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Preyssler-Structured Tungstophosphoric Acid Catalyst on Functionalized Silica for Esterification of *n*-Butanol with Acetic Acid

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Abstract The Preyssler-structured tungstophosphoric acid catalyst supported on functionalized silica (Preyssler/F-silica) was prepared by means of grafting technique with amine group as coupling media, and its catalytic behavior was investigated in the esterification of *n*-butanol with acetic acid. The catalyst was characterized by infra-red spectroscopy, UV–Vis spectroscopy, Hammett indicator and N_2 adsorption techniques. Catalysts prepared directly by impregnating Preyssler acid on silica (Preyssler/silica) were also studied for comparison. The Preyssler/F-silica catalyst with the 14.3% loading of Preyssler acid exhibits a considerable conversion of *n*-butanol of 46.7% with 100% selectivity for *n*-butyl acetate in the esterification of *n*-butanol with acetic acid, which is comparative to the 15%Preyssler/silica catalyst. Moreover, a six-cycle reaction test reveals a good reusability for Preyssler/F-silica due to the water-resistance property of the Preyssler structure on the surface of the functionalized silica, and Preyssler/silica looses its high activity immediately at the second reaction cycle. The active sites on functionalized silica can retain the Preyssler structure before and after reaction. At 120 °C of reaction temperature, 140 min of reaction time, 1:1 molar ratio of acetic acid with *n*-butanol, and 0.005 g/mL of the catalyst content in reaction media are the suitable reaction conditions over the Preyssler/F-silica catalyst.

Keywords Preyssler heteropolyacid · Grafting · Esterification · Functionalized silica

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1 Introduction

Heteropolyacid (HPA) has got extensive studies as an efficient solid acid catalyst due to its unique advantages, such as strong Brønsted acidity, structure alterability and environmental friendliness [1, 2]. Nowadays, most of studies focus on the catalytic behaviors of the Keggin-structured HPA [3], among which 12-tungstophosphoric acid with the formula of $H_3PW_{12}O_{40}$ is known to be a highly active catalyst for a variety of acid-catalyzed reactions [4, 5]. In contrast, the Preyssler-structured HPA does not attract much research attention. The Preyssler's anion $[NaP_5W_{30}O_{120}]^{14-}$ consists of a cyclic assembly of five PW_6O_{22} units and displays approximately D_{5h} symmetry [6]. The advantages of Preyssler HPA as a solid acid catalyst may include large number of balanced protons, strong acidity, high hydrothermal stability, and wide pH range stability in solution [7, 8]. A few of researchers have investigated the catalytic performances of Preyssler HPA in a number of organic synthesis processes [9–11]. Fatemeh et al. [12] reported a high catalytic activity of the Preyssler-structured compound $H_{14}[NaP_5W_{29}MoO_{110}]$ with a 100% selectivity in the direct esterification of butanol to butylbutanoate in the absence of butanoic acid. Also, Majid et al. [13] observed a high catalytic activity of Preyssler type HPA in the synthesis of 14-substituted-14-H-dibenzo [*a*,*j*] xanthene derivatives without using any solvents.

However, the extremely low surface area of HPA and its water-solubility always hinder its practical applications [14]. A solution to conquer these drawbacks is to support HPA on carriers, such as silica, active carbon, molecular sieves, Al_2O_3, etc. [15]. The impregnation is an easy way to make it. However, HPA tends to be leached out of the support into the polar reaction media, which leads to the deactivation of the solid catalyst. In order to avoid leaching, the grafting method has been chosen to immobilize HPA on the carrier. The main steps of this method involve the functionalization of carrier by organic components at first and then the linking of HPA with functionalized carriers. Waldemar et al. [16] immobilized Keggin HPA inside the pores of Si-MCM-41 by introducing amine groups into pore walls first and the obtained sample showed a stable activity in the oxidation of cyclohexane using *tert*-butyl hydroperoxide as oxidant. Li et al. [17] anchored the Keggin HPA on the amine–silane functionalized silica, which exhibited a higher catalytic activity in the oxidation of cyclohexane by oxygen and without leakage of active components. Bret et al. [18] synthesized transition-metal-substituted polyoxometalates clusters on the surface of silica supports by grafting technique and observed the higher catalytic activity in the epoxidation of cyclohexene to cyclohexene oxide in the presence of isobutyraldehyde without loss of activity in multiple catalytic runs. Using FT-IR and XPS techniques, Masahiko et al. [19] verified the adsorptivity of Keggin type HPA on silica gel, which was modified with (3-anilinopropyl) trimethoxysilane. Up to now, the study of HPA catalysts grafted on the functionalized silica was mainly based on the Keggin type HPA for oxidation reactions. To the best of our knowledge, investigation of the Preyssler HPA grafted on the functionalized silica as a catalyst for an acid-catalyzed process has not appeared so far.

