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Effect of acidity and structures of supported tungstophosphoric acid on its catalytic activity and selectivity in liquid phase synthesis of ethylbenzene

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Abstract

Silica-supported tungstophosphoric acid (SPW) with Keggin structure in liquid phase alkylation of benzene with ethylene and transalkylation of benzene with diethylbenzene was studied. The structures of SPW were characterized by nitrogen adsorption, FT-IR, and XRD; and the acidic properties characterized by pyridine adsorption FT-IR, NH_3-TPD, and Hamett indicators. Tungstophosphoric acid (PW) maintains its Keggin structure in SPW. PW is finely dispersed on the support as the loading less than 30 wt.%. SPW has both Brönsted (B) and Lewis (L) acid sites with B acid sites predominantly. The L acid sites are derived from the chemical interaction between the protons of PW and the hydroxyl groups of silica. The amount and acid strength of surface acid sites of SPW increase as the loading increased. Liquid phase alkylation indicated that catalytic activity of SPW is associated with amount and strength of surface acid sites and dispersivity of PW. Highly dispersed PW is much more effective than bulky solid ones. Liquid phase transalkylation showed that catalytic activity of SPW is determined by amount and strength of surface acid sites. SPW with large amount and strong acid strength of surface acid sites as well as relatively large specific surface areas has high activity in both alkylation and transalkylation. SPW is very active and selective in both alkylation and transalkylation.

Keywords: Supported tungstophosphoric acid; Benzene; Ethylene; Ethylbenzene; Alkylation; Transalkylation

1. Introduction

As the most important alkylbenzene, ethylbenzene is predominantly synthesized by the alkylation of benzene with ethylene using acidic catalysts [1]. In recent years, there has been a strong increase in production of ethylbenzene in China, and this trend will be maintained in the future [2].

In conventional, the acidic catalyst is aluminum chloride, which is very active in both the alkylation of benzene with ethylene and the transalkylation of benzene with polyethylbenzene (produced in alkylation, mainly diethylbenzene), but this catalyst is also very corrosive and producing large amount of wastes in processing. To overcome these shortages, solid acid catalysts have been developed, and several acidic zeolite catalysts already been used in industry [1–3].

Comparing with aluminum chloride, the advantages of zeolite catalysts are that they are environmentally benign and non-corrosive, and consume less raw materials and energy. However, the reaction temperature (T) and pressure (P) are much higher, and much more residue is produced [4]. There is an impetus to develop new solid acids with the advantages of both aluminum chloride and acidic zeolite catalysts.

For their high catalytic activity, environmental benignity and non-corrosive nature, solid heteropoly acids have been used in a variety of catalytic reactions in recent years [5–15]. For the alkylation of benzene with alkenes, many workers have used solid heteropoly acids as catalysts in either bulky or supported forms [6–8,10,16,17]. In the case of the alkylation of benzene with ethylene, silica-supported tungstophosphoric acid has been used as catalyst under gas phase conditions [18]. For the liquid phase synthesis of ethylbenzene, supported silicotungstic acid has been used as catalyst [19]. Of all the heteropoly acids, PW has the strongest acid strength and the highest thermal stability; its acid strength is much stronger than that of most inorganic liquid strong acids and acidic zeolites [6,20]. It has been reported that SPW is much more active and selective than zeolite catalysts in the alkylation of benzene with propylene and 1-dodecene [16,17].

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As solid acid catalyst, bulky solid PW has low efficiency due to its very low specific surface area and rapid deactivation. Furthermore, bulky solid PW is difficult to use in a fixed bed reactor because of its very small (micron scale) particle sizes. To improve its applicability, PW is usually supported on acidic or neutral substances with high specific surface area, such as silica, active carbon or acidic ion-exchange resins. Silica is the most often used support [21]. In this paper we reported for the first time of SPW as catalyst in liquid phase alkylation of benzene with ethylene and transalkylation of benzene with diethylbenzene. The structures and acidic properties of SPWs were characterized. Catalytic activity and selectivity of SPWs in both alkylation and transalkylation have been associated with their acidic properties and structures.

