

## The acid treatments of the H $\beta$ zeolite as the catalyst in the synthesis of ethyl tertiary butyl ether antiknock additive

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**Abstract:** Influences of acids treatments on the structure, properties and the catalytic performances of the H $\beta$  zeolite in the synthesis of ethyl tertiary butyl ether were investigated. The initial activities of catalysts treated with different acids exist maximum values with the increase of the acid concentration and have a little decrease, however, the stabilities and the stable activities of the catalysts were significantly improved, which is precisely advantages of the zeolite acid treatment. Stabilities of the treated catalysts decrease as the following order citric acid > acetic acid > hydrochloric acid. In order to make research on these changes clearly various characterizations were carried out. XRD results showed the hardly changed framework, the decrease of degree of crystallinity and the existence of the dealumination after acid treatments. Correlating to the activity results, it is also concluded that the tetragonal crystalline is beneficial for the activity. FTIR results verified the existence of the dealumination and implied the influences of the secondary building unit on the stability of the samples. XRF results verified the realumination and the necessity of the moderate n (Si)/n (Al) for the stability of the sample.

**Keywords:** H $\beta$  zeolite, acid modification, activity, stability, ETBE

### 1. Introduction

Industry booming and stricter environment relations have promoted the market of fuel additives. Ether compounds, a kind of additive of the gasoline, can increase the gasoline octane number, reduce the automobile's energy consumption and the commissioning of pollutants including CO, NO<sub>x</sub> etc. into the air. Therefore, the research of ether as gasoline antiknock additive has aroused people's widespread interest[1]. Methyl Tertiary Butyl Ether (MTBE) is a typical ether additive in the gasoline, however, it is discovered that MTBE is a kind of pollutant of ground water for its non-degradable nature. Therefore, it has been forbidden in some countries such as America and Netherlands. In contrast, ethyl tertiary butyl ether (ETBE) is more competent for its higher octane number, lower vapor pressure and lower water-solubility, and its green synthesis route with non-toxic ethyl alcohol as raw material makes it more extractive to substitute MTBE as the future antiknock additive in gasoline[2,3].

Different kinds of acidic catalysts including resins[4,5,6], modified active carbon[7], heteropolyacid and its salts, zeolites etc. were studied in the synthesis of ETBE[7,8,9,10,13]. Macroporous sulfonic acid type ion exchange resins are used as an industrial catalyst at present for the synthesis of ETBE. For the synthesis of ETBE, resin catalyst has high activity and selectivity, however, the poor thermal stability for the deformation of the resin and the sulfonate groups easy to fall off at the high temperature (more than 100°C), and the difficulty in regeneration[4,5] limited its applications in practice. On the contrary,  $\beta$  zeolites, as heterogeneous catalysts, have excellent thermal stability and regeneration ability. As a result, active, thermally stable and regenerative zeolites are attracting attentions of researchers. The ion exchanging treatment of the zeolite into H-zeolite is a kind of typical method to improve the catalytic activity of the synthetic zeolite containing sodium. However, the stability loss should be concerned in that improvements of the catalytic activity are also applicable to the vice reaction in the reaction for the coke condensation.

The proper dealumination of the H $\beta$  zeolites with acids is a kind of effective method to maintain the activity and fill up the stability loss. Adding H $\beta$  zeolite modified with phosphoric acid to the FCC catalysts, it can be seen hydrothermal stability, cracking activity, anti-carbon deposition performance of the FCC catalysts and the product distribution were all significantly improved. Moreover, it can improve the octane level of gasoline[11]. The acidities of H $\beta$  zeolites are important factors affecting the catalytic performances. The H $\beta$  zeolites modified with acids have the increased silica-alumina mole ratio and the larger pore diameter, the amount of acid, the proper ratio of Lewis to Bronsted acid can also be modified, therefore the H $\beta$  zeolite catalyst with high activity and high stability can be prepared with this method.

While the reports involving the influences of acidic modifications of H $\beta$  zeolite on its structures, properties and its activity, stability in the etherification are seldom. In this paper such issues were investigated in detail, the research work is practically significant for the effective and clean production of high-octane number components even for the production of the clean fuel in the industrial. The research results can also provide important basis for the design and preparation of better etherification catalyst[12,13,14].

## **2. Experimental Section**

### **2.1 Materials**

H $\beta$  zeolite is synthesized by NO.3 refinery in Fushun, and all the analytical grade reagents are from Sinopharm Chemical Reagent Co., Ltd.

