

Catalytic Conversion of Cellulose to Cellulose Acetate Propionate (CAP) Over $\text{SO}_4^{2-}/\text{ZrO}_2$ Solid Acid Catalyst

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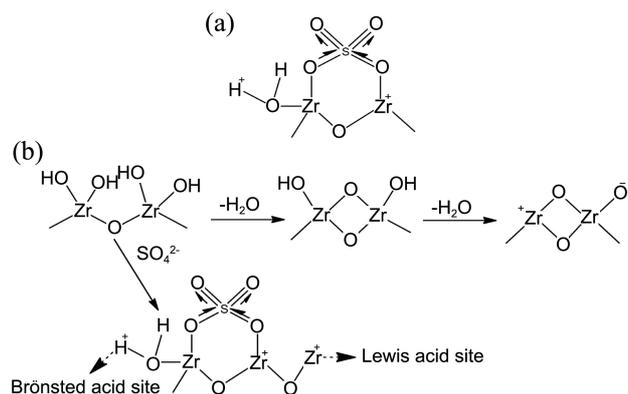
The solid super acid catalyst $\text{SO}_4^{2-}/\text{ZrO}_2$ was prepared by impregnation method using ZrO_2 as the catalyst support. Catalyst forming was taken into consideration in order to separate catalyst from the mixture of cellulose acetate propionate (CAP). Al_2O_3 and sesbania gum powder were selected as binding agent and auxiliary agent respectively. The catalytic properties were evaluated through esterification of cellulose with acetic anhydride, propionic anhydride and characterized by XRD, FTIR and NH_3 -TPD. In this paper, the effects of concentration of H_2SO_4 impregnated, calcination temperature, esterification temperature and esterification time on the yield, acyl content and viscosity of CAP were investigated. The results showed that $\text{SO}_4^{2-}/\text{ZrO}_2$ successfully catalyzed CAP synthesis over catalysts impregnated in 0.75 mol/L H_2SO_4 and calcined at 500 °C. The yield, acetyl content and propionyl content of CAP reached the maximum value of 105.3%, 29.9% and 25.8% reacted at 50 °C for 8 h.

Key Words : Cellulose acetate propionate, Solid acid catalyst, Catalyst forming, Esterification

Introduction

Eco-friendly polymers from renewable resources have attracted great attention with expertise in diverse areas,¹ because of rapidly growing concerns to environmental pollution and energy crisis.² Among the biomass-based polymers, cellulose, the major constituent of plants cell wall, is the most abundant organic compound on the earth, which offers an attractive alternative to petroleum feedstocks when making plastics.^{3,4} Cellulose acetate propionate (CAP) is a particularly interesting polymer which has been widely used in printing inks, hot-melt dip coatings, lacquer coatings, and desalination membranes.⁵

Currently, most commercial processes used for CAP Employ a homogeneous catalyst such as H_2SO_4 .⁶⁻⁸ However these acid catalysts have some disadvantages, such as pollution, separation and recycling difficulties⁹ and corroding the equipments. The use of heterogeneous catalysts to replace the homogeneous ones can be expected to eliminate the problems with homogeneous catalysts.¹⁰ The solid acid catalysts have a less corrosive nature, leading to safer, cheaper and more environment-friendly. Sulfated zirconium solid acid ($\text{SO}_4^{2-}/\text{ZrO}_2$) is a familiar catalyst widely used in esterification and other reactions due to their strong acidity and high catalytic activity.¹¹ Hino¹² proposed the surface structure to be SO_4^{2-} combined with Zr elements in the bridging bidentate state as shown in Scheme 1(a). The S=O double bond nature in the sulfate complex is much stronger than that of a simple metal sulfate; thus, the Lewis acid strength of Zr^{4+} becomes remarkably greater by the inductive effect of S=O in the complex as illustrated by arrows. In the presence of water, the Lewis acid sites are converted to Brönsted acid sites via proton transfer as seen in Scheme



Scheme 1. A surface structure of sulfated zirconia (a); Lewis acid and Brönsted acid site of the catalyst (b).