2. Experimental

2.1. Materials

PW with analytical purity was purchased from Beijing Xinhua Chemical Reagent Plant, China, and used without further purification. Mesoporous spherical silica gel was procured from Qingdao Haiyang Chemical Company Limited, China, and washed with nitric acid and baked at 450 °C before being used as support, and the size of silica gel is 18–26 in. mesh. Benzene with analytical purity was obtained from Beijing Chemical Plant, China, and dried with 4 Å molecular sieves to give water content less than 40 μg/g. Ethylene in polymerization grade with purity higher than 99 wt.% was obtained from Yanshan Petrochemical Corporation, China. Diethylbenzene containing 89.9 wt.% diethylbenzene and 9.0 wt.% 2-butylbenzene was fractionated from industrial polyethylbenzene, which was produced by the BASF-Yangzi Styrene Series Corporation, China. Diethylbenzene was also dried with 4 Å molecular sieves to a water content of 63 μg/g. Water was deionized water. Nitrogen with purity higher than 99.999% was used.

SPW was prepared by incipient impregnation. Firstly, the bulky solid PW was dissolved in deionized water, and then silica gel was added to the solution with stirring and immersed overnight in a moisture-saturated atmosphere. The catalyst was subsequently dried in an oven to remove free water at 70 °C, and then the temperature was raised to 110 °C and maintained for more than 3 h. Finally, the prepared catalyst was stored in a desiccator. Before reaction, all SPWs and PW were pretreated at 220 °C in air for 2 h to activate.

Zeolite beta and Y zeolite catalysts both containing 70 wt.% of zeolites are industrial catalysts used in ethylbenzene production, which were provided by Professor Fengmei Zhang, Research Institute of Petroleum Processing, SINOPEC. These catalysts were crashed and sieved to the size of 18–26 in. mesh and baked in the air at 550 °C for 2 h to activate before being used.

2.2. Characterization

The BET specific surface areas and pore structures of SPWs were characterized by static nitrogen physical adsorption in a Micromeritics ASAP2400 instrument. The Keggin structure of PW was confirmed by Fourier transform infrared spectra (FT-IR) in a NICOLET Magna-IP750 FT-IR spectrometer. The crystal phase of PW was characterized by using a SIEMENS D5005D X ray diffraction (XRD) diffract meter with Cu Kα radiation. The type of acid sites of the catalyst was determined by pyridine adsorption FT-IR measurements by using a Bio-Rad FTS3000 FT-IR spectrometer, ratio of peak area of absorption band at 1540 to that of 1450 cm^{-1} being used as ratio of B acid sites to L acid sites (R_{BL}). R_{BL} is derived from the peak areas after desorption of pyridine at 350 °C (strong acid sites). Hammett indicators were used to determine the strength of acid sites. Temperature programmed desorption of ammonia (NH_3-TPD) was used to determine the total amount of surface acid sites with a Dupont2100 thermal analytical instrument.

2.3. Catalytic reactions and analyzes

Liquid phase alkylation of benzene with ethylene was carried out in a 300 cm^3 stirred autoclave with controlling systems of temperature, pressure and flow rate of ethylene. After adding benzene and activated catalyst, the autoclave was purged with nitrogen and heated to a given temperature, feed in ethylene to start the reaction until the molar ratio of benzene to ethylene reached a set value.

Liquid phase transalkylation of benzene with diethylbenzene were conducted in a tubular micro fixed bed reactor system. After catalyst was loaded and activated, the reaction system was purged with nitrogen and pressurized at the set temperature, and then the mixture of benzene and diethylbenzene was added to begin transalkylation.

Integration of alkylation and transalkylation was also carried out in the same autoclave.

Liquid samples were analyzed using a HP-5890 gas chromatograph with an OV-1 capillary column and flame ionization detector; the composition was calculated from the adjusted peak areas. The composition of product mixture was determined using a HP6890GC/HP5973MS system. Selectivity to ethylbenzene (S_{EB}) was based on the consumption of ethylene in alkylation and of diethylbenzene in transalkylation, respectively. Under the conditions of transalkylation, 2-butylbenzene was inert.

3. Results and discussion

3.1. Structures of SPW

The BET specific surface areas (S_{BET}), pore volumes (V_P) and average pore diameters (d_P) of silica gel, SPWs, PW, zeolite beta and Y zeolite are listed in Table 1.

