

CATALYTIC SYNTHESIS OF 4-METHYL-2-(α -METHYL BENZYL) PHENOL OVER FE-AL-MCM-41 FOR EXTRACTION-SEPARATION RUBIDIUM FROM BRINE

Zhenhua FENG,^{a,b,c} Lianying AN,^{a,d,*} Zhenggen HUANG,^a Xianyin ZHAO^{a,d} and Bengao WANG^a

^a College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, P. R. China

^b Sichuan Bureau of Geology and Mineral Resources Chengdu Analytical & Testing Center for Mineral and Rocks, Chengdu 610081, P. R. China

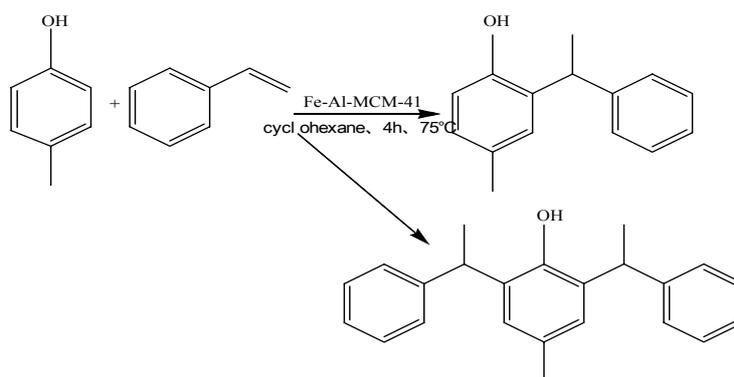
^c Evaluation and Utilization of Strategic Rare Metals and Rare Earth Resource Key Laboratory of Sichuan Province; Chengdu Analytical & Testing Center, Sichuan Bureau of Geology & Mineral Resources

(Chengdu Mineral Resources Supervision and Testing Center, Ministry of Land and Resources) Chengdu 61008, P. R. China

^d Mineral Resources Chemistry Key Laboratory of Sichuan Higher Education Institutions, Chengdu 610059, P. R. China

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A new extractant 4-methyl-2-(α -methyl benzyl) phenol had been synthesized with styrene and p-cresol through the Friedel-Crafts alkylation reaction. Fe-Al-MCM-41 which was used as molecular sieves catalyst for the synthesis of the extractant was prepared by hydrothermal synthesis method and then characterized by FT-IR, XRD, NH₃-TPD and N₂ adsorption isotherm. The catalytic synthesis conditions of 4-methyl-2-(α -methyl benzyl) phenol such as reaction time, temperature and catalyst dosage were investigated. The conversion of styrene was about 81.2%, the target product yield and selectivity can reach 74.6% and 95.7% respectively. The structure of the 4-methyl-2-(α -methyl benzyl) phenol was confirmed by ¹H-NMR. At the same time, 4-methyl-2-(α -methyl benzyl) phenol was used as extractant to separate rubidium from brine of which the rate of potassium to rubidium is 10:1 ($C_{K^+}=10.0\text{g/L}$, $C_{Rb^+}=1.0\text{g/L}$). The experiment results show that the extractant has a great extraction performance to rubidium, the extraction yields of rubidium and potassium can reach 81.1% and 9.4% respectively. The separation factor of Rb^+/K^+ can reach up to 41.4.



INTRODUCTION

Rare metals rubidium is widely used in new energy industry, aerospace industry and environmental science with the development of science. There are many subsurface brine and salt lake containing abundant rubidium but often at trace concentrations. At the same time, K^+ , Na^+ , Li^+ , Mg^{2+} and other ions also coexist with Rb^+ , the concentrations of which are tens or even hundreds

times that of Rb^+ . The key is to separate and purify rubidium from potassium efficiently because these two ions have very similar physical and chemical properties.¹⁻³ Fractional crystallization and precipitation are traditional methods for rubidium separation, However, due to increasingly stringent regulations concerning the protection of environment, the use of energy-intensive must be eliminated. Therefore, there is an urgent need to develop a new method to replace the energy-intensive method for the extraction and

* Corresponding author: anliany@cdu.edu.cn

purification of rubidium. Solvent extraction is an economical, efficient, and environmentally friendly method for the separation of low-concentration rubidium.

