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Esterification of Acetic Acid with *N*-Butanol Over the Catalysts of Surface Hydrophobicity and Lipophobicity

Qingbo Liu · Guifang Chen · Jing Li · Xiangguang Yang

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Abstract A series of silica-supported silicotungstic acid catalysts ($H_4SiW_{12}O_{40}$, abbreviated as HSiW), modified with various loadings of Teflon (HSiW/SiO_2-Teflon), were prepared by impregnation method. The surface properties of the catalysts were studied by means of XRD, BET, NH_3-TPD and the Drop Shape Analyzer (DSA) measurements. Both the surface hydrophobicity and the surface lipophobicity of HSiW/SiO_2-Teflon catalysts are enhanced by means of the addition of Teflon. HSiW/SiO_2-Teflon exhibit better activity than that of HSiW/SiO_2 in the esterification of acetic acid with *n*-butanol. Surface hydrophobicity and lipophobicity of the catalysts lead to more effective to remove product molecules and decrease the interaction between H_2O molecules and the catalyst surface, especially at low reaction temperature and appropriate WHSV.

Keywords Hydrophobicity · Lipophobicity · Teflon · Silicotungstic acid · Esterification · *n*-Butyl acetate

1 Introduction

Esterification of acetic acid with *n*-butyl alcohol is commercially important as the product *n*-butyl acetate can be used to manufacture the lacquer, artificial perfume, flavouring extract, leather, photographic films, plastics and safety glass. It can be also used as the dehydrating agent. Mineral acids such as H_2SO_4, HCl, HF, H_3PO_4, $ClSO_2OH$ have been used in the conventional esterification reaction. These liquid acids are corrosive to the reaction vessels and the excess acid has to be neutralized after the reaction, which leaves considerable amount of salts as by-products. So the replacement of the conventional hazardous, polluting and corrosive liquid acid by solid acid in acid catalysis is the demand of the day to create the cleaner technology. The aim is to minimize environmentally unacceptable wastes in acid catalysis. Many solid acid catalysts have been reported in the literature for esterification reaction, such as ion exchange resin [1, 2], H-ZSM-5 [3], zeolites-Y [4], niobic acid [5], sulphated oxides [6], Al-MCM-41 [7] and supported heteropolyacids (HPA) [8, 9]. HPAs with Keggin structure, in particular their acidic forms, have been widely studied as heterogeneous catalysts in both acid-catalyzed and oxidation processes [10]. However, pure heteropoly acids generally show very low catalytic reactivity owing to their very small surface areas. Therefore, the supported heteropoly acids, usually prepared by the impregnation of heteropoly acids on classical porous materials, are more effective in acid catalytic reactions [11, 12].

It is well known that the esterification is a reversible reaction and H_2O is formed as a by-product together with the same amount of *n*-butyl acetate in the esterification of acetic acid with *n*-butanol. On the solid acid catalysts, H_2O may lead to the deactivation of the catalysts [13], and decrease the equilibrium scale of *n*-butyl acetate formation, thereby removing H_2O by azeotropic distillation during the reaction is required. The hydrophobic nature of highly siliceous zeolites was first pointed out by Chen [14, 15]. The effect of surface hydrophobicity on catalytic performance was also observed by Namba et al. [16] in the direct esterification of acetic acid with *n*-, *iso*- and *tert*-butyl alcohol over various zeolites. Corma also found that zeolite catalysts with the high Si/Al ratio for the esterification of phenylacetic and benzoic acids with ethanol, isopropanol,

Q. Liu · G. Chen · J. Li · X. Yang (✉)
ChangChun Institute of Applied Chemistry, Chinese Academy of Sciences, ChangChun, P.R. China
e-mail: xgyang@ciac.jl.cn