Table 1
Structural data for silica gel, SPWs, PW, zeolite beta and Y zeolite

	S_{BET} (m^2/g)	V_P (cm^3/g)	d_P (nm)
Silica gel	432	0.98	9.0
10 wt.% SPW	379	0.86	9.0
20 wt.% SPW	326	0.73	9.0
30 wt.% SPW	287	0.62	8.7
50 wt.% SPW	208	0.41	7.8
75 wt.% SPW	100	0.12	4.7
PW	4.6	0.01	8.0
70 wt.% zeolite beta	378	0.54	4.24
70 wt.% Y zeolite	500	0.43	2.58

As shown in Table 1 the S_{BET} of silica gel is as high as 432 m^2/g, and the average pore size is 9.0 nm. In contrast, bulky PW is a non-porous solid, and the S_{BET} is very low, only 4.6 m^2/g. However, the S_{BET}s of all SPW are much higher than that of PW, even though the loading is as high as 75 wt.%. For SPW with different loading, the S_{BET}, V_P and d_P all decrease as the loading increased. The dramatic decreases of S_{BET}, V_P and d_P of the 75 wt.% SPW in comparison with that of 50 wt.% SPW means that much of its pores are filled with solid PW.

As shown in Fig. 1, the XRD spectrum indicates that silica gel is amorphous. As long as the loading of PW is lower than 30 wt.%, PW is finely dispersed on the pore surface of silica gel, and no crystalline phase of PW exists. As the loading reaches 30 wt.%, three weak diffraction peaks appear at 10.5°, 25.5°, and 34° in 2θ. This means that large crystals of PW begin to form in the pores of silica gel, and the dispersion becomes worse. With the increase of loading, the diffraction peaks of the crystalline phase become stronger and stronger. For bulky solid PW, there are a number of diffraction peaks ranging from 5° to 40° in 2θ indicating PW has several hydrates [15]. It was reported that for a silica support with specific surface area in the range of 200–300 m^2/g, a crystalline phase of PW began to form when the loading reached 20 wt.%. When MCM-41 was used as support, however, PW could be finely dispersed on the pore surface even though the loading reached a value as high as 50 wt.% [22]. This suggests that using a support with a high specific surface area can allow an increase in the loading of PW without any adverse effects on the dispersion of PW.

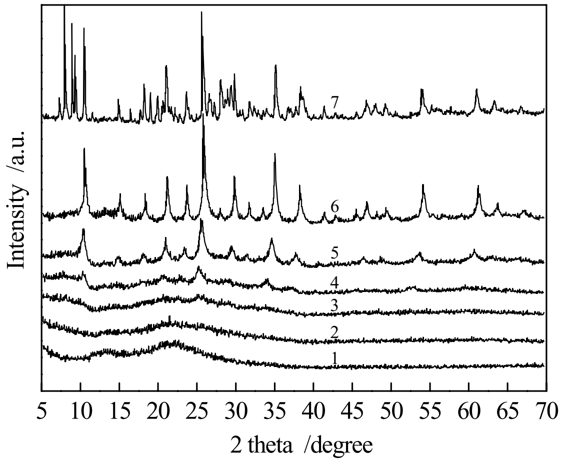

Fig. 1. XRD spectra of silica gel, SPWs and PW: (1) silica gel; (2) 10 wt.% SPW; (3) 20 wt.% SPW; (4) 30 wt.% SPW; (5) 50 wt.% SPW; (6) 75 wt.% SPW; (7) PW.

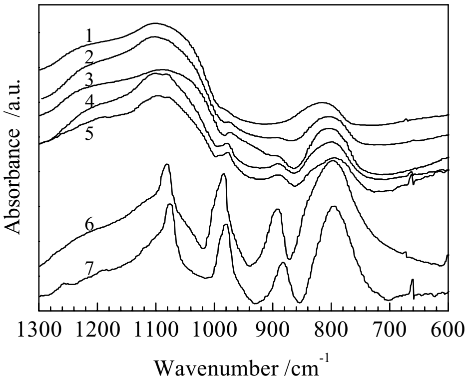

Fig. 2. FT-IR spectra of silica gel, SPWs and PW: (1) silica gel; (2) 10 wt.% SPW; (3) 20 wt.% SPW; (4) 30 wt.% SPW; (5) 50 wt.% SPW; (6) 75 wt.% SPW; (7) PW.