### **2.2 Acid treatments**

Acidic treatments for H $\beta$  zeolite with different acids including hydrochloric acid, acetic acid or citric acid solution were carried out in the 100mL volumetric flasks with stirring at 80°C in the water bath for 4h. Then the samples were washed several times with deionized water until neutral. After drying for 12h at 100°C, the samples were calcined in a muffle at 550 °C for 5h, then the final treated samples were obtained.

The sample treated with different kinds of acids are named as HA(0.3), HA(1.0), CA(0.3), CA(1.0), AA(0.3) and AA(1.0), corresponding to hydrochloric acid, citric acid and acetic acid respectively, and the number in the brackets are the concentrations of the acids.

### **2.3 Etherification**

1g catalyst was put into a fixed bed reactor, both ends of the bed were filled with inert filler material (quartz sand) roasted at 550°C for 5h. The etherification of ethanol and tert-butyl alcohol (molar ratio 1.1:1) was carried out with the WHSV of 2h<sup>-1</sup> at the desired reaction temperature. The reaction products were collected in the tank with regular sampling and analyzing on GC.

### **2.4 Catalyst characterization**

#### **XRD**

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-1AX X-ray diffractometer using Cu K $\alpha$  radiation at 40 kV and 100 mA with a scan rate of 8 °/min, scanning range of 0-80 °.

#### **FTIR**

Nicolet Magna IR 550 infrared spectrometer was used to examine the catalysts' the functional group changes before and after acidic treatments in KBr pellet (0.005g sample with 0.1g KBr) with the resolution of 4 cm<sup>-1</sup>, scanning range 4000-400 cm<sup>-1</sup>.

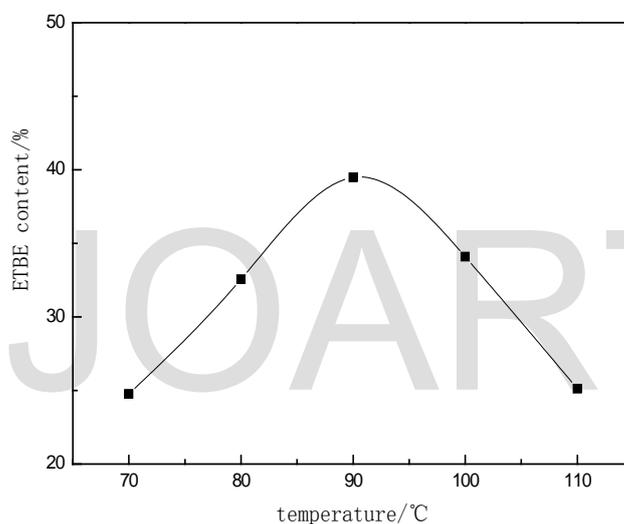
#### **XRF**

The Si/Al ratios of the treated samples were evaluated on the X-ray fluorescence with the operating conditions as follows. Under the control of the cooling system, 75kPa argon-methane mixture gas flow into the sample chamber of fluorescence spectrometer at 50kV and 50mA, then vacuum to less than 75Pa.

### 3. Results and Discussion

#### 3.1 Influences of acidic treatments on the activity of H $\beta$ zeolite

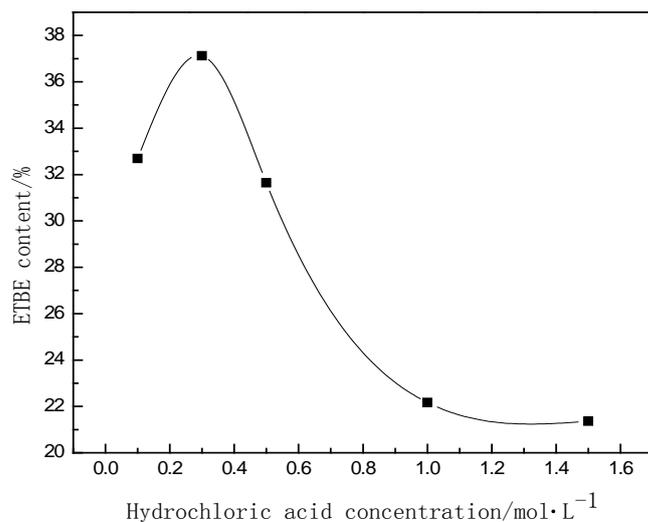
Catalytic functions of the samples treated with acids were evaluated on the fixed bed reactor. It is shown that ETBE contents in the product increased initially, decreased afterwards and reach maximum at 90°C with the reaction temperature increasing from 70 to 110°C (Figure 1). This result is not surprising because the reaction from ethanol and tert-butanol to ETBE is reversible and exothermic, the reaction at the temperature lower than 90°C is dynamically controlled, the increasing temperature is beneficial for the reaction rates, however, when the reaction temperature increase to higher than 90°C, the reaction is thermal dynamically controlled, the increasing temperature has negative influence on the reaction.



