Study of the reaction of tetramethyltin with Hβ zeolite

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Abstract

The grafting reaction of $SnMe_4$ on the surface of Hβ zeolite (Si/Al = 25.0) was studied under high vacuum conditions. The chemical compositions and structure of the resulting solid were characterized by in situ FTIR, ICP, XRD, XPS, ^{13}C and ^{119}Sn MAS NMR, UV–Vis DRS, gas phase chromatogram (GC), chemical analyses, temperature programmed decomposition (TPD), temperature programmed reduction (TPR), and N_2 adsorption at low temperature. The results showed that $SnMe_4$ reacts with Hβ zeolite quantitatively at temperature as low as 183 K and the reaction occurred on the surface of the zeolite without destroying the framework of zeolite. The BET surface area and the pore volume of the zeolite decreased and the surface properties changed, however the microporous structure was retained upon the reaction and post treatment.
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1. Introduction

Zeolites have extensive uses as adsorbents, catalysts and supports of catalysts in the chemical industry due to their special and modifiable structures and properties. The post-synthesis modification of zeolites has been extensively studied and numerous methods, such as traditional ion-exchange, pore size engineering [1–3], coordination chemistry of zeolites [4], and ship-in-bottle [5–9], etc., were developed for this purpose. Lately, a novel strategy for the modification of the solid surface, named as surface organometallic chemistry (SOMC), was reported to be also commendably applied for the surface modification of zeolites [10]. SOMC modification is based on grafting reactions between organometallic complexes and the surface hydroxyl groups to obtain surface complexes with well-defined structure and specific chemistry composition [11,12]. The advantages in using SOMC for the modification of zeolite are: (i) surface grafting occurs easily and stoichiometrically owing to high acidity and a certain amount of hydroxyls; (ii) the internal surface or external surface of zeolite can be modified selectively by well-chosen organometallic complexes; (iii) the surface compound can be introduced to a specific cavity of zeolite according to the size of the complex molecular and the selectivity of zeolite pores.

β zeolite is an effective catalyst for various reactions such as catalytic cracking and isomerization of hydrocarbons [13], disproportionation of methylbenzenes [14], isomerization of xylenes [15], the conversion of aromatics and hydrocarbons [16]. β zeolite presents a three-dimensional structure of 12-membered ring channels with pore diameters of 0.62 nm. It allows larger molecules to enter into its cavity, which is very convenient for its modification by SOMC. In the present study, the grafting reaction of tetramethyltin on the surface of Hβ zeolite and the resulting surface species were studied. This study can provide useful information leading

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to detailed knowledge on the elementary steps of catalyzed reactions on zeolite and the reactivities of zeolite and is related to our interest in the preparation of a new generation of well-defined surface bound catalysts.

2. Experimental

2.1. Materials

Hβ zeolite used for these experiments was purchased from Shanghai Oil Chemical Industry Company and had a Si/Al ratio equal to 25.0. Tetramethyltin (SnMe₄, 99.5%) was purchased from Aldrich and dehydrated before use.

2.2. Grafting reaction

The grafting reaction of tetramethyltin on Hβ zeolite was performed in a Schlenk tube equipment connected to a vacuum line. Hβ zeolite was treated under dynamic vacuum (10^{-3} Pa) at 673 K for 3 h to remove adsorbed water. After cooling to room temperature, a large excess of liquid tetramethyltin was introduced to the schlenk tube with a syringe via a septum. A trap of liquid nitrogen was used to condense the vapour of tetramethyltin. The trap was removed and then the reactor was heated to the desired temperature. The reactor was kept at the temperature 323 K for 5 h to ensure a complete reaction. The unreacted SnMe₄ was removed by a treatment under dynamic vacuum (10^{-3} Pa) for 3 h at the reaction temperature and the solid was transferred under pure nitrogen into small ampoules. The reaction was also monitored by infrared spectroscopy. 20–30 mg of Hβ zeolite was pressed as a disk (diameter 18 mm) and loaded in a self-made IR cell with CaF₂ windows. The same treatments as above were performed and the IR spectra during the treatments were recorded on a Nicolet Nexus 670 FTIR Spectrometer.

2.3. Characterization

The evolved gases were analyzed by precision pressure gauge, HP-5973 GC–MS and Agilent 6890 GC. The solid products were characterized in detail by physical and spectral techniques. The chemical compositions were analyzed by Vario EL III elemental analyzer (EA), inductively coupled plasma spectroscopy (ICP) and Philips PW1710 power diffractometer. The BET surface area was detected by N₂ adsorption with OMNISORP 100CX gas adsorb analyzer. Experiments of temperature programmed decomposition (TPD) and temperature programmed reduction (TPR) were performed on Autochem 2910 automatic catalyst Characterization System equipped with a Omnistar GSD30103 Mass Spectrograph. The loading amount of sample was