tertbutanol and *p*-cresol possibly overcame the homogeneous equilibrium limitation, and showed an average catalytic activity per proton very similar to that of sulfuric acid [4]. Generally, the severe poisoning of the acid sites by water as a weak base brings difficulties in the use of solid acids; in fact, most solid acids would only exhibit lower catalytic activities in aqueous solutions [17]. However, the poisoning from H_2O could be lowered by using the more hydrophobic high-Si/Al-ratio zeolites [18] or heteropoly compounds [19, 20], which would be more active despite only having a smaller number of acid sites [21]. Furthermore, an adsorption-based methodology for measuring zeolite hydrophobicities has been developed by Weitkamp and co-workers [22]. H_2O molecular formed in the reaction could be removed effectively due to surface hydrophobicity, in which poisoning of catalysts would be prevented. However, the effect of surface lipophobicity of the solid acid catalysts in the esterification has not been reported. In our previous studies, HSiW/SiO_2-Teflon catalysts enhance both the surface hydrophobicity and the surface lipophobicity by means of the addition of Teflon, surface-appropriate lipophobicity of catalysts are effective for decreasing the interaction between lipophilic big molecules and the catalyst surface [23]. *N*-butyl acetate is lipophilic, which is strongly adsorbed on the lipophilic surface of the catalysts and it is not easy to remove from the catalysts surface at low temperatures. Surface lipophobicity could be effective for removing *n*-butyl acetate. In this letter, the additive effect of Teflon on the catalytic in the esterification and the relation between the activity and surface properties of the catalysts are reported.

2 Experimental

HSiW/SiO_2-Teflon catalysts were prepared by the following method: first, Teflon emulsion (Teflon 60%, shuzhou fulin corp.) was added dropwise to a HSiW (analytical reagent, Beijing chemical factory) aqueous solution under constant stirring at room temperature and then treated by ultrasonic mixing for 0.5 h. Secondly, dry SiO_2 was added rapidly into this mixture and treated by ultrasonic agitation for 0.5 h again. Finally, it was dried at 110 °C for 5 h and then calcined at 250 °C in flowing air for 3 h. A series of samples having different weight percentages of Teflon were prepared in the above method. The weight ratio of HSiW to SiO_2 kept 1 to 1 in all samples and the weight ratio of Teflon to HSiW-SiO_2 varied from 10% to 50% (denoted as SWT-10, SWT-20, SWT-30, SWT-40, SWT-50, respectively). For comparison, 50 wt.% HSiW/SiO_2 (denoted as SW) was prepared in the same method.

The crystalline structures of HSiW, SW and SWT were analyzed by using a PW1710 BASED powder diffractometer with Cu Kα radiation ($\alpha = 1.5406$ Å). The working voltage and current of the X-ray tube were 40 kV and 30 mA. The samples were scanned in the range $2\theta = 2$–$70°$ at a scanning rate of 3°/min. The specific surface areas of the samples were measured on a Micromeritics ASAP 2010. NH_3-TPD spectra were performed on a homemade apparatus equipped with TCD as a detector. After treated at 300 °C for 1 h and cooled to 20 °C in the same atmosphere, the samples were exposed to NH_3 for 1 h, and then swept with helium at a rate of 50 mL/min, TPD was carried out with temperature rising rate of 20 °C/min up to 300 °C in helium. Contact angles were measured with a Drop Shape Analyzer (DSA10, KRÜSS GmbH, Hamburg 2001) at room temperature. Water droplets or bean oil droplets ($\sim$0.2 μL) were dropped carefully onto the films of catalysts and the average value of five measurements from different positions of the same sample was adopted as the contact angle. The above method was in agreement with the method as described in ref [24].

The catalytic performance was evaluated for the *n*-butanol esterification reaction in a fixed bed glass reactor with an internal diameter of 8 mm. Before the reaction, the catalyst was heated at 200 °C in N_2 stream for 1 h. Then the mixture solution of acetic acid and *n*-butanol was injected into the reactor by a syringe pump. The reactor effluent was collected in an ice-water trap and analyzed by GC using a SE-54 capillary column.

3 Results and Discussion

3.1 Characterization of Catalysts

The specific surface area of silica support is 357 $m^2\ g^{-1}$, and the specific surface areas of the samples with 0, 10, 20, 30, 40 and 50 wt.% Teflon loading is showed in Fig. 1, which decreases continuously with an increase of Teflon loading from 0 to 50 wt.%. The decrease of surface area may mainly result from the decreasing content of silica and the increasing of the non-porous component Teflon.