In this work, we study the functionalized silica-grafted Preyssler HPA catalyst and observe its considerable and stable activity in the esterification of *n*-butanol with acetic acid.

2 Experimental

2.1 Catalyst Preparation

The Preyssler's anion $[NaP_5W_{30}O_{120}]^{14-}$ was prepared according to the previous method with some modifications [6]. About 33 g $Na_2WO_4 \cdot 2H_2O$ was dissolved in 30 mL H_2O by vigorously stirring, into which 26.5 mL aqueous solution of phosphoric acid (85% by weight) was added. The mixture was sealed into a Teflon bottle at 120 °C for 18 h. Following this, 30 mL H_2O and 10 g KCl were added into the above mixture to form the precipitate with a white color. The white precipitate was obtained by filtration and washed successively by 2 M aqueous solution of CH_3COOK and methanol. The precipitate was dried and recrystallized twice to obtain the potassium salt of Preyssler HPA. The Preyssler acid was prepared by the passage of an aqueous solution of the potassium salt through a column of H^+ ion-resin, followed by the evaporation of the elute in oven.

The preparation of functionalized silica (F-silica) is as follows. About 5 g of fumed silica (CAB-O-SIL, EH-5, CABOT) suspended in 50 mL toluene was refluxed for 1 h, and then 2.5 g 3-aminopropyltriethoxy silane (KH550) was injected into the above mixture with further stirring for 24 h. The F-silica was obtained by filtration, washed successively with toluene, ethanol and water, and finally dried in vacuum at 80 °C for 12 h. The adsorption of HPA on the surface of F-silica was carried out by the following procedure: 0.2 g Preyssler acid was dissolved in 100 mL H_2O with vigorously stirring, and then 0.4 g F-silica was added into the above solution. The mixture was stirred for 24 h at room temperature. The solid was recovered by filtration, washed with water and dried at 110 °C for 12 h. The obtained sample is designated as Preyssler/F-silica.

The directly supported Preyssler HPA catalysts (Preyssler/silica) were prepared by impregnating silica into an aqueous solution of Preyssler acid. After constant stirred overnight at the room temperature, the mixture was subjected to evaporation and drying to get the solid products. The loadings of Preyssler acid for Preyssler/silica catalysts were 15% and 50%, respectively, which were prepared by changing the concentration of aqueous solution of Preyssler acid. Before charged into the reaction media, all the catalysts were activated at 300 °C in air for 3 h.

2.2 Catalytic Test

The esterification of *n*-butanol with acetic acid was performed in a three-necked glass flask with a Teflon-coated magnetic stirrer and a water-removal accessory. About 7.4 mL acetic acid and 11.9 mL *n*-butanol (1:1 molar ratio), 120 °C of reaction temperature, 140 min of reaction time, and 0.005 g/mL of catalyst content in reaction media were used as the typical reaction conditions. The products were analyzed by Gas Chromatograph using SE-54 capillary column with FID as the detector, and the conversion was determined by the internal standard method with *n*-pentane as the standard substance. The reuse ability of catalyst was tested as follows. After a reaction, the solid catalyst was separated from liquid by filtration and washed by water. Then the water-treated catalyst was dried and putted into the reactant mixture of next reaction.

