃PW₁₂O₄₀ (HPW). Heteropoly acids are polar organic liquids and readily soluble in water and have been successfully applied in homogeneous catalysis. Scholars have studied ion-

exchange resin⁷⁻⁹, aluminum oxide^{10,11}, titanium dioxide¹² and activated carbon¹³ as the carrier of the preparation of the heteropoly acid composites. Most researchers believe that activated carbon and silica as excellent carrier can be used for preparing heteropoly acid composites. The siliceous mesoporous materials (mainly SBA-15 and MCM-41) were applied as the carriers for many active substances^{14,15}. SBA-15 is a new type of SiO₂ mesoporous materials which is synthesized with a non-ionic block polymer as the template and it not only has larger diameter and thicker cell walls, but also has better stability. Wang *et al.*¹⁶ supported heteropoly acid on SBA-15 as a catalyst had studied on the alkylation reaction of 1-dodecene in benzene solvent and found that pure SBA-15 has no catalytic activity, while catalytic activity, selectivity and stability of the PW₁₂/SBA-15 are better than HY zeolite. Lapkin *et al.*¹⁷ had studied the heteropoly acid supported on SBA-15 as a chemical adsorbent and found it has good effect. The study also found that heteropoly acid supported on SBA-15 has a damaging effect on the carrier structure, even though the loading is very little.

The use of mixed heteropoly acids supported on SBA-15(PW₁₂+PMo₁₂/SBA-15) by impregnation method as solid catalysts for self-condensation reaction of cyclohexanone to synthesize 2-(1-cyclohexenyl)cyclohexanone was studied in this work.

EXPERIMENTAL

SBA-15 was supplied by Jilin University Chemical Works, China. Phosphotungstic acid (Keggin structure, PW_{12}) and phosphomolybdic acid were supplied by Beijing Chemical Works, China., Tetraethyl orthosilicate (TEOS) was supplied by Tianjin Kermel Chemical Co., Ltd., China. Templating agent $EO_{20}PO_{70}EO_{20}$ (P123) was supplied by Aldrich Chemical Co., Inc. Cyclohexanone and anhydrous ethanol were supplied by Tianjin Kermel Chemical Co., Ltd., China. These reagents were all AR. Hydrochloric acid (industrial products) was supplied by Taiyuan Chemical Industry Group Co., Ltd., China. Catalyst was homemade. The deionized water was made in our laboratory.

$EO_{20}PO_{70}EO_{20}$ (P123, 2 g) were dissolved in hydrochloric acid (2 mol/L, 80 mL) solution, heated in the constant temperature water bath and stirred for about 3 h; after it was completely dissolved, tetraethyl orthosilicate (TEOS, 4.5 mL) was added and stirred for 3-5 h in water bath, then dried of crystallization at 100 °C for 48 h in the autoclave. The samples were washed repeatedly until neutral and then dried at ambient temperature, finally calcined at 550 °C for 6 h in static air. Lastly, the pure sample of SBA-15 is obtained.

A mixed solid of phosphotungstic acid and phosphomolybdic acid (weight ratio 1:1) were added to deionized water (40 mL) and stirred to dissolve completely. The calcined SBA-15 (4 g) was added to heteropoly acid solution and then stirred with water bath at 30 °C for 24 h. After filtering and drying, activate the sample at 300 °C for 1 h. Mixed heteropoly acids catalyst was denoted by X % $PW_{12} + PMO_{12}/SBA-15$, which X represents the mass percentage share of mixed heteropoly acid in sample.

The synthesis reaction was conducted in a three-necked flask (250 mL) with a thermometer, a reactor, a water separator and a reflux condenser; the mixture of the (80 mL) cyclohexanone and catalyst were added into a three-necked flask (250 mL). They were heated, refluxed under 145-150 °C and reacted for some times. In this reaction, the production of water was brought out by the condensation method of evaporation with the help of cyclohexanone¹⁸, which facilitates the reaction to be in the positive direction. In addition to bringing out of the water, part of unreacted cyclohexanone was continued to react under reflux. After the reaction finished, the catalyst was recovered by filtration and the distillate that boiling point at 64-67 °C (vacuum degree of 0.09 MPa) was collected by distillation with a pressure-relief device. Then the colorless and transparent cyclohexanone, which is unreacted, was obtained. Finally, the distillate whose boiling point was 132-135 °C was collected by distillation with a pressure-relief device.