The XRD patterns of SWT samples are presented in Fig. 2. For pure HSiW, the three main diffraction peaks that appeared at 10.3°, 25.5° and 34.7° can be assigned to the characteristic peaks of crystalline HSiW Keggin structure [25]. As formerly observed, amorphous silica only displays a very weak and abroad band, which could not bring any effect on HSiW. For the samples with various Teflon loading, three typical characteristic peaks still appear, but they are very diffuse pattern and shift to lower 2θ angles, indicating an increase in *d*-space. This could be attributed to two factors: (i) the change of crystallization water number of HSiW in the step of impregnation [26] and (ii) the strong interaction between HSiW and silica

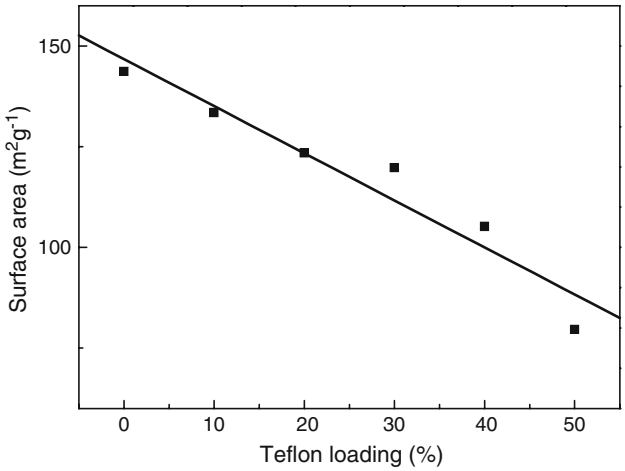

Fig. 1 BET surface area for various loading of Teflon on HSiW/SiO2

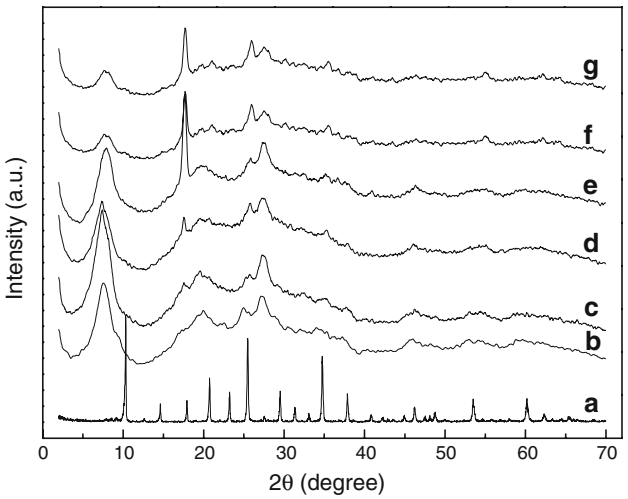

Fig. 2 XRD patterns of: (**a**) $H_4SiW_{12}O_{40}$; (**b**) SW; (**c**) SWT-10; (**d**) SWT-20; (**e**) SWT-30; (**f**) SWT-40; (**g**) SWT-50

[27] in Fig. 2b. For the samples with various Teflon loading, the intensity of the characteristic diffraction peaks of HSiW decreases obviously with the increasing loading of Teflon, as shown in Fig. 2. A new peak around 17° gradually sharpens, which may be assigned to the diffraction peak of Teflon.

The NH_3-TPD profiles of SW, SWT-10, SWT-20, SWT-30, SWT-40 and SWT-50 are shown in Fig. 3, a broad NH_3-TPD peak around ~120 °C appear at SW. The desorption temperature in the experiment was not exceeded 300 °C because Teflon would become unstable above 300 °C. As can be seen from Fig. 3, the intensity of desorption peak a little decreases with the increasing loading of Teflon. This can be attributed to the decrease of the total amount of HPA in the samples with an increase of Teflon loading. A very weak shoulder peak around 180 °C appeared in Teflon containing samples which may be

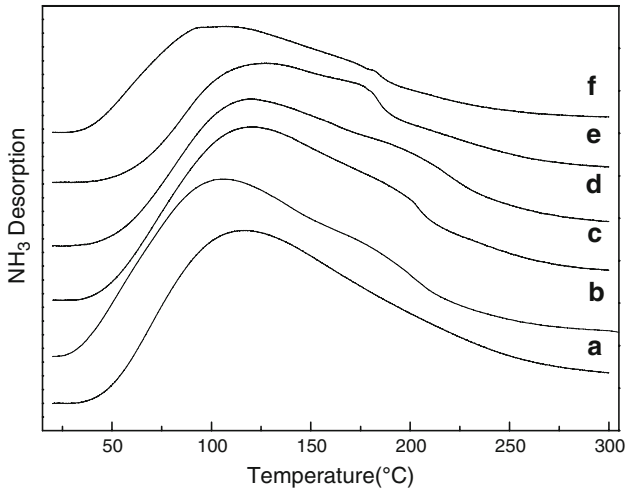

Fig. 3 NH_3-TPD profile obtained on the catalysts: (**a**) SW; (**b**) SWT-10; (**c**) SWT-20; (**d**) SWT-30; (**e**) SWT-40; (**f**) SWT-50

composed of HPA and Teflon corresponding to the stronger acid sites.