2.3 Characterization

The FT-IR spectra were measured on Nexus 870 FT-IR spectrometer by KBr pellets. BET surface area was achieved by N_2 adsorption on the ASAP2020 Micromeritics analyzer. The loading of Preyssler acid for prepared Preyssler/F-silica sample was measured by the UV–Vis spectra. After the adsorption of Preyssler acid onto the surface of F-silica during the preparation of Preyssler/F-silica, heteropoly species were leached into the filtrate, the amount of which were estimated by using a Perkin Elmer Lambda 35 spectrometer with a quartz cell of 10 mm optical path. For the quantitative analysis, a standard curve was obtained by using the aqueous solutions of Preyssler acid with different concentrations. The Preyssler acid loading of 14.3% by weight for the sample Preyssler/F-silica was obtained by calculating the weight difference of initially used HPA and leached HPA in filtrate. The acid strengths of catalysts were measured with Hammett indicators, including anthraquinone (pKa = −8.20), *p*-nitrotoluene (pKa = −11.35), *p*-nitrochlorobenzene (pKa = −12.70), *m*-chloronitrobenzene (pKa = −13.60), and 2,4-dinitrofluorobenzene (pKa = −14.52).

3 Results and Discussion

3.1 Comparison of Various Catalysts

Figure 1 compares the FT-IR spectra of the Preyssler HPA, Preyssler/F-silica, 15%Preyssler/silica, and pure silica. From Fig. 1, it can be seen that the Preyssler HPA sample prepared in this work showed all the IR vibration peaks assigned to a Preyssler structure, and the locations of featured peaks are in well agreement with those in the previous reports [6, 20]. In detail, the Preyssler HPA sample displayed vibrations at 1,165, 1,082 and 1,021 cm^{-1} for P–O stretching in Preyssler structure, 940 and 913 cm^{-1} for W–O–W stretching, 788 cm^{-1} for W=O stretching, and 573 cm^{-1} for P–O bending. For pure silica, a very broad Si–O–Si stretching peak occurred around 1,100 cm^{-1} [21]. This may hindered the clear observation of the three P–O stretching peaks in this area for Preyssler/F-silica due to the strong background. However, the two W–O–W stretching peaks at 940 and 913 cm^{-1} could be clearly detected for Preyssler/F-silica, which strongly suggest that the Preyssler's anions chemically adsorbed onto the surface of F-silica through KH550 retain their Preyssler structure. A previous study showed that the reaction of Preyssler HPA with functionalized silica affected the position of the W–O–W stretching peaks [20]. However, in our case, Preyssler/F-silica in Fig. 1 only showed a widening for W–O–W stretching peaks without observing a clear shift. On the other hand, for Preyssler HPA/silica, no peaks assigned to Preyssler structure could be observed obviously. This is partially because of the strong background of pure silica, but the more important reason may be that the interaction between Preyssler's anions and hydroxyls in the surface of silica mostly caused the distortion of anions, and thus substantially weakened the IR vibrations and covered up by the silica background.

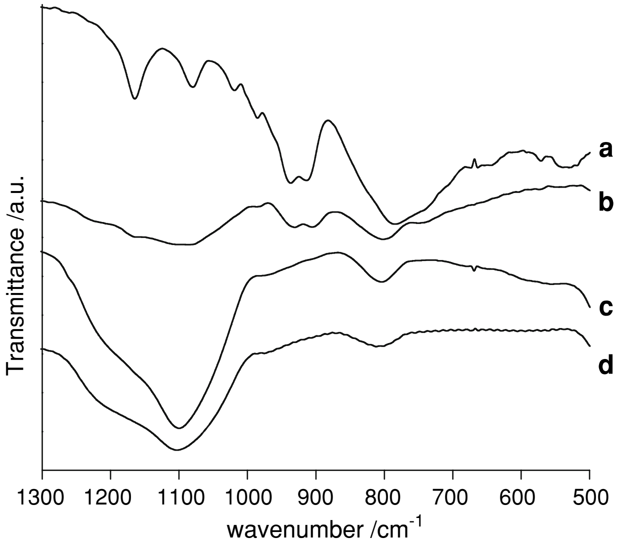

Fig. 1 The FT-IR spectra of Preyssler HPA (**a**), Preyssler/F-silica (**b**), 15%Preyssler/silica (**c**), and pure silica (**d**)