**Fig. 1 Reaction temperature effect on the activity of H $\beta$  the molecular sieve**

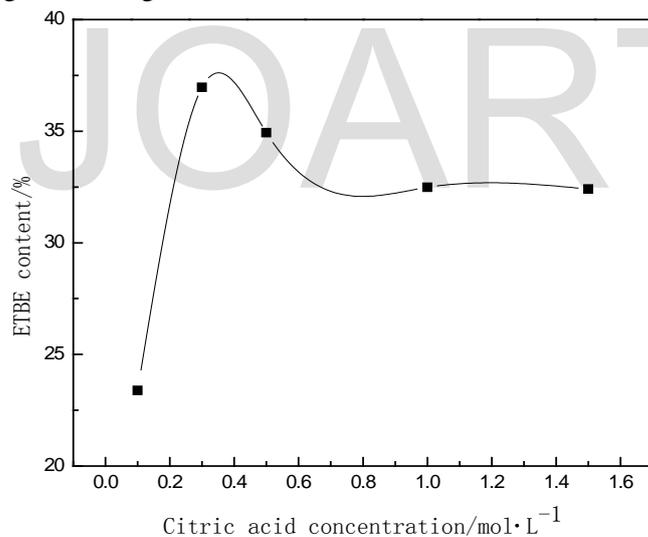
The activities of acid modified H $\beta$  zeolite catalysts were evaluated in the synthesis of ETBE at 90°C, and the reaction results are shown in Figure 2~4. It is shown that the increase of the hydrochloric acid concentration makes the content of ETBE in the products increasing a little firstly but then decreasing rapidly in Figure 2. When the concentration of hydrochloric acid is 0.3mol / L, H $\beta$  zeolite has the highest activity; the content of ETBE was 37.1%. Hydrochloric acid is a kind of strong acid, the dilute one can remove the extra-framework aluminum and transition state aluminum on the surface, dissolve the amorphous material in the pores, while the crystalline structure remains intact, which render the increase of H $\beta$  zeolite catalytic activity, therefore more ETBE was collected in the products.

However, it should be noted that when the concentration of the hydrochloric acid is more than 0.3mol/L, the activity of molecular sieve declined rapidly, the concentrated acid may remove the framework aluminum, which may lead to the destruction of crystalline and pore structure [15], the reduction of the degree of crystallinity of the zeolite or the changes of the acidities. Which is the real reason? The answer depends on the further studies with characterization.

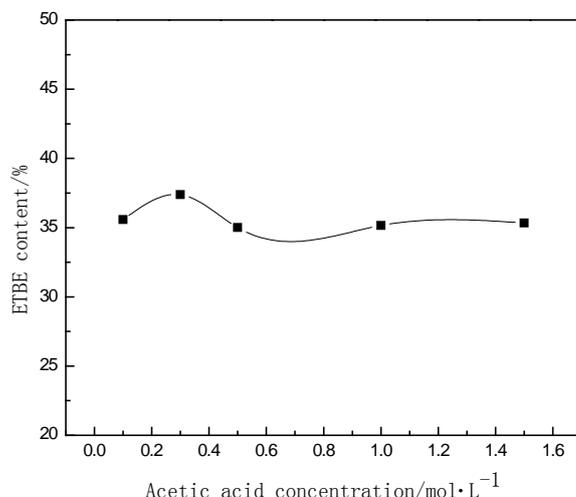


**Fig.2 Influences of hydrochloric acid concentration on the activity of H $\beta$  zeolite**

The reaction results of H $\beta$  zeolites modified respectively with citric acid and acetic acid are shown in Figure 3~4. Similar results to hydrochloric acid treatments were obtained. However, the differences are that concentrations of these two kinds of acids especially the acetic acid haven't so strong influences on the activities of the H $\beta$  zeolite. Why? Maybe the dealuminations of these two acids aren't as strong as the inorganic acids.