It has been reported that 4-tert-butyl-2-(α -methyl benzyl) phenol (t-BAMBP), a kind of extractant for rubidium, the separation factor of Rb^+/K^+ is only 15.^{4,6} Replace tert-butyl with methyl to reduce the steric effect of tert-butyl and so reduce the obstacles to larger rubidium ions, may improve the reaction efficiency between rubidium and extractant, 4-methyl-2-(α -methyl benzyl) phenol was designed as an effective extractant for extracting rubidium from brine.

It is crucial to develop new solid acid catalysts for the synthesis of new rubidium extractant 4-methyl-2-(α -methyl benzyl) phenol. Based on MCM-41 have numerous advantages of mesoporous molecular sieves and Fe-Al has a significant alkylation catalyst activity, multiple metals molecular sieve catalyst Fe-Al-MCM-41 are obtained by ion substitution method.⁷⁻⁸ The catalyst was used to synthesize 4-methyl-2-(α -methyl benzyl) phenol, the catalytic performance of Fe-Al-MCM-41, the effects of synthesis reaction conditions such as the reaction time, temperature, the amount of catalyst, the ratio of raw materials, the yield and selectivity of the main product 4-methyl-2-(α -methyl benzyl) phenol were studied. Finally, the extraction and separation performance of 4-methyl-2-(α -methyl benzyl) phenol to high potassium low rubidium brine were also tested. For the advantage of simple synthesis process, mild synthetic conditions and low cost, the new extractant 4-methyl-2-(α -methyl benzyl) phenol has a good application prospect for separate rubidium from salt lake brine.

EXPERIMENTAL

1. Reagents

Sodium aluminate, cetyl trimethyl ammonium bromide, ferric chloride, tetraethyl orthosilicate, rubidium chloride, sodium hydroxydatum, potassium chloride, styrene, p-cresol, cyclohexane, D60. All the chemicals were AR grade purity and purchased from Kelong Chemical & Co. Ltd, China.

2. Synthesis of Fe-Al-MCM-41

First, the CTAB was dissolved in purified water, successively added $NaAlO_2$, TEOS, NaOH with constant stirring for 2h; Second, adjusting the pH of the solution to about 10.5 using 2mol/L H_2SO_4 stirring for 1h into a uniform gel phase, and then transferred to a teflon-lined stainless steel autoclave, the reaction was continued 48h by hydrothermal method at 150°C; Third, the product was filtered, washed with water, dried and calcined at 550 °C with temperature programmed to remove the templating agent; Last, the Al-MCM-41 was added to the methanol solution containing $FeCl_3 \cdot 6H_2O$, stirring for 2h at 25 °C, and Fe-Al-MCM-41 mesoporous molecular sieve catalyst was obtained in which silica-alumina molar ratio was 10.⁹ The catalysts were characterized with Fourier Transform Infrared (FT-IR), X-Ray diffraction (XRD), temperature-programmed desorption of ammonia (NH_3 -TPD) and N_2 adsorption isotherm.

3. Synthesis of extractant 4-methyl-2-(α -methyl benzyl) phenol

p-cresol, styrene, cyclohexane were used as materials, Fe-Al-MCM-41 as catalysts, the 4-methyl-2-(α -methyl benzyl) phenol was synthesized. The product was purified with silica gel column chromatography. The selectivity of the reaction and the recovery of product were calculated by using styrene as the reference. The structure of the products was confirmed by 1H -NMR (ACE300 (300MHz)). The synthesis mechanism was presented in Fig. 1.

4. Rb/K extraction-separation method

The material liquid and extractive agent are placed in the automatic shaker according to certain scale, mixing a certain time in the shake, and then stand to layer. Determine the concentration of Rb^+ and K^+ in the remaining aqueous, calculation extraction rate and separation factor of Rb^+ and K^+ .