Table 1 listed the BET surface areas of various catalysts. The pure Preyssler HPA only had a negligible surface area, and pure silica possessed a higher specific surface area of 380 m^2/g. The surface areas of supported Preyssler HPA catalysts prepared simply by impregnation decreased with increasing the HPA loading. On the other hand, after functionalizing the silica support, the surface area of F-silica drastically dropped to 71 m^2/g, which can be attributed to the increase in agglomeration of silica particles and/or occupation of organic of pores after modification with 3-aminopropyltriethoxy silane [20]. By supporting Preyssler HPA onto F-silica, the surface area of the Preyssler/F-silica sample further decreased to a low value of 34 m^2/g. The acid strength (H_0) for various catalysts is also displayed in Table 1. Both pure Preyssler HPA and 50%Preyssler/silica show superacidity with H_0 of −14.52 and −13.6, respectively. 15%Preyssler/silica gives a lower H_0 value of −11.35 compared with pure Preysslar HPA and 50%Preyssler/silica. After Preyssler HPA anchored on F-silica, the acidity is very comparable with 15%Preyssler/silica. It means that no substantially differences happen between HPAs supported on functionalized silica and on unfunctionalized silica with the similar loadings in term of acid strength.

The catalytic activities of various catalysts for esterification of *n*-butanol with acetic acid are compared in Table 1. Under the employed reaction conditions, *n*-butyl acetate was the only detected product for all catalysts. One can see from Table 1 that without any added catalysts, 14.6% of conversion of *n*-butanol was obtained due to the acid environment provided by one of the reactants, acetic acid. The pure silica and F-silica showed very similar

Table 1 BET surface areas, acid strengths, and catalytic activities of various catalysts for esterification of *n*-butanol with acetic acid[a]

Entry	Catalyst	S_{BET} (m^2/g)	Acid strength (H_0)	Conversion (%)	TON[b]
1	Blank	–	–	14.6	–
2	Silica	380	–	18.8	–
3	F-silica	71	–	15.7	–
6	Preyssler HPA	0.3	−14.52	98.5	2.3×10^3
4	15%Preyssler/silica	276	−11.35	49.4	4.8×10^3
5	50%Preyssler/silica	179	−13.6	74.5	2.2×10^3
7	Preyssler/F-silica	34	−11.35	46.7	3.6×10^3

[a] Reaction conditions: 7.4 mL acetic acid, 11.9 mL *n*-butanol, 120 °C of reaction temperature, 140 min of reaction time, 0.1 g Preyssler/F-silica (0.05 g Preyssler HPA, 0.08 g 15%Preyssler/silica, or 0.1 g 50%Preyssler/silica)

[b] Turnover number calculated as moles of *n*-butyl acetate formed on one mole of Preyssler HPA within 140 min of reaction time

conversion to the blank test for the absence of acidic sites. The pure Preyssler HPA exhibited a very high conversion of 98.5%. 50%Preyssler/silica catalyst behaved a higher conversion (74.5%) than 15%Preyssler/silica catalyst did (49.4%) due to the more active sites delivered by the higher HPA loading of the former one. Preyssler/F-silica catalyst owned a similar HPA loading to that of 15%Preyssler/silica (14.3% vs. 15%) and it gave a slightly lower conversion of 46.7%. This very similar conversion in esterification of fresh Preyssler/F-silica and 15%Preyssler/silica corresponds well with the observed same acid strength of them. In term of turnover number, it is seen from Table 1 that Preyssler/F-silica and 15%Preyssler/silica were more active than the pure Preyssler acid and 50%Preyssler/silica. Considering the much lower surface area of Preyssler HPA/F-silica than that of 15%Preyssler/silica, it is certain that Preyssle/F-silica showed a higher activity per square meter of catalyst surface than 15%Preyssler/silica.