According to the literatures [24], the surface hydrophobicity and lipophobicity of the samples with 0, 10, 20, 30, 40 and 50 wt.% Teflon loading is determined by means of the contact angles for water and bean oil, as shown in Fig. 4. It can be seen that the surface hydrophobicity and lipophobicity of the samples containing Teflon are increased with an increase of Teflon loading and reach a maximum at 30 wt.% Teflon loading. The shapes of water, bean oil droplets on the films of SW and SWT-30 are shown in Fig. 5. The contact angles for water and bean oil are 40.6 ± 0.5°and 0 ± 1.0° over SW in Fig. 5a and c, respectively. In contrast, the contact angles for water and bean oil are 127.1 ± 0.1°and 60.2 ± 0.2°over SWT-30 in Fig. 5b and d, respectively. The results show that SW

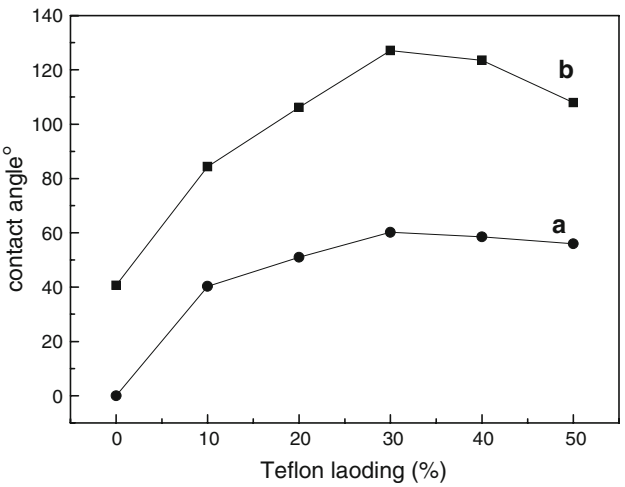

Fig. 4 Contact angles of SWT samples with various Teflon loading: (**a**) bean oil; (**b**) water