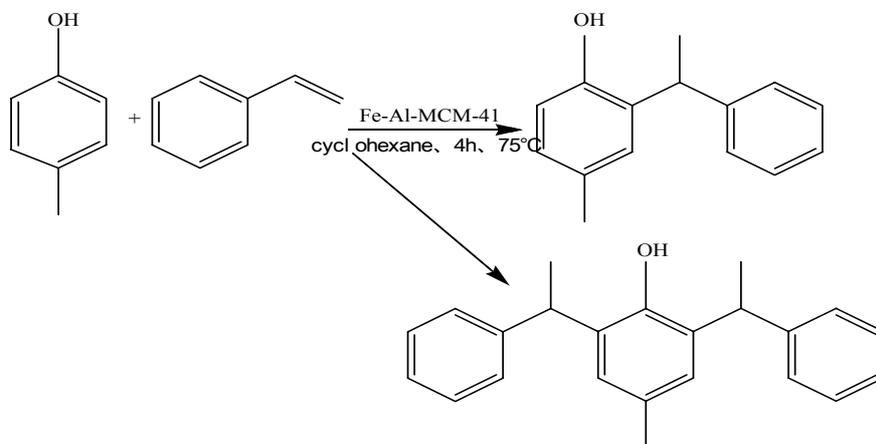


Fig. 1 – The mechanism of synthesis of 4-methyl-2-(α -methyl benzyl) phenol.

5. Analysis method

The concentration of Rb^+ and K^+ in aqueous phase were determinate by ICP-OES (Perkin Elmer, Optima5300DV).

RESULTS AND DISCUSSION

1. Characterization of Fe-Al-MCM-41

1.1. Fourier Transform Infrared (FT-IR)

Figure 2 show the FT-IR of Al-MCM-41 and Fe-Al-MCM-41 respectively. The antisymmetric and symmetric stretching vibration of Pure MCM-41 Si-O-Si were at 1123 cm^{-1} and 814 cm^{-1} respectively. The antisymmetric and symmetric stretching vibration of Al-MCM-41, of which Si was partly replaced by Al, were at 1077 cm^{-1} and 799 cm^{-1} . At this time, the peak is sharper and stronger, and move to lower wave number, which is for the reason of being replaced by Al, Al-O is longer than Si-O, indicating Al have entered the framework of molecular sieves. The antisymmetric and symmetric stretching vibration at 1070 cm^{-1} and 794 cm^{-1} , illustrated that not only Al has substituted Si, but also some of the Si in the molecular sieves framework has been replaced by Fe.

1.2. X-Ray diffraction (XRD)

The XRD patterns of Al-MCM-41 and Fe-Al-MCM-41 are shown in Figure 3. As it can be

observed, for these two catalysts, these samples exhibited a strong peak at $2\theta=2.4^\circ$ with a wide and weak reflection between 3.0 and 5.0 which correspond to the diffraction of the planes (100), (110) and (200) respectively. These signals are characteristic of MCM-41 type mesoporous materials¹⁰. However, the peak of Fe-Al-MCM-41 shows a certain deviation, which is because the atomic radius of Fe is larger than that of Si, and the crystal cell becomes larger after Fe enters the framework of Al-MCM-41, and there is a small deviation of $2\theta=2.4^\circ$, indicating that Fe has successfully entered the framework of molecular sieve Al-MCM-41.¹¹

1.3. Temperature-programmed desorption of ammonia (NH_3 -TPD)

As can be observed from Fig. 2 and Table 1, both Al-MCM-41 and Fe-Al-MCM-41 showed desorption peaks at 100°C and 300°C , corresponding to weak acid center and strong acid center respectively, while Fe-Al-MCM-41 also showed desorption peaks at 600°C , indicating that there was a new strong acid center here. By comparing the total acid amount and acid strength of Al-MCM-41 and Fe-Al-MCM-41, the total acid amount and acid strength of Fe-Al-MCM-41 increased significantly with the Fe load, indicating that the number of active points of catalysts increased due to the Fe load.¹²

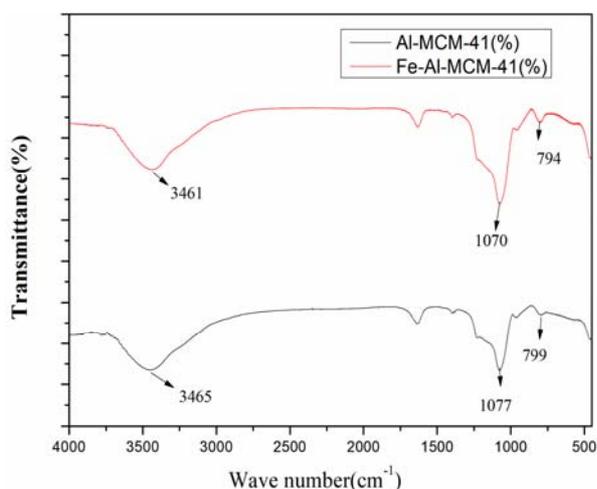


Fig. 2 – The FT-IR spectra of catalysts.