Detection method: Samples were analyzed by different techniques. X-ray diffraction (XRD) patterns of the catalyst were obtained by Japanese Rigaku motor X-ray diffractometer (Rigaku D/2500 X-Ray diffractometer) instrument operating at 40 kV and 100 mA with Cu target K_{α} -ray irradiation. Fourier Thermo Gravimetric Analyzer (TGA) were conducted under an air flow using a Rigaku thermal analyzer with 10 °C/min ramp for the determination of the material quality changes with temperature, in the temperature range of 30-700 °C. The specific surface areas were determined from the nitrogen adsorption/desorption isotherms (at 77 °K) measured with a

micromeritics NOVA 1200e volumetric system. Transform Infrared (FT-IR) spectra of samples were measured using a BIO2RAD/FT3165 spectrometer at room temperature and analyses performed using KBr pellet technique with a resolution at 2 cm^{-1} . Gas Chromatography (GC) spectrum of dimer was obtained by GC-900 which was supplied by Shanghai Analysis Instrument Factory Co., Ltd., China.

The reaction products were separation by means of distillation, the structure of product determined by infrared spectrum (IR) and its content was determined by gas chromatography (GC). The progress of the reaction was indicated by conversion of cyclohexanone. The conversion of cyclohexanone W was $W = (A-B)/A \times 100 \%$, where A and B was volume of cyclohexanone (unit is mL). The A was the volume of cyclohexanone before the reaction and the B was the volume of cyclohexanone after the reaction.

RESULTS AND DISCUSSION

The XRD patterns of pure SBA-15 and different concentrations of $PW_{12} + PMO_{12}/SBA-15$ are shown in Fig. 1. As shown in Fig. 1, for all the samples the hexagonal structure of SBA-15 is confirmed by a typical XRD pattern consisting of a strong peak (at 2 θ around 0.8°) along with two weak peaks (at 2 θ around 1.6° and 1.8°) and the characteristic crystal plane (100) plane, (110) plane, (200) plane are clearly visible. When the mixed heteropoly acids loading is low (3 %), zeolite SBA-15 crystal surface of the characteristic peaks almost has no change, which indicated that a little amount of mixed heteropoly acid ions did not have much impact on the pore of zeolite SBA-15 and it is more evenly distributed on its surface. With increasing of the loading amount of $PW_{12} + PMO_{12}/SBA-15$, the three characteristic peaks of zeolite SBA-15 crystal surface have different degree of decreasing. The reason is that with increasing of the heteropoly acid loading, the pores of SBA-15 are partially clogged by heteropoly acid ions, which leads to reducing inner diameter of the pore.

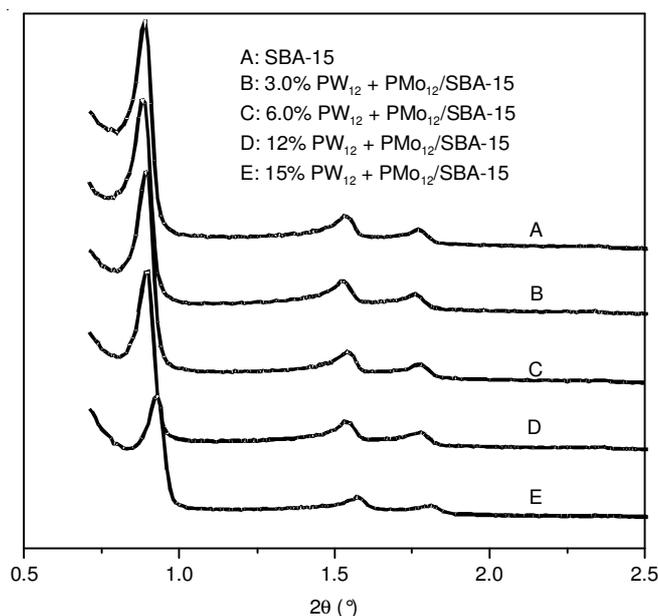


Fig. 1. XRD patterns of SBA-15(A) and X % $PW_{12} + PMO_{12}/SBA-15$

To further ascertain the structural properties of the catalyst, the adsorption-desorption isotherm of nitrogen analysis is carried out on the $\text{PW}_{12} + \text{PMo}_{12}/\text{SBA-15}$ (29 %). Fig. 2 shows the $\text{PW}_{12} + \text{PMo}_{12}/\text{SBA-15}$ (29 %) of nitrogen adsorption-desorption isotherms. The figure shows adsorption and desorption branches all have a steep jump branch and appear obvious hysteresis loops in a relatively high pressure area, both of them can not overlap and forming a ring. This phenomenon indicates that the samples will not only have a relatively neat uniform pore, but also have relatively large pore. Pore size distribution was shown in Fig. 3 and it shows that the pore size of $\text{PW}_{12} + \text{PMo}_{12}/\text{SBA-15}$ (29 %) is significantly smaller than pure SBA-15, which proved that mixed heteropoly acids had already existed in the mesoporous zeolite.