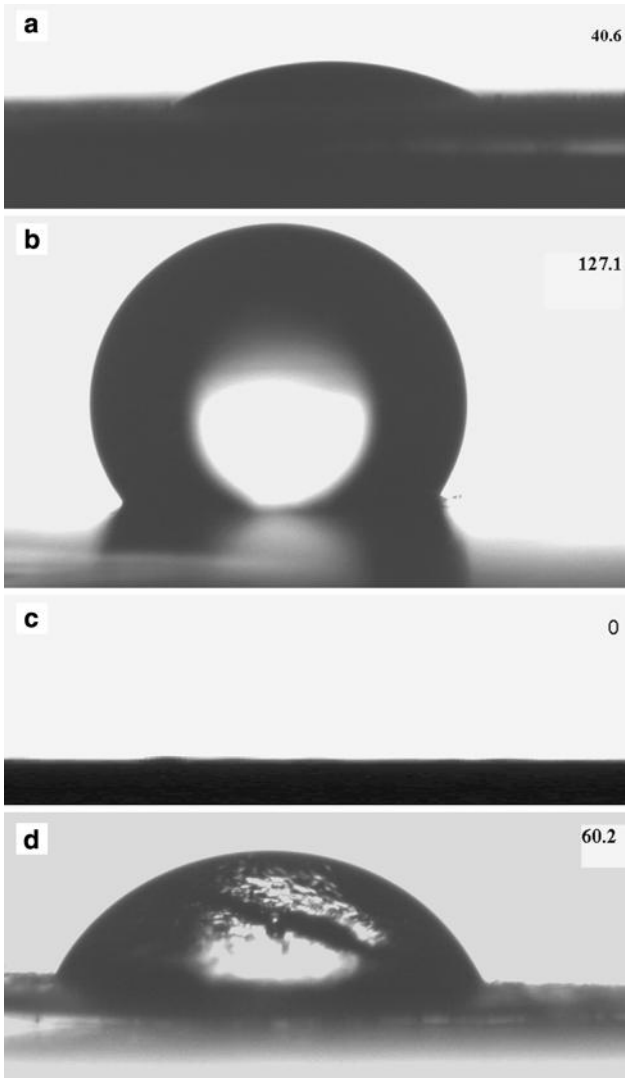

Fig. 5 Shapes of water, bean oil droplets (~0.2 μL) on catalysts films: (**a**) water droplet on the SW film; (**b**) water droplet on the SWT-30 film; (**c**) bean oil droplet on the SW film; (**d**) bean oil droplet on the SWT-30 film

possesses certain surface hydrophobicity and completely lipophilic, which is implied disadvantageous to the desorptions of the products in the esterification. But the SWT-30 enhances both the surface hydrophobicity and the surface lipophobicity, which will be advantaged to the desorptions of water and *n*-butyl acetate in the esterification.

3.2 Catalytic Activity

The effect of Teflon loading in the catalysts on the *n*-butanol conversion is shown in Fig. 6. When the esterification was carried out at 70 °C, the product analysis by GC showed that the selectivity of *n*-butyl acetate is ~100%, therefore only conversion of *n*-butanol was reported for simplicity.

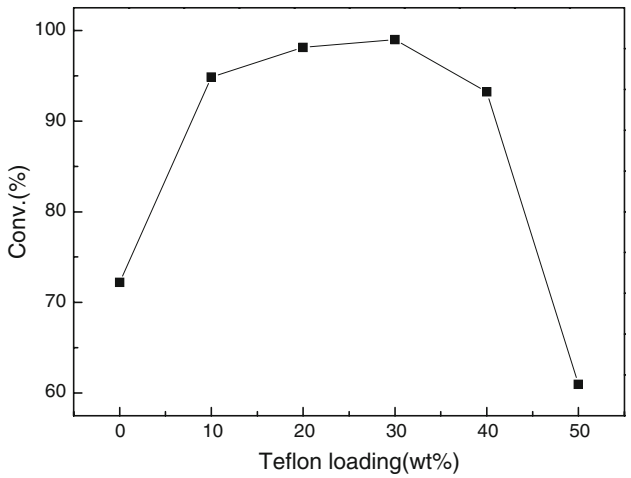

Fig. 6 Effect of the loading of Teflon on the conversion of *n*-butanol Reaction Conditions: $T = 70$ °C, WHSV = 1.08 h^{-1}, Catalyst charge = 0.50 g, Acetic acid: *n*-butanol = 1:1, time on stream = 1 h

From Fig. 6, the conversion of *n*-butanol is 72.2% over SW without Teflon. After the catalysts were modified with Teflon, the conversion had a dramatic increase with the loading of Teflon first, and reached a maximum at 30 wt.% Teflon loading, then followed by a decline. A maximum appears at 30 wt.% Teflon loading, which could be attributed to both the stronger hydrophobicity and lipophobicity of the catalyst surface with Teflon loading. SWT-30 shows the strongest hydrophobicity and lipophobicity among all the catalysts, as shown in Fig. 4. Both H_2O and *n*-butyl acetate are the products of the esterification, which are in liquid phase at the reaction temperature, the existence of Teflon enhances both the surface hydrophobicity and the surface lipophobicity of the catalyst, so both H_2O and *n*-butyl acetate are easier to be removed from the catalyst surface. The easier removal of H_2O and *n*-butyl acetate from the catalyst surface, which accelerates the desorptions of products, increases the conversion of *n*-butanol and prevents the severe poisoning of the acid sites by water simultaneously. When the Teflon loadings increased to 50 wt.%, the decrease of *n*-butanol conversion mainly results from the decrease of HSiW content in the catalyst due to the increase of the non-porous component Teflon.