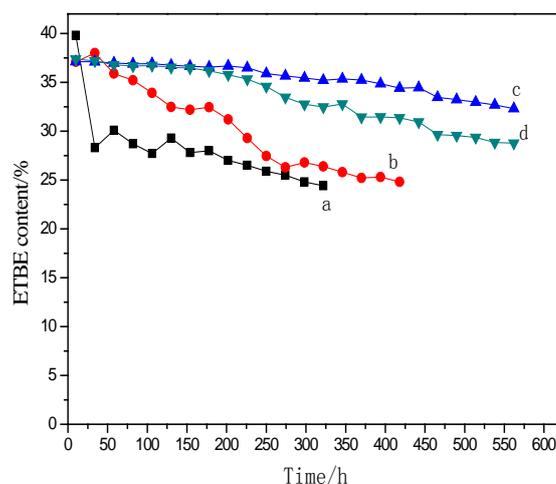
**Fig.3 Influences of citric acid concentration on the activity of H $\beta$  zeolite**



**Fig.4 Influences of acetic acid concentration on the activity of H $\beta$  zeolite**

**3.2 Influences of acid treatment on the stability of H $\beta$  zeolite**

The stabilities of the H $\beta$  zeolite modified with 0.3mol / L acids were compared with the untreated one in Figure5, it is shown that untreated H $\beta$  has good initial catalytic activity but not good stability, the ETBE content declined to less than 36% after only about 24h; Although the H $\beta$  zeolites modified by 0.3 mol / L acids have a little lower initial activity, their stabilities were improved obviously. H $\beta$  zeolite modified by 0.3mol / L citric acid has the best stability, and the content of ETBE is up to 36% after 220h. H $\beta$  zeolite modified by 0.3mol / L acetic acid has better stability than the zeolites modified by 0.3mol / L hydrochloric acid, while the content of ETBE dropped to 36% after 170h. The stabilities of the H $\beta$  zeolites modified with different acids decrease in this order citric acid > acetic acid > hydrochloric acid. Such results may be related to the acid strength and acid amounts, the detailed explanations are concerned with the characterization results.

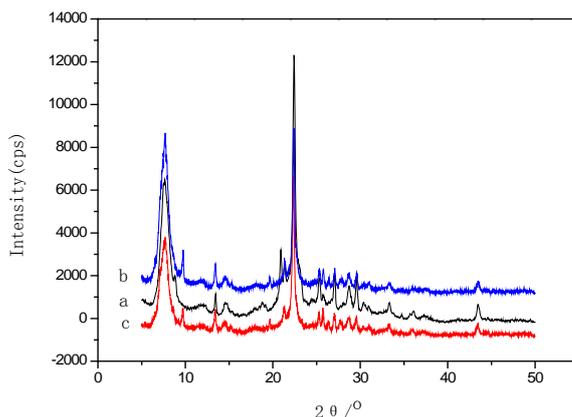


**Fig.5 Influences of acid treatment on the stability of H $\beta$  zeolite**  
 a. Untreated catalyst, b. HA(0.3), c. CA(0.3), d. AA(0.3)