3.2 Catalytic Stability

The catalytic reusability of three different silica supported Preyssler HPA catalysts in the esterification of *n*-butanol with acetic acid is illustrated in Fig. 2. It can be seen that although the fresh 50%Preyssler/silica catalyst is very active with a high conversion of 74.5%, it dropped largely to 31.7% for the second run. Very similarly, over 15%Preyssler/silica the conversion of *n*-butanol decreased rapidly from 49.4% for the first run to 32.4% for the second run. This indicates a very instable catalytic activity for the Preyssler/silica catalyst prepared by impregnation mostly due to the severe leaching property of HPA. According to the previous report [22], for the catalyst prepared directly by impregnation, only slight interaction exists between the supported HPA and the silica support and this weak interaction cannot avoid the extraction of the HPA out of the silica by water. In contrast, Fig. 2 showed that the Preyssler/F-silica catalyst the conversion reduced very slowly when the catalyst was reused, and at the forth run the conversion was 43.8%, which is comparative to 46.7% over fresh catalyst. On the other hand, the decrease of conversion arising from the catalyst lost during the separation and transfer of the catalyst into the next reaction recycle cannot be excluded. This observation reveals a satisfied reusability for the Preyssler/F-silica catalyst, which means that the Preyssler HPA has only a slight tendency to leach from the functionalized silica. The well stability of Preyssler HPA on F-silica is suggested to ascribe to the strong chemical interaction of $Si(CH_2)_3NH_3^+$ and $[NaP_5W_{30}O_{120}]^{14-}$ [23, 24]. Figure 3 compares the FI-IR spectra of fresh Preyssler/F-silica and the used one. They were very similar to each other. The W–O–W stretching peaks for Preyssler

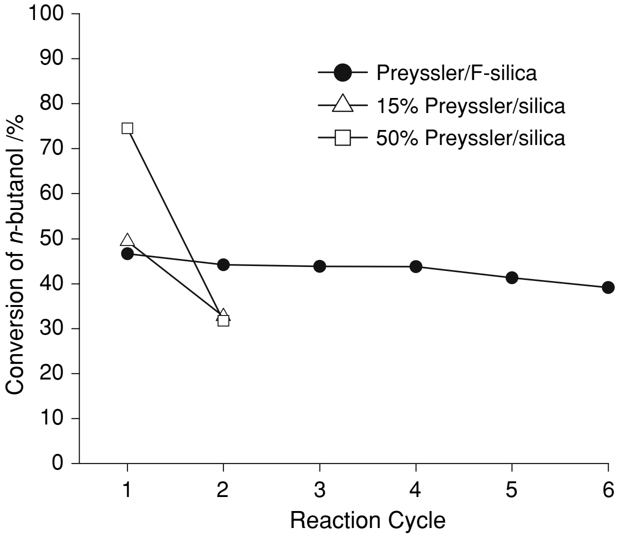

Fig. 2 Conversions of *n*-butanol in the esterification of *n*-butanol with acetic acid over different silica supported Preyssler HPA catalysts as a function of reaction cycles. Reaction conditions: 7.4 mL acetic acid, 11.9 mL *n*-butanol, 120 °C of reaction temperature, 140 min of reaction time, 0.1 g Preyssler/F-silica (0.08 g 15%Preyssler/silica, or 0.1 g 50%Preyssler/silica)

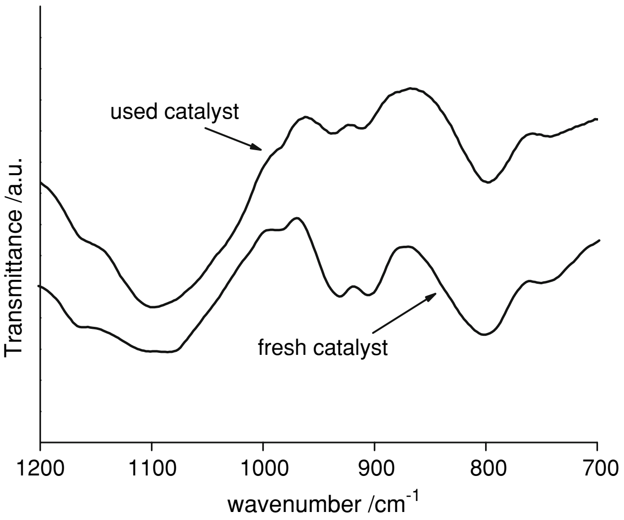

Fig. 3 IR spectra of Preyssler/F-silica sample before and after reaction

structure at 940 and 913 cm^{-1} were still clearly recognized after reaction, demonstrating that the Preyssler HPA still stayed on the surface of F-silica for the used catalyst. Owing to the stable activity of Preyssler/F-silica, the effects of some important reaction conditions were measured over this catalyst in the following.

3.3 Effect of Reaction Time

Figure 4 shows the influence of reaction time on the conversion of *n*-butanol over Preyssler/F-silica. It was obvious that the conversion increased greatly with the increase of reaction time up to 140 min, and after that, the conversion of *n*-butanol increased comparatively slowly along with the increase of reaction time.