Characteristic FT-IR absorption bands in the range of 600–1300 cm^{-1} are used to confirm the presence of the Keggin structure [5]. The FT-IR spectra of silica gel, SPWs and PW are shown in Fig. 2. For PW, there are four absorption bands at 800, 880–900, 976–995 and 1080 cm^{-1}, characterizing of the Keggin structure. In the case of the SPWs, because of the overlap with two broad absorption bands from the support near 800–820 and 1000–1100 cm^{-1}, the absorption bands at 800 and 1080 cm^{-1}, respectively, cannot be clearly distinguished especially at low loadings of PW. Although the absorption bands at 880–900 and 976–995 cm^{-1} are weak, they can easily be distinguished. It is evident that PW maintains its Keggin structure after being supported.

3.2. Acidic properties of SPW

The data of acidic properties of SPWs, PW, zeolite beta and Y zeolite are listed in Table 2. For all SPWs, there are two types of acid sites, B acid sites and L acid sites and B acid sites are predominant. While for PW, it only has B acid sites. The support is neutral and 10 wt.% SPW only demonstrates weak acidity. While 20 wt.% SPW exhibits strong acidity as that of most zeolites. As the loading larger than 30 wt.%, SPWs demonstrate super acidity. Among all these solid acids PW is the strongest. The total amounts of surface acid sites in SPWs increase with the loading almost linearly except that of the 10 wt.% SPW. As the loading is higher than 30 wt.%, there are more surface acid sites in SPWs than in PW.

As shown in Fig. 3, the FT-IR spectra indicated that there are many hydroxyl groups on the surface of silica gel, and the amounts of hydroxyl groups are markedly decreased as the loading of PW increased. In fact, there exists a chemical

Table 2
The data of acid properties of SPWs, PW, zeolite beta and Y zeolite

Solid acid	Type of acid sites	H_0	A_A (mmol H^+ g^{-1})	R_{BL}
10 wt.% SPW	B, L	0.8 to −3.2	0.02	2.00
20 wt.% SPW	B, L	−8.2	0.23	2.90
30 wt.% SPW	B, L	−11.99 to −12.7	0.36	3.83
50 wt.% SPW	B, L	−12.7 to −13.16	0.66	7.43
75 wt.% SPW	B, L	−13.16	0.75	10.0
PW	B	−13.16	0.39	–
70 wt.% zeolite beta	B, L	−8.2	0.71	0.22
70 wt.% Y zeolite	B, L	−8.2	0.75	1.74

interaction between the protons in PW and the hydroxyl groups on silica gel which lead to form $\equiv SiOH_2^+$ especially at low loading of PW, the strength of B acid sites become weak and non-uniform, only a fraction of the B acid sites can maintain their strength [23]. For its low loading of PW and high dispersion and chemical interaction with the hydroxyl groups, the acid strength of 10 wt.% SPW is very weak and cannot adsorption enough ammonia in comparison with its theoretical amount of acid sites. The L acid sites in SPWs can only be the result of chemical interaction between PW and hydroxyl groups on silica gel. The dehydration of $\equiv SiOH_2^+$ will form the Lewis acid site $\equiv Si^+$.

3.3. Liquid phase alkylation

Liquid phase alkylation of benzene with ethylene was carried out under the following conditions: stirrer speed 10 s^{-1}, 100.0 g benzene, 2.86 g catalyst, $P = 1.6$ MPa, $T = 180\,°C$, reaction time 1 h. The experimental results are listed in Table 3. The catalytic activity r_E was calculated from the total consumption of ethylene in alkylation and in the unit of kilogram ethylene (E) per kilogram catalysts (cat) per hour (h), kg E kg_{cat}^{-1} h^{-1}.