1(b).¹³ From the perspective of specific surface area, $\text{SO}_4^{2-}/\text{ZrO}_2$ powder is much larger than any other forms of catalysts, however the separation of $\text{SO}_4^{2-}/\text{ZrO}_2$ powder from the mixture of CAP is extremely difficult. So catalyst forming is much of importance for separation convenience. In this study, Al_2O_3 and sesbania gum powder are treated as binding agent and auxiliary agent respectively. Dilute nitric acid is used to stir the mixture of Al_2O_3 , sesbania gum powder and $\text{SO}_4^{2-}/\text{ZrO}_2$. Then the mixture is extruded by banded extruder.

In this paper, the effects of concentration of H_2SO_4 impregnated, calcination temperature, and esterification temperature and time on the yield, acyl content and viscosity of CAP have been studied.

Experimental

Reagents. $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (Analytical pure) used for pre-

paration of $Zr(OH)_4$ was obtained from Rongruida micro materials plant (Zibo, Shandong, China). Ammonia solutions, sulfuric acid, acetone, methanol, butyl acetate obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) were all of analytical grade. Acetic acid, acetic anhydride, propionic acid and propionic anhydride obtained from Changmao Biochemical Engineering Co., Ltd (Changzhou, Jiangsu, China) were all of technical grade. Sesbania gum powder was obtained from Midwest Group (Beijing, China). Cellulose was obtained from Wuxi Chemical Industry Research & Design Institute Co., Ltd (Wuxi, Jiangsu, China).

Catalyst Preparation.

Zr(OH)₄: $Zr(NO_3)_4 \cdot 5H_2O$ was dissolved in deionized water to prepare Zr ion containing solution into which 28 wt % aqueous ammonia was added to adjust the pH value to 9-10. The precipitate was aged for 24 h followed by filtration, washing for several times with water until pH value of filtrate changed to 7, and then drying at 105 °C for 10 h to obtain the precipitate $Zr(OH)_4$.

SO₄²⁻/ZrO₂: $Zr(OH)_4$ was impregnated in a certain concentration of H₂SO₄ for 10 h followed by evaporated at 105 °C until being dried to powder into which Al₂O₃ and sesbania gum powder which were served as binding agent and auxiliary agent respectively were added. And then dilute nitric acid was added into the above mixture to stir and extruded into rod-shaped which was calcined in muffle furnace at the calcination temperature range of 450 °C, 500 °C, 550 °C, 600 °C. In order to distinguish the type of catalysts, catalysts were denoted using some letters and figures. 0.75M-SZ-500 was taken as an example in which 0.75M, SZ and 500 indicated concentration of H₂SO₄ impregnated, SO₄²⁻/ZrO₂ and calcination temperature respectively.

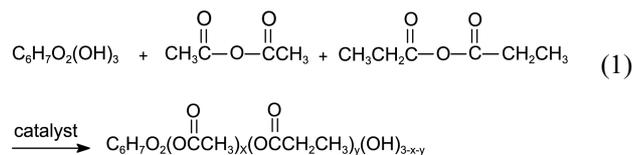
Catalyst Characterization. X-ray diffraction (XRD) patterns of the catalysts were recorded on a DX-1000 diffractometer, operating at 40 kV and 100 mA and using nickel-filtered Cu K_α radiation. The scanning range was over 10-80°.

Fourier transform infrared spectroscopy (FTIR) on the catalysts was recorded on Nicolet PROTÉGÉ 460 FTIR. The scanning range was over 11000-400 cm⁻¹.

NH₃-temperature-programmed desorption (NH₃-TPD) was performed in a fixed-bed reactor at atmosphere pressure. The catalysts were swept by He flow (30 mL/min) at 277 °C for 1 h and then cooled to 80 °C. NH₃ gas with a flow rate of 20 mL/min was introduced about 20 min till the samples achieved saturated adsorption. Then He flow (50 mL/min) was input into the reactor at 100 °C for 2 h to remove physisorbed NH₃. The samples were heated from 134 °C to 506 °C at a rate of 10 °C/min.