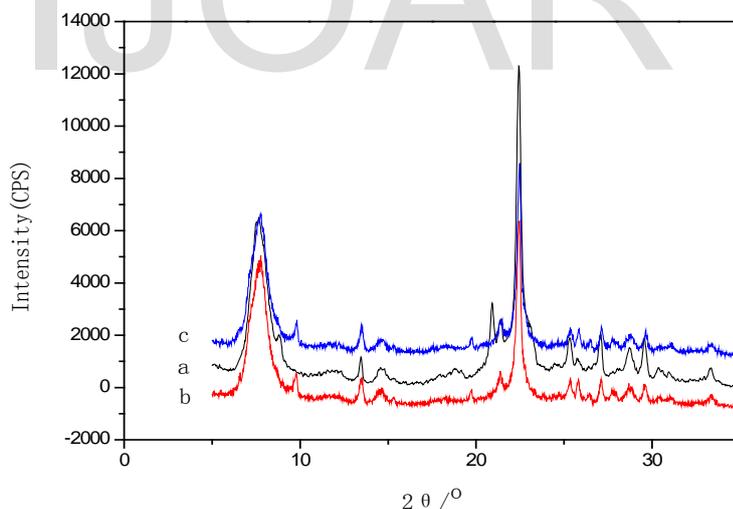
### 3.3 Characterizations

#### 3.3.1 XRD

The XRD diffraction patterns of samples treated by different concentrations of acid were shown in Figure 6~7. The samples remained characteristic diffraction peaks of H $\beta$  zeolite at 7.8 ° and 22.5 ° and high crystallinity [16]. After acid treatment, the area ratio of high-angle peak (at 22.5°) to the total peaks reduced, which is the evidences of the framework dealuminization. The peak (at 22.5°) represent the tetragonal type aluminum in the zeolite, relating such results to the reaction results, it is found that the tetragonal type in H $\beta$  zeolite contributes to the increase of the activity. Here the results of the changes of the activities with the acid concentration can be understood.



**Fig.6 XRD spectra of Hydrochloric acid treatment on  $\beta$  zeolite**  
 a. Untreated catalyst, b. HA(0.3), c. HA(1.0)

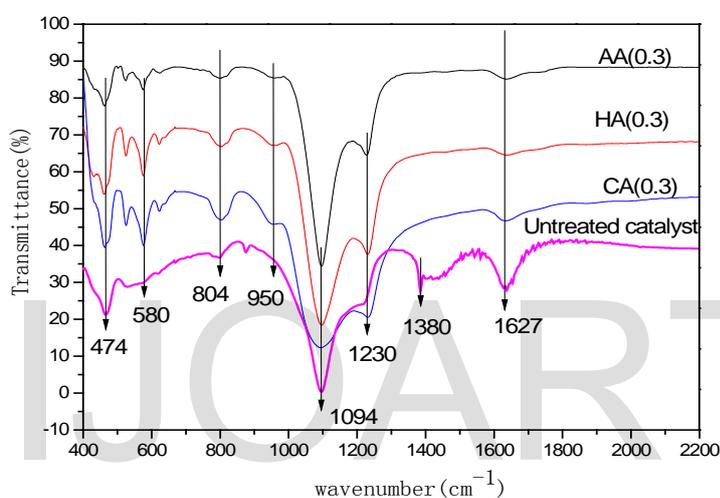


**Fig.7 XRD spectra of Citric acid treatment on  $\beta$  zeolite**  
 a. Untreated catalyst, b. CA(0.3), c. CA(1.0)

#### 3.3.2 FTIR

The FTIR spectra(2200-400cm<sup>-1</sup>) of the H $\beta$  zeolite samples after different acids treatment were compared with the untreated one in Figure 8. The fingerprint bands of H $\beta$  zeolite observed at 1627, 1380, 950, 804, are usually assigned to  $\nu(\text{Al-H})$ ,  $\nu_{\text{as}} [\text{Al-OR} (\text{R}=\text{H} \text{ or } \text{OH})]$ ;  $\nu[\text{Si-O}]$  and  $\nu_{\text{s}}$  (T-O-T, T= Si or Al) respectively. They are regarded as experimental evidences for the existence the

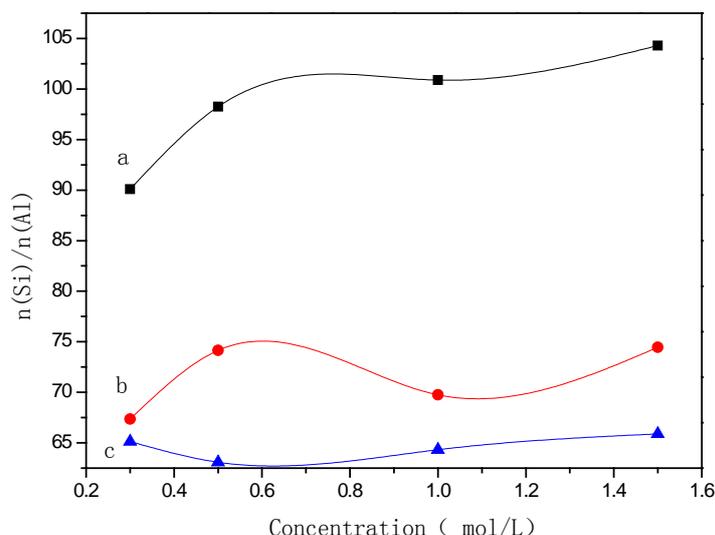
molecular fractions such as silicon oxides and/or aluminum oxides. Compared with the untreated zeolite, bands of the treated ones at  $1627$  and  $1380\text{cm}^{-1}$  decreased sharply, but bands at  $950$  and  $804\text{cm}^{-1}$  increase more or less, they are the powerful evidences for the dealumination. Bands at  $580$  and  $474\text{cm}^{-1}$  may be assigned to the vibration of the secondary building units (SUB) and the bending vibration of (T-O-T, T= Si or Al)[17]. Bands at around  $580\text{cm}^{-1}$  increased significantly than the untreated catalyst. It is can be seen that for CA with the highest stability the area ratio of the bands around  $474\text{cm}^{-1}$  and  $580\text{cm}^{-1}$  is almost similar. And according to the reaction stability order, the more the area ratio of the bands area at  $474\text{cm}^{-1}$  to  $580\text{cm}^{-1}$ , the worse stability the modified H $\beta$  zeolite has. Here at least it can be concluded that the coordination of the SUB and the framework has influence on the catalyst stability.