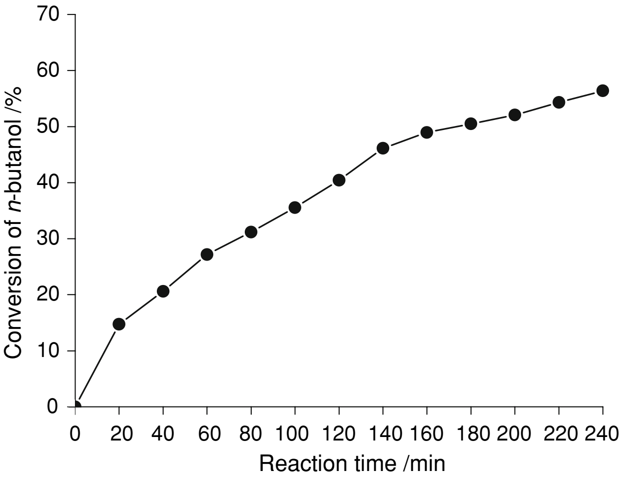

Fig. 4 Conversion of *n*-butanol in the esterification of *n*-butanol with acetic acid over Preyssler/F-silica catalyst as a function of reaction time. Reaction conditions: 7.4 mL acetic acid, 11.9 mL *n*-butanol, 120 °C of reaction temperature, 0.1 g Preyssler/F-silica

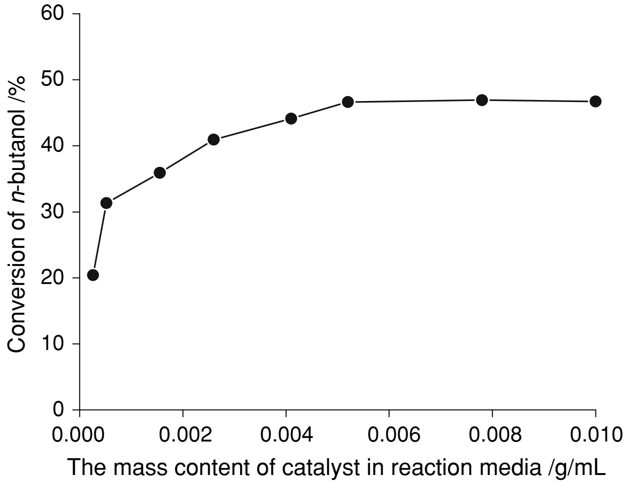

Fig. 5 Conversion of *n*-butanol in the esterification of *n*-butanol with acetic acid over Preyssler/F-silica catalyst as a function of catalyst content in reaction media. Reaction conditions: 7.4 mL acetic acid, 11.9 mL *n*-butanol, 120 °C of reaction temperature, 140 min of reaction time

3.4 Effect of Catalyst Content in Reaction Media

Influence of catalyst content in reaction media on the conversion of *n*-butanol over Preyssler/F-silica is shown in Fig. 5. One can see that the conversion reached a plateau value at the catalyst content of 0.005 g/mL, and beyond this point, no increase of conversion could be observed.

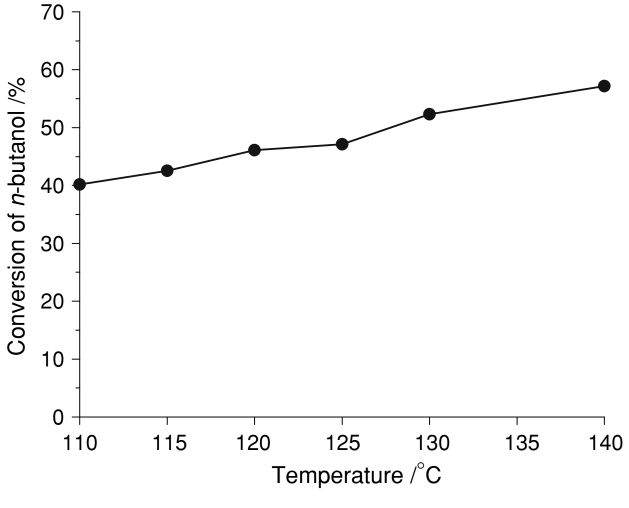

Fig. 6 Conversion of *n*-butanol in the esterification of *n*-butanol with acetic acid over Preyssler/F-silica catalyst as a function of reaction temperature. Reaction conditions: 7.4 mL acetic acid, 11.9 mL *n*-butanol, 140 min of reaction time, 0.1 g Preyssler/F-silica