Catalytic Tests. Acid activation of cellulose (5.0 g) needed to be taken into consideration in which acetic acid and acetic anhydride were treated as activation fluids. Activation time and temperature were 0.5 h and 60 °C respectively. The purpose of activation was to lift the role of hydrogen bonds and increase active surface area. Besides that activation could improve microcellular structure of

cellulose and promote permeation, diffusion and swell of reagents through the cellulose. Acid activation treatments could enhance the reaction performance. The activity of SO₄²⁻/ZrO₂ solid acid catalyst for the esterification of cellulose treated by acid activation with acetic anhydride and propionic anhydride were determined at a certain temperature of water-bath in a 250 mL of four-neck flask equipped with a reflux condenser under continuous stirring for several hours. CAP was synthesized from cellulose through esterification over the catalyst of SO₄²⁻/ZrO₂ as shown in Eq. (1)



The molar ratio of acetic anhydride to propionic anhydride was 1:3. At the end of reaction, catalyst was separated by centrifuging. CAP was gradually precipitated by dropping the transparent reaction solution into deionized water with controllable rate. CAP was filtrated followed by shattering, washing until the pH value of filtrate changed to 7 and then being dried to powder at 105 °C in the oven.

Structure Characterization of CAP.

Contents of Acetyl and Propionyl: The contents of acetyl and propionyl of CAP were determined by means of end group titration according to standard of Designation 817-96(2004).¹⁴ Initially, acetyl and propionyl group of CAP were substituted and then contents of acetyl and propionyl group of CAP were determined under the provision of different distribution rate of acetic acid and propionic acid in butyl acetate.

Viscosity: 2 g of CAP (accurate to 0.002 g) sample was added into a 50 mL of beaker followed by adding 10 mL of acetone to dissolve the sample. The dissolved CAP was shifted into a 25 mL of volumetric flask. The sample remaining in the beaker was washed repeatedly with 10 mL of acetone and then the washed solution was transferring into volumetric flask. Volumetric flask was put into a water-bath at 25 °C for 15 min and then acetone which was put in 25 °C of water-bath in advance was added into the volumetric flask to the mark. Viscosity of CAP was determined by NDJ-5S digital display viscometer in constant temperature water-bath.

Determination of Yield: CAP is cellulose mixed ester. Glucosyl ring of cellulose has three reactive hydroxyls which are substituted by acetyl and propionyl, thus theoretical mass of the CAP cannot be calculated. In this study, yield of CAP was used to evaluate the catalytic activity as shown in Eq. (2)

$$\text{Yield (\%)} = \frac{\text{actual mass of CAP}}{\text{mass of cellulose}} \times 100 \quad (2)$$

Results and Discussion

Effects of Preparation and Reaction Conditions on Catalytic Performance.

Effect of Concentration of H₂SO₄ Impregnated: The

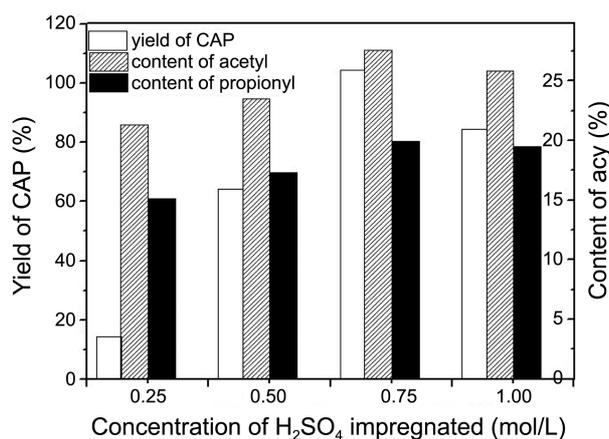


Figure 1. Effect of concentration of H₂SO₄ impregnated on the yield and content of acyl of CAP. Reaction conditions: 60 °C of esterification temperature, 5 h of esterification time, 2 g of catalyst.

content of acyl is a key factor to determine the properties of CAP. The activity of catalyst is evaluated by yield of CAP and content of acyl. The concentration of H₂SO₄ impregnated is an essential factor which will make a great difference to the activity of SO₄²⁻/ZrO₂ solid acid catalyst.

The catalytic activity of 0.25M-SZ-500, 0.50M-SZ-500, 0.75M-SZ-500 and 1.00M-SZ-500 for the esterification of CAP were examined shown in Figure 1. The relative activity order was 0.25M-SZ-500 < 0.50M-SZ-500 < 1.00M-SZ-500 < 0.75M-SZ-500. After 5 h, the maximum yield of CAP and contents of acetyl and propionyl were 104.12%, 27.6% and 19.9% respectively over catalyst of 0.75M-SZ-500. It could be found that activity of catalyst was relevant to the concentration of H₂SO₄ impregnated. Low concentration of H₂SO₄ impregnated was not conducive to the catalytic activity, which was due to the insufficient amount of sulfur species in the catalyst. However the concentration of H₂SO₄ higher than 0.75 mol/L could cover surface acid species and resulted in decreasing catalytic activity of SO₄²⁻/ZrO₂.¹⁵