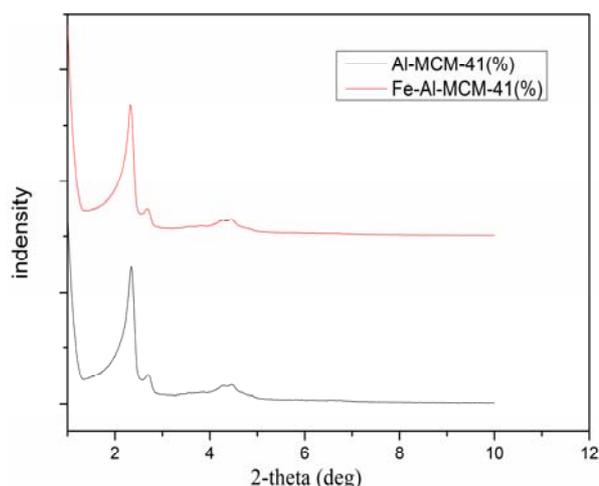
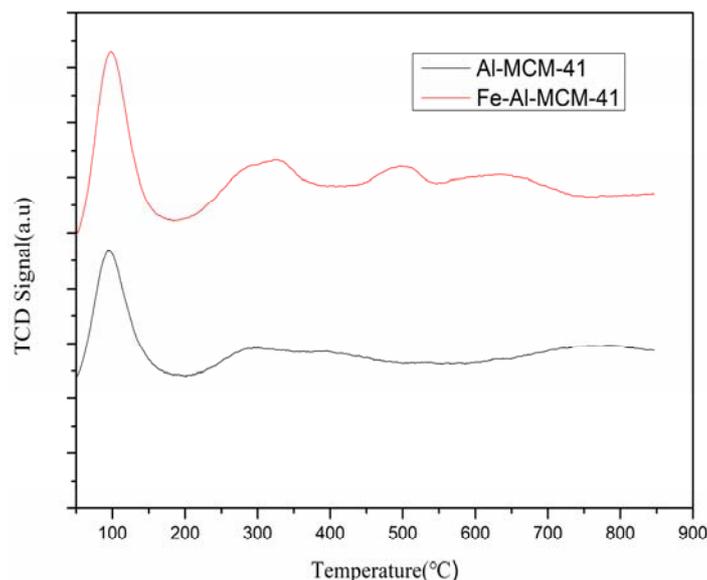


Fig. 3 – The XRD patterns of catalysts.

Table 1

Acid amount of catalysts

Sample	Acid amount (mmol/g)		
	Weak	Strong	Total
Al-MCM-41	0.4214	0.1147	0.5361
Fe-Al-MCM-41	0.5381	0.2846	0.8227

Fig. 4 – NH₃-TPD profiles of the catalysts.

1.4. N₂ Adsorption Isotherm

The nitrogen adsorption isotherm was carried out and the typical isotherm for catalysts Fe-Al-MCM-41 and Al-MCM-41 were presented in Figs. 5-6, respectively. Surface area, pore volume and pore size distribution of Fe-Al-MCM-41 catalysts were measured using the BET and BJH method, and the results were depicted in Table 2. Samples from the table were prepared at an average pore size of 2.7 nm, the synthesized molecular sieve belongs to prove mesoporous material, the catalyst of after ion exchange surface area and pore volume of the load have declined, while the performance of molecular sieve adsorption has been improved.

The adsorption isotherm was type IV, typical materials adsorption curve mesoporous.¹³ The results from figure show that Fe-Al-MCM-41 has narrow pore size distribution curve and high degree of regularity synthetic material.

2. Synthesis of 4-methyl-2-(α -methyl benzyl) phenol

The effects of main product yield and selectivity at different feed mole rate (p-cresol/styrene), reaction time, temperature, amount of catalyst over Fe-Al-MCM-41 were presented in Figs. 7–10.