From the data shown in Fig. 7, the *n*-butanol conversion is increased with the reaction temperature over SW, which can be attributed to the easier formation of carbonium ion at higher temperature, then forming *n*-butyl acetate [28]. At the reaction temperature lower than 100 °C, both reactants and products are in the form of liquid phase. The activity of the catalysts is in the order of SWT-30 > SWT-20 > SWT-10 > SW and it is also identical with the sequence of the contact angles for water and bean oil. The surface properties of the catalysts become the main factors which affect the conversion. When the reaction temperature increased

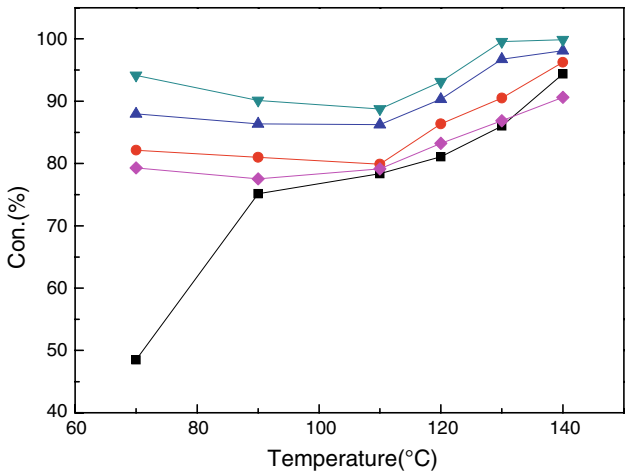

Fig. 7 Effect of the reaction temperature on the conversion of *n*-butanol with different Teflon loadings SW (■), SWT-10 (●), SWT-20 (▲), SWT-30 (▼), SWT-40 (□) Reaction Conditions: WHSV = 1.62 h^{-1}, Catalyst charge = 0.50 g, Acetic acid: *n*-butanol = 1:1, time on stream = 1 h

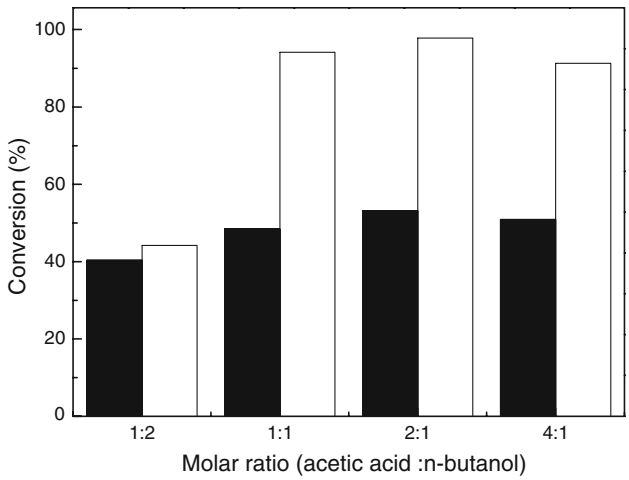

Fig. 8 Effect of molar ratio of reactants (acetic acid: *n*-butanol) on the conversion of *n*-butanol SW (■), SWT-30 (□). Reaction Conditions: T = 70 °C, WHSV = 1.62 h^{-1} Catalyst charge = 0.50 g, time on stream = 1 h

100 °C, H_2O was no longer in liquid phase and is easily removed from the catalyst surface, the effect of surface hydrophobicity on the conversion becomes weak. But the surface lipophobicity was still effective. With the temperature further increased, both H_2O and *n*-butyl acetate were not in liquid phase, the surface hydrophobicity and surface lipophobicity is no longer effective.

Molar ratios of acetic acid to *n*-butanol are varied from 1:2 to 4:1, the catalytic performances of the catalysts are shown in Fig. 8. In any cases, *n*-butyl acetate always is the main product. It is found that the conversion of *n*-butanol over SWT-30 increases markedly with the increase of the mole ratio of acetic acid to *n*-butanol from 1:2 to 1:1, which is due to unequivalence of stoichiometry. But the conversion of *n*-butanol increases slightly with the increase of the mole ratio of acetic acid to *n*-butanol from 1:1 to 2:1. With further increase in mole ratio of acetic acid to *n*-butanol from 2:1 to 4:1, a slight decrease in conversion is observed. In the case of SW, the conversion increases from 40.4 to 53.2% with the molar ratio increase of acetic acid to *n*-butanol from 1:2 to 2:1, the conversion over SW is only one half of that of SWT-30 (97.8% conversion was obtained) in the same reaction condition. Decrease in conversion in higher molar ratio of acid to alcohol (4:1) may be due to the strong adsorption of acetic acid on the catalysts surface. SWT-30 has much more decrease than SW, which may be owing to its smaller surface area. The surface hydrophobicity and lipophobicity of catalysts are effective in the range of molar ratio of acetic acid to *n*-butanol from 1:2 to 4:1,which is shown in Fig. 8.