Table 3
Alkylation activity and selectivity of SPWs and PW

Catalyst	r_E (kg E kg_{cat}^{-1} h^{-1})	S_{EB} (%)	S_E (%)
10 wt.% SPW	1.11	73.2	99.3
20 wt.% SPW	2.28	71.9	99.4
30 wt.% SPW	2.48	71.2	99.4
50 wt.% SPW	3.16	70.7	99.5
75 wt.% SPW	1.68	69.9	99.4
PW	1.05	72.2	99.2

S_{EB} and S_E are based on the molar ratio of benzene to ethylene (n_B/n_E) of 4.3

For SPW, the catalytic activity increases as the loading increased, reaches its maximum at the loading of 50 wt.%, and then decreases, and bulky solid PW has the lowest activity. Although 75 wt.% SPW has the largest amount of acid sites and strongest acid strength, its activity is much lower than that of 50 wt.% SPW. This may be explained from two aspects. Firstly, the determined amount of surface acid sites by NH_3-TPD may include part internal acid sites. The small polar molecules such as ammonia can penetrate into the inner of bulky solid heteropoly acids for their pseudo liquid phase phenomena [5]. This is also testified by the pyridine adsorption FT-IR that the characteristic peak areas of B acid sites and L acid sites in 75 wt.% SPW is less than that in 50 wt.% SPW. Secondly, as mentioned above, for 75 wt.% SPW, much of its pores are filled with solid PW, reactants have much less opportunity to react on the surface acid sites. Although bulky solid PW is the strongest solid acid used and has much more surface acid sites in comparison with SPWs with loading less than 30 wt.%, for the same reason mentioned above and its very low specific surface areas, it has the lowest activity. It is evident that highly dispersed PW is much effective in liquid phase alkylation than bulky solid ones. Based on the same mass of PW, the 10 wt.% SPW and 20 wt.% SPW have the same activity and are higher than 10 times of that of bulky sold PW. With the increase of loading and the poor dispersion, this relative activity decreases step by step, but the absolute activity increases until the loading higher than 50 wt.%.

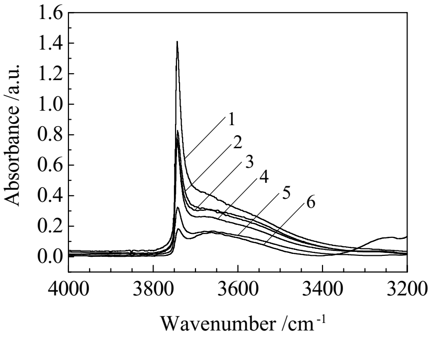

Fig. 3. Hydroxyl groups' FT-IR spectra of silica gel, SPWs and PW: (1) silica gel; (2) 10 wt.% SPW; (3) 20 wt.% SPW; (4) 30 wt.% SPW; (5) 50 wt.% SPW; (6) 75 wt.% SPW; (7) PW.

As shown in Table 4, under the same reaction conditions, 50 wt.% SPW is much active than zeolite beta and Y zeolite;

Table 4
Alkylation activity and selectivity of SPW, zeolite beta and Y zeolite

Catalyst	r_E (kg E kg_{cat}^{-1} h^{-1})	S_{EB} (%)	S_E (%)
50 wt.% SPW	3.16	65.2	99.4
70 wt.% zeolite beta	2.56	80.2	99.7
70 wt.% Y zeolite	2.53	58.2	97.9

S_{EB} and S_E are based on $n_B/n_E = 3.0$.

the zeolite catalysts are only as active as that of 30 wt.% SPW. These results are easy to explain according to the acid properties of the catalysts. Both zeolite beta and Y zeolite have large amounts of surface acid sites, but the acidity of which are only strong as that of 20 wt.% SPW. 50 wt.% SPW also has large amount of surface acid sites as well as much strong acid strength and is the most active catalyst. It is also evident that both B acid sites and L acid sites are active acid sites according to the great difference of R_{BL} in zeolite beta and Y zeolite.

Since the alkylation of benzene with ethylene is a consecutive reaction, ethylbenzene can react further with ethylene to form polyethylbenzenes including diethylbenzene and triethylbenzene, etc. These reactions will lower the selectivity to ethylbenzene of alkylation. In considering that polyethylbenzene can be transalkylated with benzene to produce ethylbenzene further, the alkylation selectivity of ethylation (S_{E}) is more important in practice. That is the molar ratio of ethylene to produce ethylbenzenes including monoethylbenzene and polyethylbenzenes to the total consumed in alkylation. The selectivity to ethylbenzene and the selectivity of ethylation are also listed in Tables 3 and 4.