Table 2

Physiochemical properties of catalysts

Sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
Al-MCM-41	899.336	0.608	2.703
Fe-Al-MCM-41	809.781	0.565	2.790

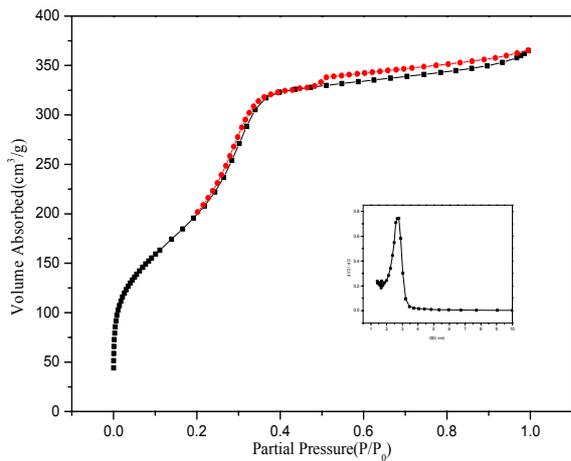
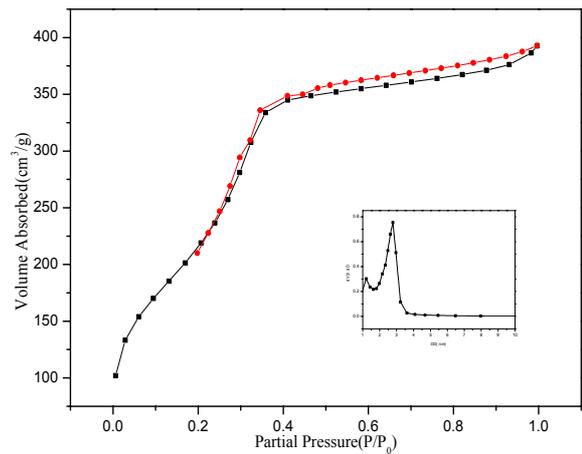
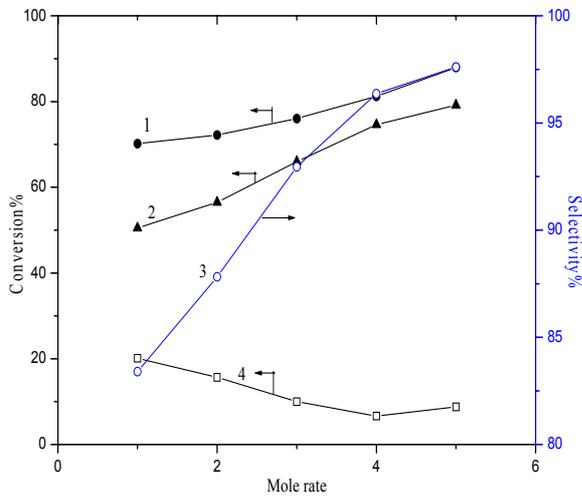
Fig. – 5 N₂ adsorption isotherm of Fe-Al-MCM-41.Fig. 6 – N₂ adsorption isotherm of Al-MCM-41.

Fig. 7 – The effect of feed mole rate on alkylation reactions.

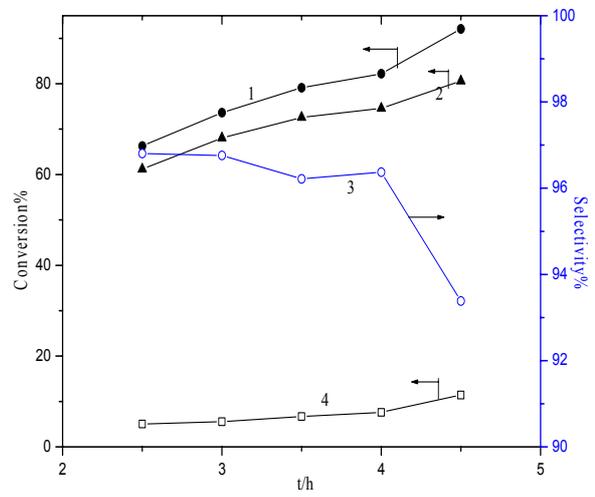


Fig. 8 – The effect of time on alkylation reactions.

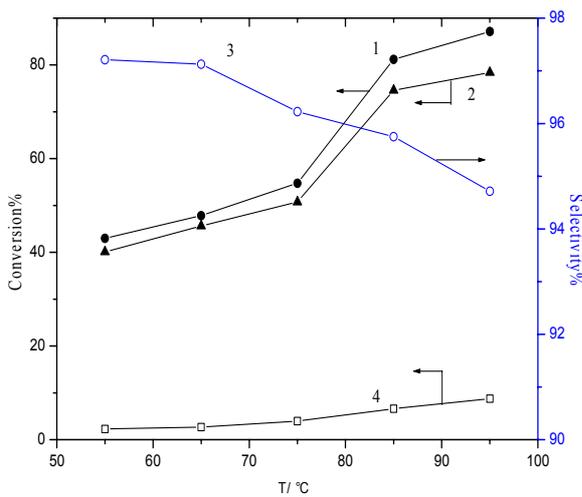


Fig. 9 – The effect of temperature on alkylation reactions.