The effects of WHSV on the conversion of *n*-butanol at 70 °C, 110 °C, and 140 °C are shown in Fig. 9a, b and c, respectively. As shown in Fig. 9a, with the increase of WHSV from 1.08 h^{-1} to 7.2 h^{-1} at 70 °C, the conversion of *n*-butanol over SW and SWT-30 decreased from 72.2% and 99.0% to 40.2% and 83.2%, respectively. The effect of the catalyst surface hydrophobicity and surface lipophobicity at higher WHSV was less effective. This result could be attributed to two factors: (i) short contact time at high WHSV, which is disadvantaged to the conversion, (ii) the products is in liquid phase at 70 °C, which could be easily removed from the catalyst surface due to the surface hydrophobicity and lipophobicity of SWT catalysts at the appropriate WHSV. While the reaction temperature was at 110 °C and 140 °C (Fig. 7b, c), the difference between SW and SWT is no longer evident and an almost isochronous decrease appears in the conversion with the increase of WHSV. This suggests that surface hydrophobicity and lipophobicity were not effective when the products are in gas phase. Significant influence of WHSV on the catalytic activity is presented in Fig. 9, it was crucial that whether the products are removed effectively at appropriate WHSV and low reaction temperature.

The performance of catalytic activity on stream over SW and SWT-30 at 70 °C is also presented in Fig. 10. The conversion of *n*-butanol over SWT-30 only decreases from 94.1% to 89.2% for 3 h, while the conversion of *n*-butanol over SW decreases from 48.5% to 40.9%. As seen from Fig. 10, the conversion of *n*-butanol over SW and SWT-30 had a slightly decrease with stream, which may be due to the solubility of HSiW by water from silica support, the SWT-30 catalyst had a better stability as well as SW. Doping of Teflon did not weaken the interaction between HSiW and the support.