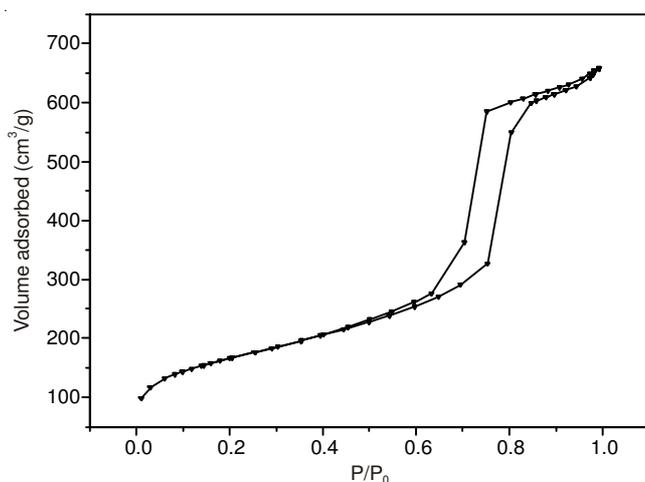


Fig. 2. N_2 adsorption isotherms of $\text{PW}_{12} + \text{PMo}_{12}/\text{SBA-15}$ (29 %)

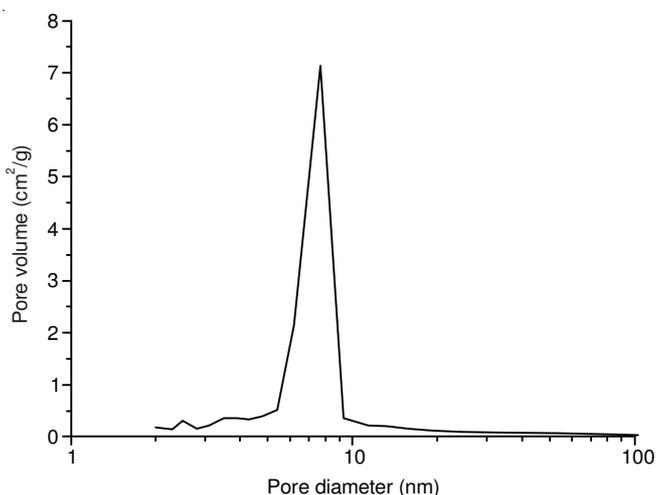


Fig. 3. Pore size distribution of $\text{PW}_{12} + \text{PMo}_{12}/\text{SBA-15}$ (29 %)

Figs. 4 and 5 show the TG-DTA curves for pure SBA-15 and 29 % $\text{PW}_{12} + \text{PMo}_{12}/\text{SBA-15}$. As shown in Fig. 4, the exothermic peak appeared at 197 °C attributed to the removal of templating agent P123 from SBA-15, which is corresponded to the significantly weight loss at 197 °C in TG curve. Fig. 5 shows that it has an endothermic peak at 54 °C where the physically adsorbed water lost from (29 %) $\text{PW}_{12} + \text{PMo}_{12}/\text{SBA-15}$ and an abroad exothermic peak appeared at 560 °C where the structure of mixed heteropoly acids is destroyed.