**Fig.8 FTIR spectra of different acids treatment on  $\beta$  zeolite**

### 3.3.3 XRF

$n(\text{Si})/n(\text{Al})$  results of modified samples were shown in Figure 9, from a brief look, it can be found that the acids treatments make the  $n(\text{Si})/n(\text{Al})$  increase more or less, the hydrochloric acid concentration has the greatest impact on  $n(\text{Si})/n(\text{Al})$ , hydrochloric acid is a strong acid,  $\text{H}^+$  will induce  $\text{AlO}_4^-$  of H $\beta$  zeolite in acidic medium, resulting framework dealumination[18]. However, both of other kinds of acids especially acetic acid concentration have not so obvious effects on the  $n(\text{Si}) / n(\text{Al})$ , because their molecules include -OH group can replenish the aluminum. The citric acid treatment of zeolite may have functions of dealumination at a Si(2Al) site but realumination at a Si(0Al) site[19,20]. The sample treated with the citric acid has the moderate  $n(\text{Si}) / n(\text{Al})$  and it has the highest stability. This is concerned with the modulation of the acid treatment on the acidity [21].



**Fig.9 Influences of acid treatment concentration on the n(Si)/n(Al)**  
**a. Hydrochloric acid, b. Citric acid, c. Acetic acid**

#### 4. Conclusion

Acids treatment of H $\beta$  zeolite with hydrochloric acid, citric acid and acetic acid may maintain the relative high catalytic activity; in order to get the high activity the suitable acid concentration is necessary. Acids treatments can improve the catalytic stability remarkably in the synthesis of ETBE. The stability order is citric acid > acetic acid > hydrochloric acid. Acids treatment made effective dealumination but didn't destroy the framework of the zeolite, the tetragonal crystalline in H $\beta$  zeolite contributes to the increase of the activity. Compared with hydrochloric acid, acids with -OH group are more beneficial for the improvement of the stability for their replenishing the aluminum ability. For the citric acid treated sample, its moderate n(Si)/n(Al) and its good coordination of SBU and the framework make it have the highest stability.

#### References:

- [1] Ronald, W. F. , "Lead-Gasoline Additives Still Contaminate Ground Water", Environm Ental Science & Technology, vol.11, pp.279-283, 2005.
- [2] Daughtrey, W. C., M. W. Gill, I. M. Pritts, et al, "Neurotoxicological Evaluation of Methyl Tertiary Buthyl Ether in Rats," App Toxicol. vol. 36, pp. 287-312, 2007.
- [3] Sakiko, F., K. Yabea, M. Furukawaa, et al, "A One-Generation Reproductive Toxicity Study of Ethyl Tertiary Butyl Ether in Rats," Reproductive Toxicology, vol. 30, pp.414-421, 2010.
- [4] Vlasenko, N.V., Yu. N. Kochkin, A. V. Topka, et al, "Liquid-Phase Synthesis of Ethyl Tert-Butyl Ether over Acid Cation-Exchange Inorganic-Organic Resins," Applied Catalysis A: General. vol.362, pp.82-87, 2009.
- [5] Muhammad, U., A. R. Saleemi, S. Qaiser, "Synthesis of Ethyl Tert-Butyl Ether with Tert-Butyl Alcohol and Ethanol on Various Ion Exchange Resin Catalysts," Communications. vol.9, pp. 721-727, 2008.
- [6] Yang B. L., S. B. Yang, R.Q. Yao, "Synthesis of Ethyl Tert-Butyl Ether from Tert-Butyl Alcohol and Ethanol on Strong Acid Cation-Exchange Resins," Reactive & Functional Polymers. Vol.44, pp.167-175, 2000.