Effect of Calcination Temperature of SO₄²⁻/ZrO₂: Cal-

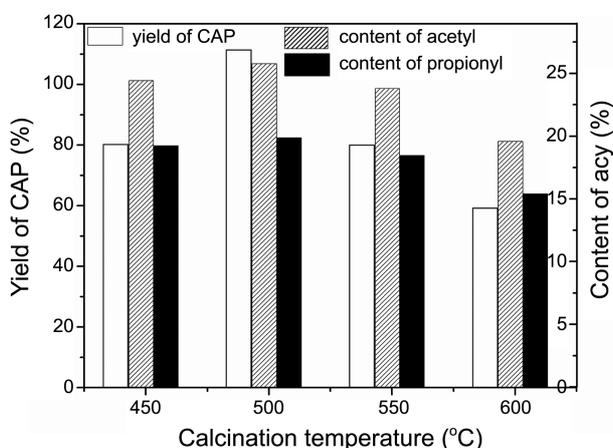


Figure 2. Effect of calcination temperature of SO₄²⁻/ZrO₂ on the yield and content of acyl of CAP. Reaction conditions: 60 °C of esterification temperature, 5 h of esterification time, 2 g of 0.75M-SZ-(450, 500, 550, 600).

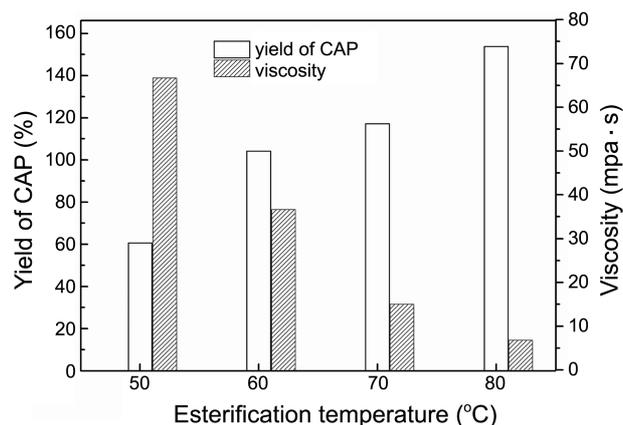


Figure 3. Effect of esterification temperature on the yield and viscosity of CAP. Reaction conditions: 5 h of esterification time, 2 g of 0.75M-SZ-500.

ination temperature plays a critical role in the catalytic activity of SO₄²⁻/ZrO₂. The yield of CAP and acyl content over the catalysts calcined at temperature range from 450 °C to 600 °C were examined shown in Figure 2. The yield of CAP, contents of acetyl and propionyl calcined at 500 °C were larger than those calcined in 450 °C, 550 °C and 600 °C. The decreasing activity of SO₄²⁻/ZrO₂ calcined higher than 500 °C could be mainly ascribed to the decomposition of sulfur species. Therefore SO₄²⁻/ZrO₂ calcined in 500 °C was appropriate for CAP synthesis.

Effect of Esterification Temperature on the Yield and Viscosity of CAP: The effect of esterification temperature on the yield and viscosity of CAP was shown in Figure 3. The yield of CAP increased with the esterification temperature. But the viscosity of CAP sharply decreased with the esterification temperature over the range from 50 °C to 80 °C, which could be attributed to the degradation and oxidation of cellulose. Glycosidic bond among glucose base rings in the cellulose macromolecules was very unstable under high temperature and acid condition. Increasing temperature usually could intensify hydrolysis, and decreased the viscosity of CAP. It was found from Figure 3 that viscosity reached 66.7 mpa·s reacted at 50 °C, though yield of CAP was not higher than those reacted in 60 °C, 70 °C and 80 °C. Extending esterification time usually could increase the yield of CAP.

Effect of Esterification Time on the Yield and Viscosity of CAP: Figure 4 showed the relationship between the esterification time and the yield, and viscosity of CAP, confirming that the esterification time contributed greatly to the yield of CAP while viscosity slightly decreased with the increase of esterification time. The yield and viscosity of CAP reached 105.28% and 57.2 mpa·s in 8 h which were approximately equal to 105.53% and 57.1 mpa·s in 9 h. Therefore esterification temperature and time should be 50 °C and 8 h in the next work.