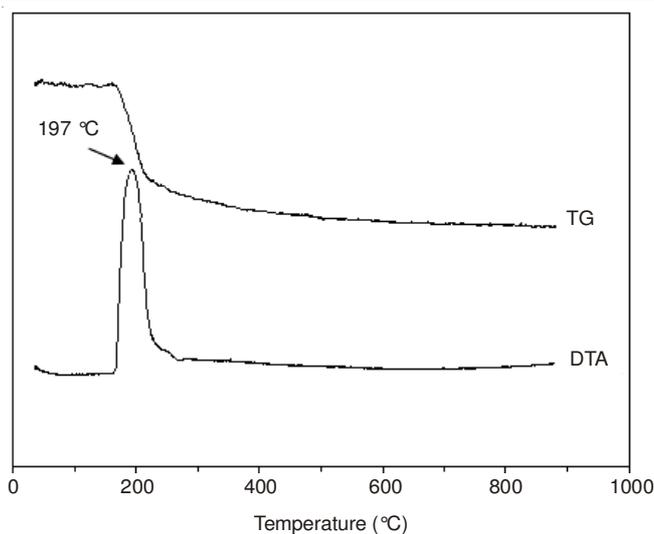


Fig. 4. TG-DTA patterns of SBA-15

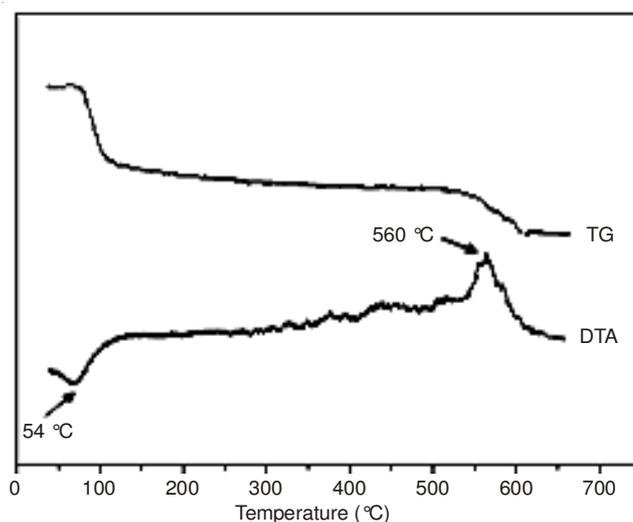


Fig. 5. TG-DTA patterns of $\text{PW}_{12} + \text{PMo}_{12}/\text{SBA-15}$ (29 %)

Comparing different TG/DTA curves, it is concluded that the structure of mixed heteropoly acid loading on the support of SBA-15 is damaged and the reduction of temperature is the strong evidence that heteropoly acids and the carrier interact with each other.

Effect factors of conversion rate: Fig. 6 shows there is an increase in the conversion rate of the cyclohexanone with the loading amount increasing. The conversion rate is the highest when the loading amount is 29 %. While the amount above 29 %, the reactions conversion rate were not distinctly increased. It is well-known that the more loadings amount is, the smaller pore volume of the carrier is. Then reactants are limited to enter into the pore of catalyst. Thereby, the conversion of the product decreases gradually.

The role of the catalyst is to reduce the activation energy of the reaction, which ultimately contributes to crossing the energy barrier more easily and generating products more quickly. As can be seen from the Fig. 7, conversion rate increases with the increasing amount of catalyst. Greater the amount of catalyst is, the higher the conversion rate is. However, when the amount of catalyst is excessive, it can help reduce the activation energy of the side-reaction and promote the adverse