As the loading increased, S_{EB} is almost at the same level, and decreases very slowly. These largely because of that the SPWs are large porous material and the pores are only partly narrowed as the loading increased. However, this effect has little influence on the selectivity for the pores are large enough to let molecules transfer freely. By contrary, bulky solid PW has no pores, reactants are easy to transfer to the surface acid sites, and products are easy to transfer to the liquid phase, hence S_{EB} is a little better than SPWs. As for zeolite beta, which has micro pores fitting to the size of molecule of benzene and ethylbenzene, that has the property of shape selectivity, hence has the highest S_{EB}. Y zeolite also has micro-pores, but the relatively large pores and the super cages structures of pores lead to the lowest selectivity.

The S_{E}s for SPWs and PW are higher than 99% and has little differences. This means that the amounts and acid strength of surface acid sites have little effect on the selectivity of ethylation. These S_{E}s are comparable with that of zeolite beta, and high than that of Y zeolite. The lower selectivity of Y zeolite is also due to its super cages that lead to more side reactions of molecular cracking (which form toluene and methyl ethylbenzene, etc.) and decreases the selectivity.

3.4. Liquid phase transalkylation

Liquid phase transalkylation was conducted under such conditions: $T = 200\,^{\circ}\mathrm{C}$, $P = 2.1\,\mathrm{MPa}$, molar ratio of benzene to diethylbenzene 10, total weight hourly space velocity $5\,\mathrm{h}^{-1}$, and water content in the reactants $38\,\mu\mathrm{g/g}$. The results are shown in Figs. 4 and 5.

The initial conversion of diethylbenzene (X_{D}) increases rapidly from 38.3% to 90.3% as the loading of PW increased from 10 to 75 wt.%. Furthermore, as the loading of PW is increased, the deactivation rate of the catalyst is also markedly reduced. For 75 wt.% SPW, the conversion of diethylbenzene is 78.6% after 6 h, which is 87.0% of the initial conversion; while for the 10 wt.% SPW, after the same time the conversion is 12.5%, only 33% of the initial conversion.

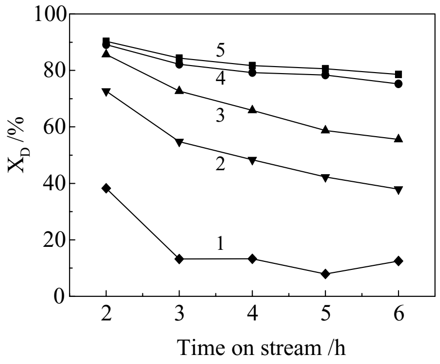

Fig. 4. Effect of the loading of PW on conversion of diethylbenzene: (1) 10 wt.% SPW; (2) 20 wt.% SPW; (3) 30 wt.% SPW; (4) 50 wt.% SPW; (5) 75 wt.% SPW.

Fig. 5 indicates that the initial S_{EB}s for all SPWs are higher than 99% and has little differences. As the time on stream increased, the S_{EB} decreases as the loading decreased. This trend is in accordance with that of the conversion of diethylbenzene. The great differences in diethylbenzene conversion with little variation in ethylbenzene selectivity indicate that there are very few byproducts in the transalkylation reaction. As for the 10 wt% SPW, even very few byproducts have much important effect on its S_{EB} for its very low conversion of diethylbenzene.

The activity of 75 wt.% SPW is slightly higher than that of 50 wt.% SPW. This suggests that the activity of SPW in liquid phase transalkylation is mainly correlated with the amounts and strength of surface acid sites and hardly affected by the specific surface areas. Transalkylation conducted in autoclave under the same temperature and molar ratio of benzene to diethylbenzene indicated that 50 wt.% SPW ($X_{\mathrm{D}} = 79.7\%$) is more active than bulky solid PW ($X_{\mathrm{D}} = 50.1\%$) while zeolite beta has no activity. The loading of