Recycle Time of SO₄²⁻/ZrO₂: The stability of SO₄²⁻/ZrO₂ was shown in Figure 5. The yield and acyl content of CAP over catalyst of 0.75M-SZ-500 diminished with the reuse

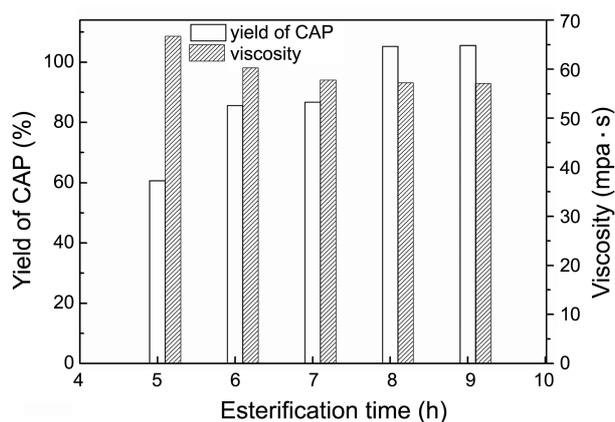


Figure 4. Effect of esterification time on the yield and viscosity of CAP. Reaction conditions: 50 °C of esterification temperature, 2 g of 0.75M-SZ-500.

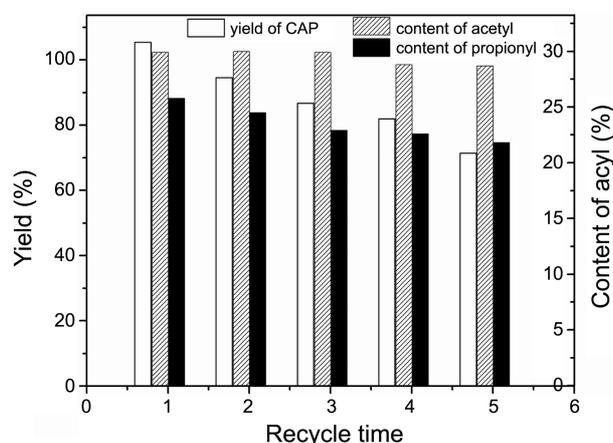


Figure 5. Yield of CAP as a function of the catalyst reuse cycle. Reaction conditions: 50 °C of esterification temperature, 8 h of esterification time, 2 g of 0.75M-SZ-500.

cycle of the catalyst. After the fifth reuse, the yield, acetyl and propionyl content of CAP over $\text{SO}_4^{2-}/\text{ZrO}_2$ reduced to 71.3%, 28.7% and 21.8%, which were less than the initial yield (105.3%), and acetyl content (29.9%), propionyl content (25.8%).

Characterization.

XRD: Either tetragonal (t) or monoclinic (m) zirconia crystal phases or both were found in as-prepared catalysts. The phase transition of both crystal phases was dependent on calcination temperature.¹⁶ The XRD patterns of catalyst calcined at 450 °C showed that *t*- ZrO_2 , *m*- ZrO_2 and $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ co-existed in $\text{SO}_4^{2-}/\text{ZrO}_2$. The formation of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ might be due to the long time immersion and the dissolution of $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ in H_2SO_4 .¹⁷ Diffraction peak of $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ weakened gradually with the increase of calcination temperature. Catalysts mixed with sesbania calcined at higher temperature could lead to generate carbon laydown which might be severer with the increase of calcination temperature. It was suggested that the existence of carbon laydown could decrease the intensity of diffraction peaks of *t*- ZrO_2 and *m*- ZrO_2 according to the diffraction

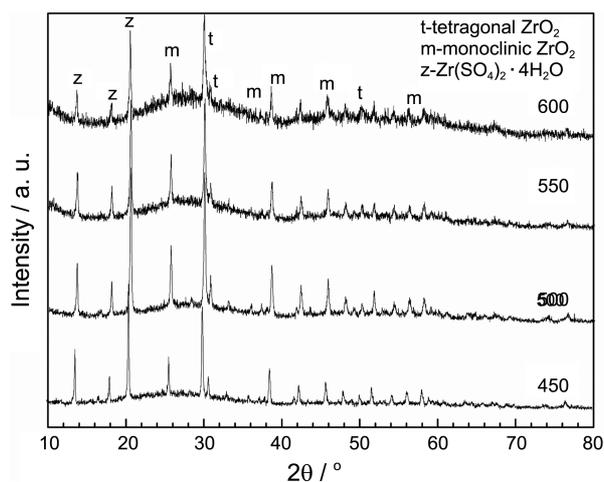


Figure 6. XRD patterns of $\text{SO}_4^{2-}/\text{ZrO}_2$ calcined at different temperatures.