- [7] Puziy, A.M., O. I. Poddubnaya, Yu. N. Kochkin et al, "Acid Properties of Phosphoric Acid Activated Carbons and Their Catalytic Behavior in Ethyl-Tert-Butyl Ether Synthesis," *Carbon*. vol. 48, pp. 706-713, 2010.
- [8] Poz´niczek, J., A. Micek-Ilnicka, A. Luban´ska, et al, "Catalytic Synthesis of Ethyl-Tert-Butyl Ether on Dawson Type Heteropolyacid," *Applied Catalysis A: General*. vol.286, pp.52-60, 2005.
- [9] Poz´niczek, J., A. Luba´nska, D. Mucha, et al, "Cesium Partly Substituted Salts  $Cs_xH_{6-x}P_2W_{18}O_{62}$  of Wells–Dawson Heteropolyacid as Catalysts for Ethyl-Tert-Butyl Ether Synthesis," *Journal of Molecular Catalysis A: Chemical*. vol.257, pp. 99-104, 2006a.
- [10] Poz´niczek, J., A. Luban´ska, A. Micek-Ilnicka, et al, "TiO<sub>2</sub> and SiO<sub>2</sub> Supported Wells-Dawson Heteropolyacid H<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub> as the Catalyst for ETBE Formation," *Applied Catalysis A: General*. vol.298, pp.217-224, 2006b.
- [11] Xie, C. X., Zhao J., Pan H. F., Ning S. K. , "Beta-Zeolite Modified by Phosphorous as FCC Catalyst Additive," *Petrochemical Technology*. vol.31, pp.691-703, 2002.
- [12] Collignon, F., G. Poncelet, "Comparative Vapor Phase Synthesis of ETBE from Ethanol and Isobutene over different acid zeolites," *Journal of Catalysis*. vol.202, pp.68-77, 2001.
- [13] Collignon, F., M. Mariani, S. Moreno, "Gas Phase Synthesis of MTBE from Methanol and Isobutene over Dealuminated Zeolites," *Journal of Catalysis*. vol.166, pp.53, 1997.
- [14]Levent, D., N. Oktar , G. Dogu, "ETBE Synthesis over Silicotungstic Acid and Tungstophosphoric Acid Catalysts Calcined at Different Temperatures," *Fuel Processing Technology*.vol. 91, pp.737-742, 2010.
- [15] Liu, A. Q., L. J. Ma, "The Effect of Dealumination of  $\beta$  Zeolite with HCl on Its Structure and Catalytic Civity," *Journal of Bei Jing University of Chemical Technology*. vol.30, pp.31-35, 2003.
- [16] Newsam, J. M., M. J. Treacy, W. T. Koetsier, "Structural Characterization of Zeolite Beta," *Proc. R. Soc. Lond. A*. vol.420, pp.375-4051, 1988.
- [17] Jiang, J., D. S. Mao, W. M. Yang, G. Z. Lu, "Influence of Preparation Methods on Reaction Activity of the Aldehyde-Ammomia Condensation over Co/HZSM-5 Catalysts," *Chemical Communication*. vol.66, pp.4, 2003.
- [18] Zhai, L. J., M. Liu, X. M. Dong, et al , "Dehydration of 2-(4'-Ethylbenzoyl)-benzoic Acid to 2-Ethylanthra-quinone over H $\beta$  Zeolite Modified with Organic Acids," *Journal of Catalysis*. vol.30, pp.9-13, 2009.
- [19] Xie, Z. K., Q. L. Chen, C. Zhang, J. Bao, Y. Cao, "Influence of Citric Acid Treatment on the Surface Acid Properties of Zeolite Beta," *J. Phys. Chem. B*. vol.104, pp.2853-2859, 2000.
- [20] Tian, Z., Z. F. Qin, G. F. Wang, et al, "Alkylation of Benzene with Propene over H $\beta$  Zeolite Modified with Citric Acid," *Journal of Fuel Chemistry and Technology*. vol.34, pp.359-363, 2006.
- [21] Yin, Z. Q., C. A. Ruan and X. D. Chen, "Effect of Non-Framework Aluminium on Catalytic Activity of Zeolites," *Fushun Research Institute of petroleum and Petrochemical College Newspaper*. vol.2, pp.43-48, 1994.