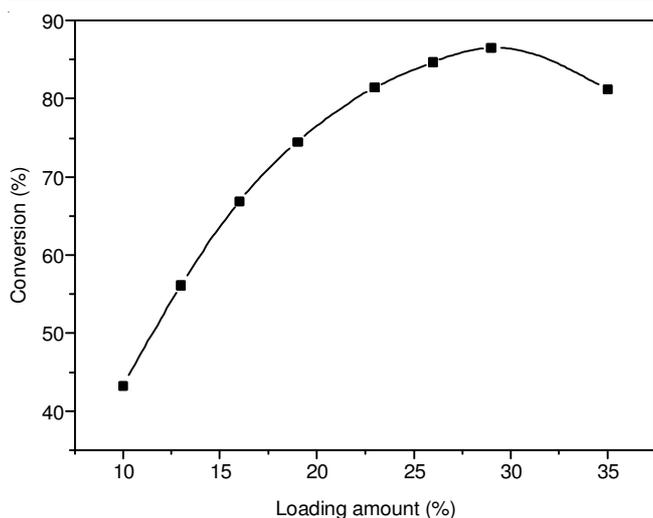


Fig. 6. Effect of loading amount on conversion

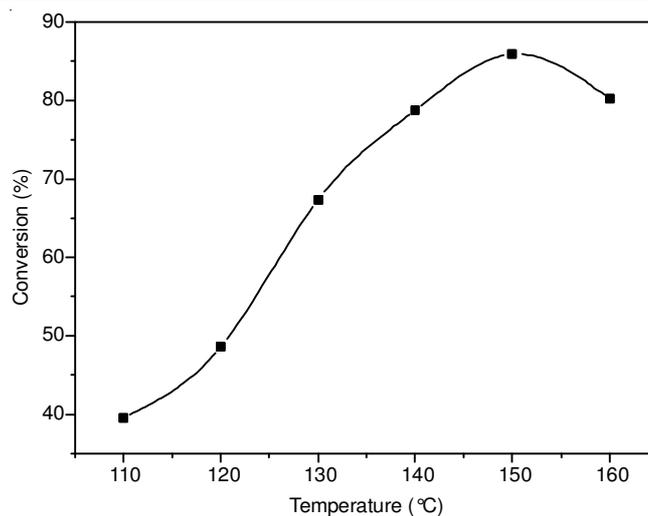


Fig. 8. Effect of reaction temperature on conversion

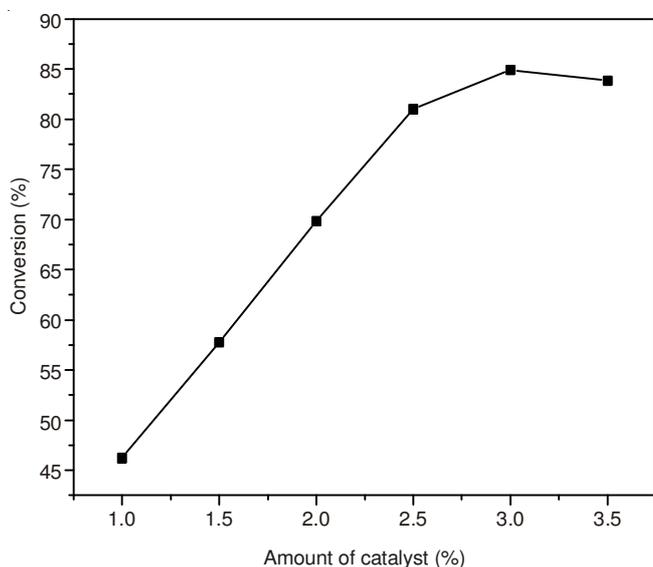


Fig. 7. Effect of quantity of catalyst on conversion

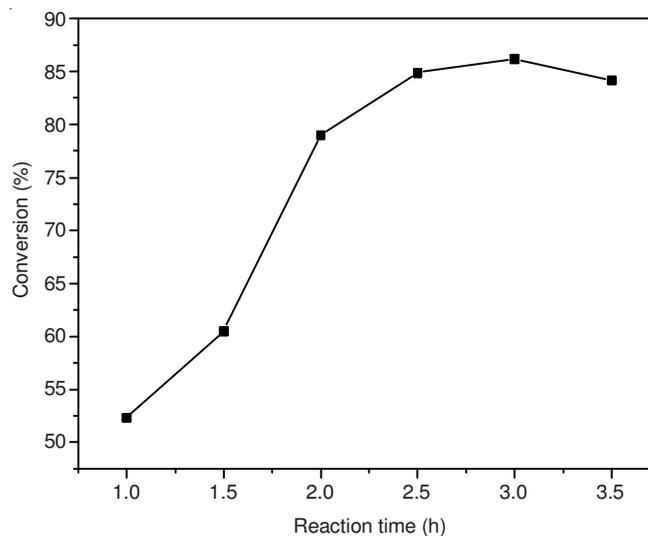


Fig. 9. Effect of reaction time on conversion

reactions. Fig. 7 shows the amount of catalyst is 3 % for the optimum condition.

Temperature is considered as an important factor to conversion rate. Raising the temperature is apparently favourable for the acceleration of the forward reaction. From Fig. 8, it is found that when the temperature reaches 150 °C, conversion rate can reach to a high value. With further increasing of the temperature, the conversion rate does not increase, even decrease. When the temperature surpassed 150 °C, the conversion rate reduced evidently which explained that high temperature could prompt the production of by-products. Therefore, the optimum reaction temperature should be selected at 150 °C. At the same time, the reaction time also played an important role in the conversion rate. Fig. 9 indicates that there was a variation in the conversion rate with the increasing of reaction time. The longer the reaction time was, the higher the conversion rate of the cyclohexanone. When the reaction time is 2.5 h, the conversion rate reached 86.5 %. When the reaction time is 3 h, the conversion rate of the cyclohexanone was still slightly improved. While we take the energy factors into consideration, the best reaction time is 2.5 h.