peaks for ZrO_2 shown in Figure 6. Literatures reported that the presence of *t*- ZrO_2 was required to become super acid, whereas it was hard to form the strong acid site on *m*- ZrO_2 .^{18,19} When 0.75M-SZ was calcined at 550 °C or higher temperature, the reduction of yield of CAP was possibly attributed to the weakness intensity of diffraction peak of *t*- ZrO_2 and the decomposition of surface sulfur species.

FTIR: As seen from Figure 7, the presence of the band at 3383.6 cm^{-1} was assigned to stretching vibration absorption peak of -OH which indicated that associated hydroxyl group existed in catalyst. The IR band at 1635.1 cm^{-1} was deformation vibration absorption peak of -OH due to the absorbed water of metal oxide surface. It is generally acknowledged that there are three existence patterns of SO_4^{2-} integrated with metal oxide, which are unidentate, chelating bidentate and bridged bidentate. Schoonheydt R. A *et al.*²⁰ have proposed that absorption peak above 1200 cm^{-1} indicated SO_4^{2-} existed at patterns of chelating bidentate while absorption peak below 1200 cm^{-1} indicated SO_4^{2-} existed at pattern of bridged bidentate. Thus IR band at 1255.2 cm^{-1} indicated

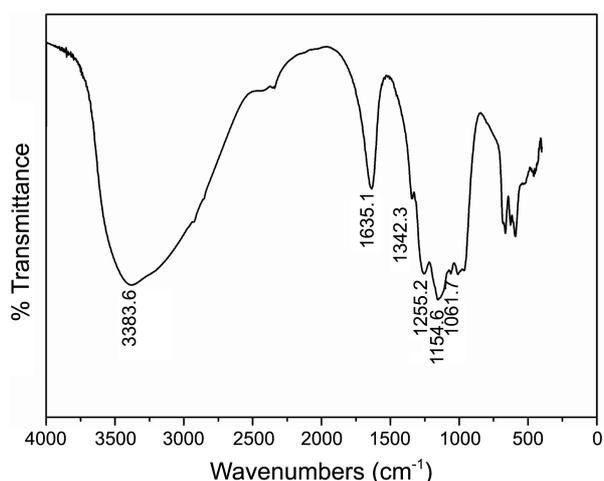


Figure 7. FTIR spectra of 0.75M-SZ-500 solid acid catalyst.

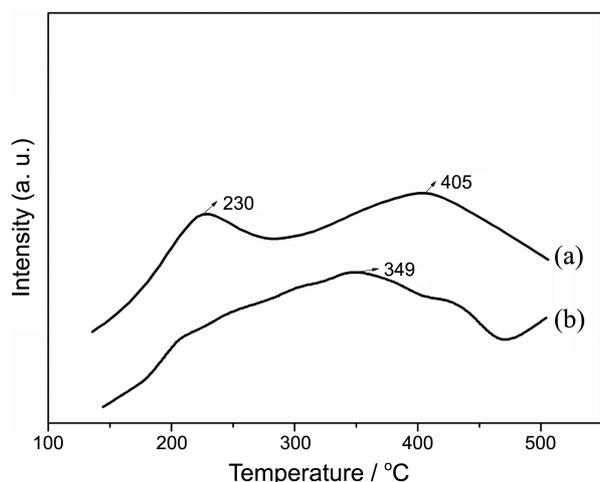


Figure 8. NH_3 -TPD curves of 0.75M-SZ-500 (a) and 1.00M-SZ-500 (b).

that SO_4^{2-} integrated with Zr^{4+} at pattern of chelating bidentate. IR band at 1154.6 cm^{-1} showed that SO_4^{2-} integrated with Zr^{4+} at pattern of bridged bidentate.