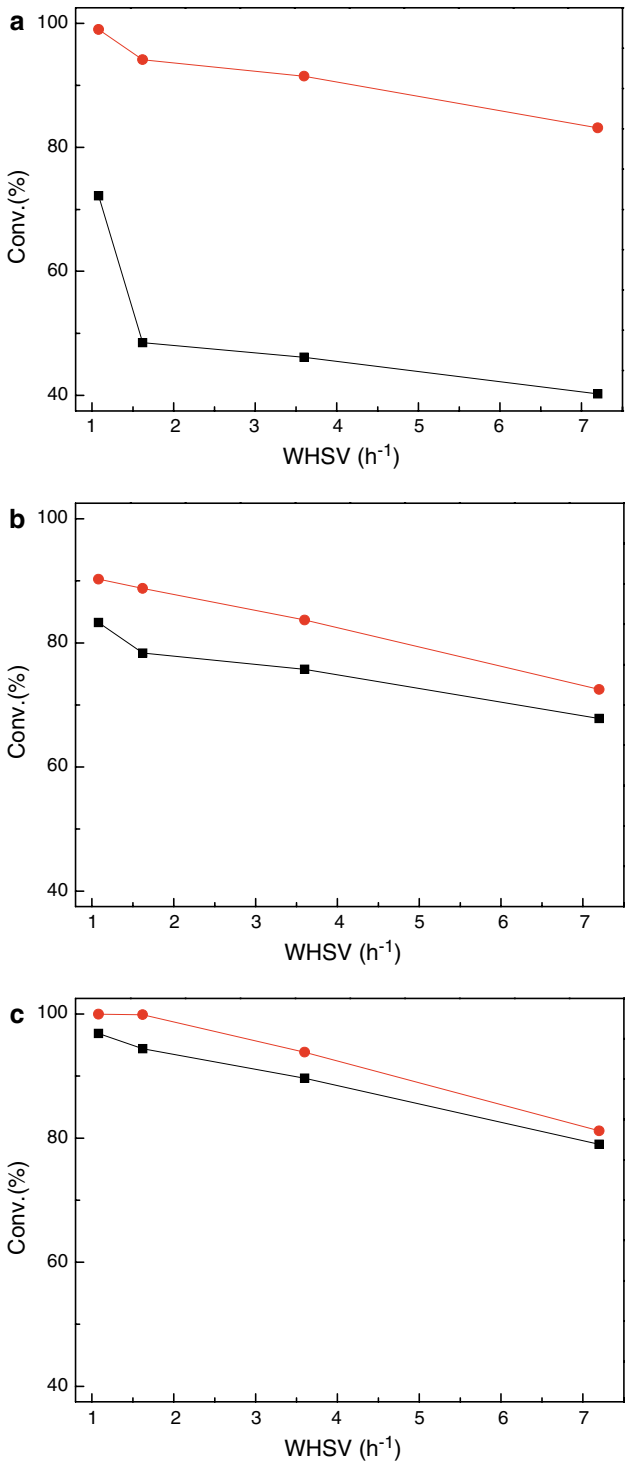

Fig. 9 Effect of WHSV on the conversion at different reaction temperature SW (■), SWT-30 (●) (**a**) 70 °C; (**b**) 110 °C; (**c**) 140 °C. Reaction Conditions: Catalyst charge = 0.50 g Acetic acid: *n*-butanol = 1:1, time on stream = 1 h

HSiW/SiO_2 catalysts modified by Teflon exhibit better catalytic activity than that of HSiW/SiO_2 (SW) in the esterification of acetic acid with *n*-butanol same as HSiW/SiO_2-30%Teflon (SWT-30) in the isobutene oligomerization

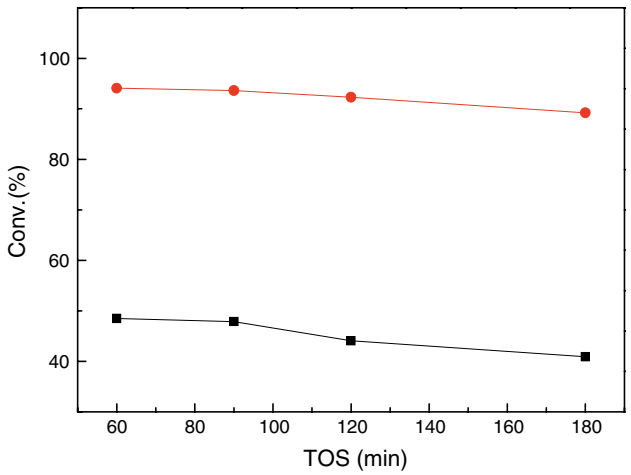

Fig. 10 Effect of reaction time on esterification. Reaction Conditions: T = 70 °C, Catalyst charge = 0.50 g SW (■), SWT-30 (●) acetic acid: *n*-butanol = 1:1, WHSV = 1.62 h^{-1}

reaction [23]. This can be attributed to the surface properties of the catalysts due to Teflon modification. This modification enhances both the surface hydrophobicity and the surface lipophobicity. In the isobutene oligomerization reaction, lipophilic coke precursor moleculars could be easily removed from the surface of catalysts because of the surface-appropriate lipophobicity of catalysts, thus, surface lipophobicity can be effective for controlling the selectivity of the purpose product, decreasing the formation of coke and lengthening the lifetime of the solid acid catalyst. In the esterification of acetic acid with *n*-butanol, the surface lipophobicity accelerates the desorptions of the product *n*-butyl acetate, which can increases the conversion of *n*-butanol and the surface lipophobicity accelerates the desorptions of the product H_2O, which can prevent the poisoning of the H_2O molecular to the catalysts.

4 Conclusions

Teflon modified HSiW/SiO_2-Teflon catalyst such as HSiW/SiO_2-30%Teflon (SWT-30) exhibits better catalytic activity than that of HSiW/SiO_2 (SW) in the esterification of acetic acid with *n*-butanol. This can be attributed to the modification to silica-supported silicotungstic acid by Teflon. This modification enhances both the surface hydrophobicity and the surface lipophobicity of SWT-30. The surface lipophobicity could be effective for removing *n*-butyl acetate more easily and the surface hydrophobicity could be effective to remove H_2O molecular to prevent its poisoning to the catalyst. The desorptions of products could be accelerated, which lead to increase the conversion of *n*-butanol because of the products easier removing from the catalysts surface easier, especially at low reaction temperature and appropriate WHSV.

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