3.5 Effect of Reaction Temperature

Figure 6 showed the effect of the reaction temperature on the conversion of *n*-butanol over Preyssler/F-silica. The conversion increased steadily when the reaction temperature was enhanced from 110 °C to 140 °C, and the conversion exceeded 50% when the temperature reached to 130 °C. However, by-products were showed up when the reaction temperature was up to 130 °C. Therefore, 120 °C was considered as a suitable reaction temperature.

4 Conclusions

In this work, the catalyst Preyssler/F-silica is obtained by grafting the Preyssler-structured heteropoly acid onto the 3-aminopropyltriethoxy silane-functionalized silica. Over this functionalized silica supported acid catalyst for the esterification of *n*-butanol with acetic acid, a conversion of *n*-butanol of 46.7% with 100% selectivity for *n*-butyl acetate is achieved, which is comparative to the 15%Preyssler/silica catalyst prepared directly by impregnating Preyssler acid on silica. However, the activity of the Preyssler/silica catalyst decreases drastically to a very low value at the second reaction cycle, in contrast, Preyssler/F-silica shows a good reusability during a six-cycle test due to the strong interaction of Preyssler HPA and F-silica.

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References

1. Kozhevnikov IV (1998) Chem Rev 98:171
2. Okuhara T (2002) Catal Today 73:167
3. Kozhevnikov IV (2007) J Mol Catal A Chem 262:86
4. Mizuno N, Misono M (1997) Curr Opin Solid State Mater Sci 2:84
5. Okuhara T, Mizuno N, Misono M (2001) Appl Catal A Gen 222:63
6. Alizadeh MH, Harmalker SP, Jeannin Y, Frère JM, Pope MT (1985) J Am Chem Soc 107:2662
7. Heravi MM, Zadsirjan V, Bakhtiari K, Oskooie HA, Bamoharram FF (2007) Catal Commun 8:315
8. Alizadeh MH, Razavi H, Bamoharram FF, Hassanzadeh MK, Khoshnavazi R, Zonoz FM (2003) Kinet Catal 44:524
9. Feizi N, Hassani H, Hakimi M (2005) Bull Korean Chem Soc 26:2087
10. Arabi M, Amini MM, Abedini M, Nemati A, Alizadeh M (2003) J Mol Catal A Chem 200:105
11. Alizadeh MH, Kermani T, Tayebee R (2007) Monatsh Chem 138:165
12. Bamoharram FF, Heravi MM, Roshani M, Jahangir M, Gharib A (2007) J Mol Catal A Chem 271:126
13. Heravi MM, Bakhtiari K, Daroogheha Z, Bamoharram FF (2007) J Mol Catal A Chem 273:99
14. Kozhevnikov IV, Kloetstra KR, Sinnema A, Zandbergen HW, Bekkum HV (1996) J Mol Catal A Chem 114:287
15. Gu YB, Wei RP, Ren XQ, Wang J (2007) Catal Lett 113:41
16. Kaleta W, Nowińska K (2001) Chem Commun 6:535
17. Li HL, Perkas N, Li QL, Gofer Y, Koltypin Y, Gedanken A (2003) Langmuir 19:10409
18. Johnson BJS, Stein A (2001) Inorg Chem 40:801
19. Kamada M, Komiinami H, Kera Y (1996) J Colloid Interface Sci 182:297
20. Tarlani A, Abedini M, Nemati A, Khabaz M, Amini MM (2006) J Colloid Interface Sci 303:32
21. Li HL, Fu AP, Xu DS, Guo GL, Gui LL, Tang YQ (2002) Langmuir 18:3198
22. Lefebvre F (1992) J Chem Soc Chem Commun 756
23. Kim H, Jung JC, Yeom SH, Lee KY, Yi J, Song IK (2007) Mater Res Bull 42:2132
24. Li WJ, Li LD, Wang ZC, Cui AL, Sun CQ, Zhao JZ (2001) Mater Lett 49:228