Product analysis and identification: The test of the samples selected hydrogen flame ionization detector (FID), quartz capillary column (OV-1 type). The temperature of chromatographic column: 220 °C; vaporization temperature: 250 °C; detection temperature: 260 °C; column pressure: 0.15 MPa; sample size is 0.5 μ L; sample shunt rate: 10 mL/min. GC spectrum of dimer was showed in Fig. 10. We could see three different peaks from the Fig. 10 as follows: Peak of the cyclohexanone at around 2 min; peak of 2-(1-cyclohexenyl) cyclohexanone at around 4.17 min; peak of 2-cyclohexyl alkylene cyclohexanone at around 4.28 min. And the peak areas of 2-(1-cyclohexenyl)cyclohexanone was largest, which indicated the largest amount of 2-(1-cyclohexenyl)cyclohexanone.

IR analysis: Spectroscopic method for identifying of surface molecules usually relied on the frequency of chemical groups or compared with standard IR spectra of the known reference. IR spectrum of main product was shown in Fig. 11, the characteristic peaks are vested as follows: 1708.81 cm^{-1} is the stretching vibration of C=O; 2927.74 cm^{-1} , 2858.31 cm^{-1} is the stretching vibration of the C=C in the cyclohexenyl ring; 1448.44 cm^{-1} is corresponding to the in-plane bending of C-H. Compared with the standard IR spectrum of 2-(1-cyclohe-

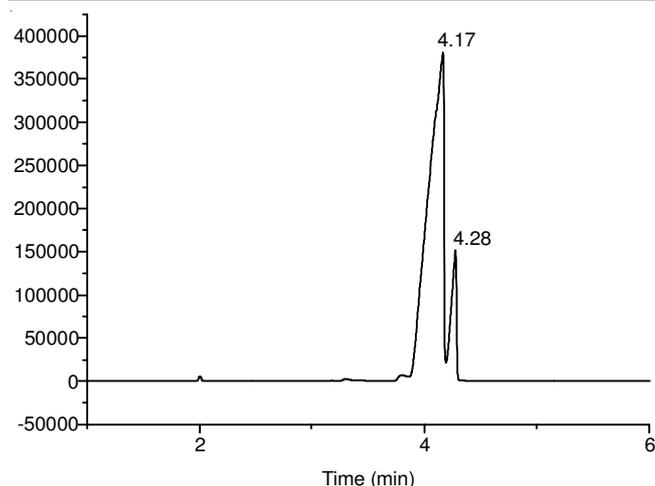


Fig. 10. GC spectra of dimer

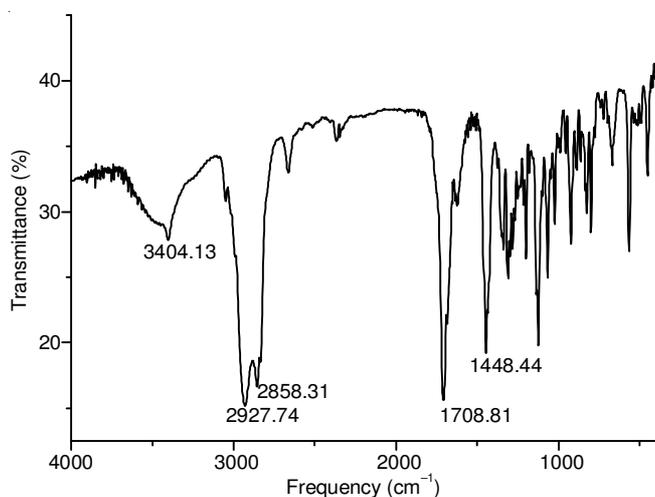


Fig. 11. IR spectra of product

xenyl)cyclohexanone, they are almost the same and it shows that the main product is 2-(1-cyclohexenyl)cyclohexanone.

Conclusion

In this section, the mixed heteropoly acids supported on SBA-15 which was used as catalysts of self-condensation reaction of cyclohexanone to synthesize the 2-(1-cyclohexenyl)cyclohexanone were studied. The effects of various parameters on the conversion ratio were also discussed. The experimental results show that: (1) The testing result of XRD

and the adsorption-desorption isotherm of nitrogen analysis all proved when the mixed heteropoly acids were supported on SBA-15, the pore size of SBA-15 is reduced, which proved that mixed heteropoly acids had already existed in the mesoporous zeolite. (2) Mixed heteropoly acid catalysts ($\text{PW}_{12} + \text{PMo}_{12}/\text{SBA-15}$) were prepared using impregnation method, which had greatly improved the BET surface area and catalytic activity and also had given full play to the catalysis of heteropoly acids. Meanwhile, 2-(1-cyclohexenyl) cyclohexanone with high purity could be obtained after distillation separation and the product conversion rate of the catalytic reaction reached 86.5 %.

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