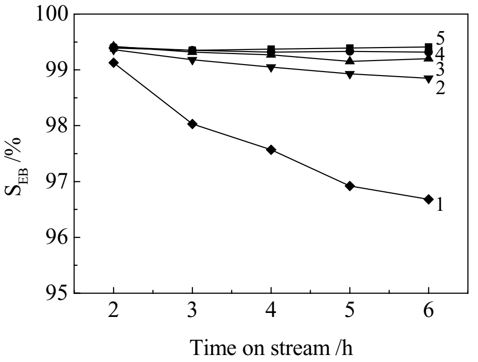

Fig. 5. Effect of the loading of PW on selectivity to ethylbenzene: (1) 10 wt.% SPW; (2) 20 wt.% SPW; (3) 30 wt.% SPW; (4) 50 wt.% SPW; (5) 75 wt.% SPW.

SPW should be higher than 30 wt.% to obtain enough activity and selectivity.

3.5. Integration of alkylation and transalkylation

The selectivity to ethylbenzene in alkylation can be further improved by conducting transalkylation immediately after alkylation without separating of products. At 180 °C and stirrer speed of $10\,\mathrm{s}^{-1}$, 117.2 g benzene and 4.83 g catalyst were added and ethylene was feed in to $n_\mathrm{B}/n_\mathrm{E} = 3$ to carry out alkylation for 2 h. After that, 23.41 g diethylbenzene was added to continue transalkylation for another 2 h. S_EB is as high as 95.8%, much higher than that of 66.1% in alkylation only. If diethylbenzene was added with benzene and catalyst simultaneously and carried out alkylation and transalkylation for 4 h, S_EB is 66.8% only. If transalkylation was conducted for 2 h and then feed in ethylene to alkylate another 2 h, S_EB is 80.1%. Taking this advantage of high selectivity to ethylbenzene, alkylation and transalkylation could be integrated in one reactor without separating operation as that in conventional aluminum chloride catalyst system.

3.6. Stability of SPW catalyst in liquid phase alkylation

Liquid phase alkylation was also conducted in the same fixed bed reactor. In considering that even though $n_\mathrm{B}/n_\mathrm{E}$ of the feed is as low as 4–5, this value in alkylation zone of the reactor is higher than 20 in general in industry. This is easy to realize by multistage feeding or recycling part of the mixture of alkylation. Hence, the liquid phase alkylation was carried out under the conditions as follow: 30 wt.% SPW used as catalyst, $T = 180\,^\circ\mathrm{C}$, $P = 2.6\,\mathrm{MPa}$, $n_\mathrm{B}/n_\mathrm{E} = 14$, weight hourly space velocity of benzene is $2.0\,\mathrm{h}^{-1}$. The alkylation was carried out for 336 h and has no signs of deactivation of the catalyst. In the whole run, the conversion of ethylene is 100%, S_EB is higher than 88% and S_E is higher than 99% and maintained. These results indicate that SPW is relatively stable in liquid phase alkylation.

4. Conclusions

Taking the advantages of the mesoporous structure and high specific surface area of silica gel, PW can be finely dispersed on the support as long as the loading is lower than 30 wt.%. SPW has both B and L acid sites whereas bulky solid PW only has strong B acid sites. It is suggested that a physicochemical interaction exists between supported PW and the hydroxyl groups on silica gel. The interaction leads to the formation of L acid sites and weakens the acidity of strong B acid sites such that only part of them maintain their original acid strengths. The amount of strong B acid sites and the acid strength increase as the loading of PW increased.

Under liquid phase conditions, in both alkylation and transalkylation, all SPWs are very active and selective. Their catalytic activities in alkylation are associated with the amount and strength of surface acid sites as well as the dispersivity of PW. While in transalkylation, the activities are mainly correlated with the amount and strength of surface acid sites. SPW with large amount and strong acid strength of surface acid sites as well as relatively large specific surface areas is the most active catalyst in both alkylation and transalkylation. The acid properties and structures have little influence on selectivity. For alkylation, the loading of PW should be higher than 20 wt.% for high catalytic activity. As for transalkylation, a loading higher than 30 wt.% is more preferable. In comparison with zeolite catalysts, reaction temperature and pressure in liquid phase alkylation and transalkylation could be much lower by using SPW.

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