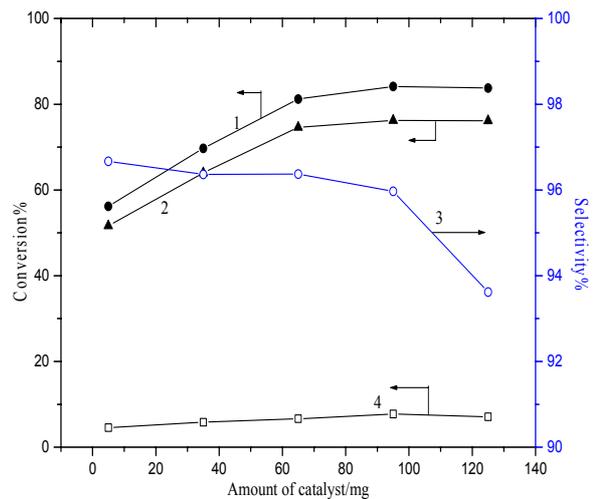


Fig. 10 – The effect of amount of catalyst on alkylation reactions.

1. the styrene conversion; 2. the main product yield; 3. selectivity of 4-methyl-2-(α -methyl benzyl) phenol; 4. byproducts yield..

According to the results, the yields of main product and byproduct have been increased with the increase of the reaction time, temperatures and amount of catalyst, which indicates a negative relationship. However, the selectivity of 4-methyl-2-(α -methyl benzyl) phenol has decreased. The conversion rate of styrene and the selectivity of the main product increased with greater the feed mole ratio of (p-cresol/Styrene) However, excessive alkylating reagent will cause the formation of 4-methyl-2,6-(α -methyl benzyl) phenol through further alkylation reaction. Therefore, the refluxing time of 4h, the appropriate starting material molar ratio of 4:1, reaction temperature at 85°C, ratio of catalyst to styrene of 1mmol styrene/65mg catalyst, were selected as optimal operation parameters for the alkylation reactions. The yield and selectivity of 4-methyl-2-(α -methyl benzyl) phenol was 74.6% and 95.7% respectively.

3. $^1\text{H-NMR}$ analysis of 4-methyl-2-(α -methyl benzyl) phenol

$^1\text{H-NMR}$ (300MHz, CDCl_3) : δ 7.30-7.21 (m, 6H, CH), δ 7.15-7.12 (m, 1H, CH), δ 6.95-6.82 (m, 1H, CH), δ 6.79-6.73 (m, 1H, CH), δ 4.56 (m, 1H, OH).

4. 4-methyl-2-(α -methyl benzyl) phenol extraction performance

Extraction experiments were carried out in an automatic shaker. The effect of the extractants was evaluated by extraction rate and separation factor. The rubidium and potassium ratio in brine was 10:1. The results were shown in Table.3. With 4-methyl-2-(α -methyl benzyl) phenol as the extractant, the extraction rate of rubidium can up to 80% and Rb^+/K^+ separation factor was 41.4.¹⁴