NH_3 -TPD: Two acid sites existed in the surface of 0.75M-SZ-500 solid acid catalyst, strong acid site (desorption temperature at $405\text{ }^\circ\text{C}$) and weak acid site (desorption temperature at $230\text{ }^\circ\text{C}$) shown in Figure 8. 1.00M-SZ-500 only had one desorption peak at $349\text{ }^\circ\text{C}$. Compared with two curves in Figure 8, it could be found that 0.75M-SZ-500 showed a strong acid site and weak acid site at $405\text{ }^\circ\text{C}$ and $230\text{ }^\circ\text{C}$ respectively. However 1.00M-SZ-500 show there was no desorption peak in the corresponding temperature, which might indicate 1.00M-SZ-500 had no the corresponding acid site. The amount of acid sites of 0.75M-SZ-500 was larger than those of 1.00M-SZ-500 according to the area of desorption peak. Thus concentration of H_2SO_4 impregnated more than 0.75 mol/L was not in favor of catalytic activity.

Conclusions

Cellulose could be converted to CAP over the catalyst of $\text{SO}_4^{2-}/\text{ZrO}_2$ and yield of CAP was up to 105.3%, when concentration of H_2SO_4 impregnated, calcination temper-

ature, esterification time and esterification temperature were 0.75 mol/L, $500\text{ }^\circ\text{C}$, 8 h and $50\text{ }^\circ\text{C}$ respectively. The activity of catalyst could be almost recovered, and yield, acetyl and propionyl content of CAP was still up to 71.3%, 28.7% and 21.8% after the fifth reuse. The excellent activity of 0.75M-SZ-500 was ascribed to the existence of two acid sites coupled with the firm combination of sulfur species with *t*- ZrO_2 .

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References

1. Jeon, G. W.; An, J. E.; Jeong, Y. G. *Composites: Part B* **2012**, *43*, 3412.
2. Scott, G. *Polym. Deg. Stab.* **2000**, *68*, 1.
3. Park, H. M.; Liang, X. M.; Mohanty, A. K.; Misra, M.; Drzal, L. T. *Macromolecules* **2004**, *37*, 9076.
4. Mohanty, A. K.; Wibowo, A.; Misra, M.; Drzal, L. T. *Polym. Eng. Sci.* **2003**, *43*, 1151.
5. Gedon, S.; Fengl, R. In *Krik-Othmer Encyclopedia of Chemical Technology*; Wiley: New York, 1993; p 496.
6. Sivaprakasam, S.; Saravanan, C. G. *Energ. Fuel.* **2007**, *21*, 2998.
7. Georgogianni, K. G.; Kontominas, M. G.; Pomonis, P. J.; Avlonitis, D.; Gergis, V. *Fuel. Process. Technol.* **2008**, *89*, 503.
8. Ataya, F.; Dube, M. A.; Ternan, M. *Energ. Fuel.* **2008**, *21*, 2450.
9. Yan, H. P.; Yang, Y.; Xiang, X.; Hu, C. W. *Catal. Commun.* **2009**, *10*, 1558.
10. Su, Q.; Zhang, Q.; Xu, G. H. *Fuel. Process. Technol.* **2009**, *90*, 1002.
11. Jiang, K. H.; Tong, D. M.; Tang, J. Q. *Appl. Catal. A-gen.* **2010**, *389*, 46.
12. Hino, M.; Kurashige, M. *Thermochim. Acta* **2006**, *441*, 35.
13. Wang, B.; Zhu, J. P.; Ma, H. Z. *J. Hazard. Mater.* **2009**, *164*, 256.
14. D817-96. Standard Test Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrates [S].
15. Su, W. Y.; Chen, Y. L.; Fu, X. Z.; Wei, K. M. *Chinese J. Catal.* **2001**, *22*, 175.
16. Zhang, C.; Liu, T.; Wang, H. J.; Wang, F.; Pan, X. Y. *Chem. Eng. J.* **2011**, *174*, 236.
17. Cai, Y. S.; Tong, D. M.; Wu, X.; Jiang, K. H.; Hu, C. W. *Chin. J. Chem. Res. Appl.* **2008**, *20*, 996.
18. Hino, M.; Aratab, K. *J. Chem. Soc.* **1988**, *18*, 1259.
19. Martínez, A.; Prieto, G.; Arribas, M. A.; Concepción, P.; Sánchez-Royo, J. F. *J. Catal.* **2007**, *248*, 288.
20. Schoonheydt, R. A.; Lunsford, J. H. *J. Catal.* **1972**, *26*, 261.