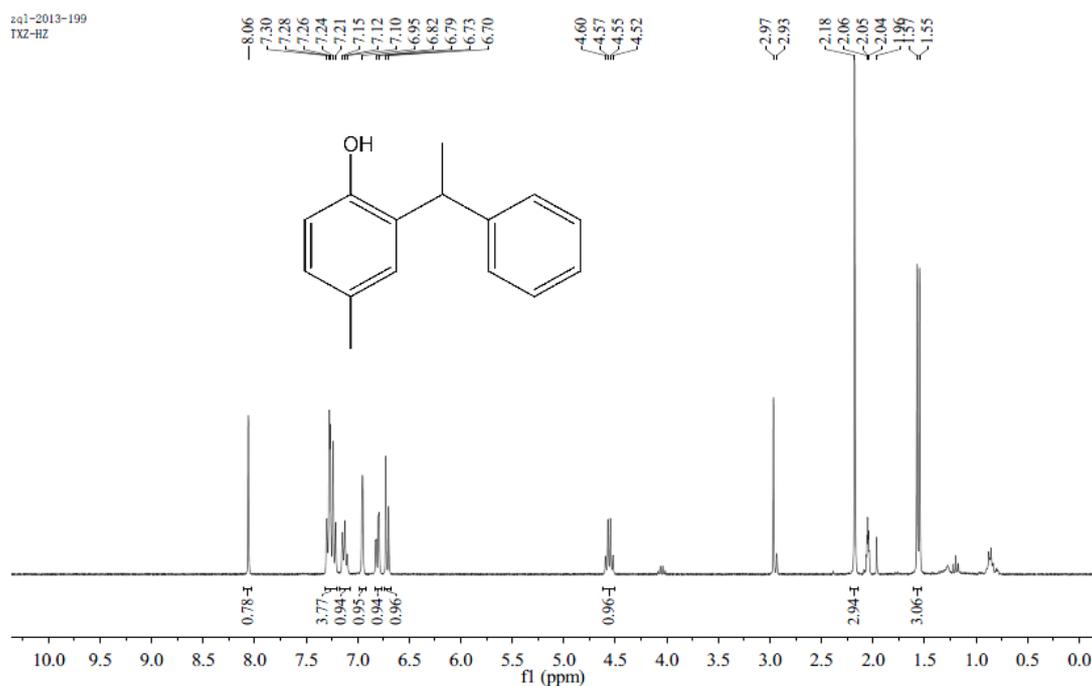


Fig. 11 – $^1\text{H-NMR}$ of 4-methyl-2-(α -methyl benzyl) phenol.

Table 3

4-methyl-2-(α -methyl benzyl) phenol extraction separation experiments

	C_{NaOH} (M)	Extraction of Rb^+ (%)	Extraction of K^+ (%)	Separation factor
1	0.20	81.1	9.4	41.4
2	0.20	77.6	9.7	33.4
3	0.50	77.7	14.8	23.9
4	0.50	60.5	14.5	11.2

- $\text{C}_{\text{Rb}^+}=0.1\text{g/L}$, $\text{C}_{\text{K}^+}=1\text{g/L}$, organic phase: 4-methyl-2-(α -methyl benzyl) phenol (0.5M)+D60, O/A=3, extraction time=2min;
- $\text{C}_{\text{Rb}^+}=1.0\text{g/L}$, $\text{C}_{\text{K}^+}=10.0\text{g/L}$, organic phase:4-methyl-2-(α -methyl benzyl) phenol (0.6M)+D60, O/A=3, extraction time=2min;
- $\text{C}_{\text{Rb}^+}=6.0\text{g/L}$, $\text{C}_{\text{K}^+}=60.0\text{g/L}$, organic phase: 4-methyl-2-(α -methyl benzyl) phenol (1.0M)+D60, O/A=3, extraction time=2min;
- $\text{C}_{\text{Rb}^+}=6.0\text{g/L}$, $\text{C}_{\text{K}^+}=60.0\text{g/L}$, organic phase: t-BAMBP (1.0M)+D60, O/A=3, extraction time=2min.

CONCLUSIONS

The molecular sieves catalyst Fe-Al-MCM-41 was synthesized by hydrothermal method and ion substitution method. It was proved that Fe-Al-MCM-41 have the characteristics of mesoporous molecular sieve, as well as the active point of Fe-Al-MCM-41 is increased due to the Fe load, which was characterized by FT-IR, XRD, NH₃-TPD and N₂ adsorption isotherm.

Using p-cresol and styrene as materials 4-methyl-2-(α -methyl benzyl) phenol was synthesized by Fe-Al-MCM-41 as molecular sieves catalyst. The structure of 4-methyl-2-(α -methyl benzyl) phenol was confirmed by ¹H-NMR. The yield and selectivity of the main product were 74.6% and 95.7% respectively.

3,4-methyl-2-(α -methyl benzyl) phenol was used as extractant to separate rubidium from brine in which the rate of potassium to rubidium is 10:1 ($C_{K^+}=10.0\text{g/L}$, $C_{Rb^+}=1.0\text{g/L}$), the extraction yields of rubidium and potassium can reach 81.1% and 9.4% respectively, the separation factor of Rb^+/K^+ can reach up to 41.4.

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