0.2000 g. the flow rate of the supporting gas (He for TPD and 10% H₂/Ar for TPR) was 30 mL min⁻¹ and the heating rate is 5 K min⁻¹. XPS spectra were recorded on PHI-5300/ESCA Spectrometer (Al/Mg dianode, 0.8 eV energy resolution, 45° angle resolution and 80 kcps sensitivity, energy 3.0 kV, current 25 mA,). Powder samples were mounted on sample stubs with conductive carbon tape. The binding energies for each peak were referenced to the C 1s peak at 284.6 eV. MAS NMR spectra were recorded on a Bruker AV300 spectrometer equipped with a standard 4 mm multinuclear probe head with a frequency of 111.94 MHz and a spinning rate at 10.92 Hz for ¹¹⁹Sn, a frequency of 75.47 MHz and a spinning rate at 10.33 Hz for ¹³C CP-MAS NMR. TMS was used as external standard.

3. Results and discussion

3.1. Grafting reaction of SnMe₄ on Hβ zeolite

The FTIR spectra of Hβ zeolite in the region of OH groups were shown in Fig. 1. After treated under vacuum at 673 K for 3 h, zeolite showed three vibration adsorptions at 3742, 3607 and 3665 cm⁻¹, which can be assigned to terminal silanol OH groups, bridging OH (Si–(OH)–Al groups having strong Brönsted acidity [17–21]) and OH connected to extra framework Al [18,19], respectively. When SnMe₄ contacted with the treated zeolite at 323 K for 5 h, both infrared spectroscopy and gas phase chromatography analysis revealed that methane was the only gaseous product. The intensities of the three hydroxyl vibration bands decreased signicantly. In the meantime two characteristic bands, which related to the vibration absorption band of methyl (C–H), appeared in the range of 3000–2900 cm⁻¹ along with the evolvement of methane (Fig. 1(b)). After the reaction, the IR of the resulting product treated under vacuum at the
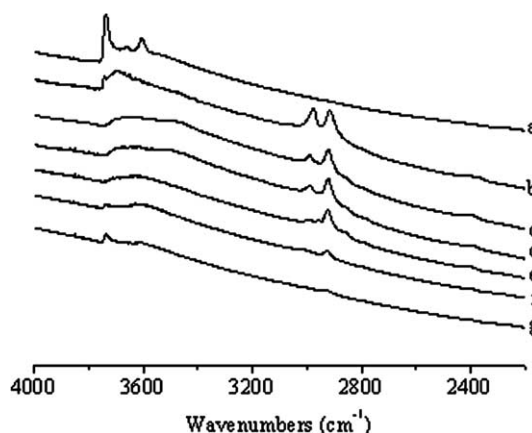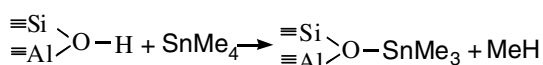

Fig. 1. IR spectra of Hβ before and after reaction with SnMe₄. (a) Hβ dehydroxylated at 673 K; (b) Hβ after reaction with SnMe₄ at 323 K for 5 h; (c), (b) at 323 K for 3 h under vacuum; (d), (c) at 473 K; (e), (d) at 523 K; (f) (e) at 573 K; (g) (f) at 623 K.

reaction temperature for 3 h showed no hydroxyl group band and decreased bands between 3000 and 2900 cm^{-1} (Fig. 1(c)), suggesting a complete reaction between surface hydroxyls and SnMe$_4$ and the removal of the unreacted SnMe$_4$.

In order to accurately analyze the reaction products, 500 mg of Hβ zeolite was used to redo the experiment under the same conditions. After reacting for 24 h, 0.53 mmol of methane was detected by GC analysis. EA and ICP analysis on the resulting solid product found 3.58 wt% of C and 12.22 wt% of tin, i.e., the ratio of carbon to tin on the solid was 2.91. The above results indicated that the reaction of tetramethyltin with the hydroxyl groups on Hβ zeolite occurred and a surface methyltin complex and methane were formed.

$$\begin{matrix} \equiv Si \\ \equiv Al \end{matrix} \!\!> \!\! O-H + SnMe_4 \longrightarrow \begin{matrix} \equiv Si \\ \equiv Al \end{matrix} \!\!> \!\! O-SnMe_3 + MeH$$

The formation of MeH can be detected by GC at a reaction temperature as low as 183 K. This temperature is lower than those reported for the grafting reaction of SnMe$_4$ on silica (298 K)[22], MCM-41(343 K) [23], and HY zeolite (193 K) [24]. It suggested that the acidity of the surface hydroxyl groups and pore structure of the solid have important effects on the grafting reaction of methyltin molecule. However in terms of the reaction products these reactions are quite similar.

Infrared spectroscopy (Fig. 1) also showed that the trimethyl tin groups grafted on the surface of Hβ zeolite were thermally stable under dynamic vacuum at temperatures below 473 K, as confirmed by no change of the IR absorption band of C–H below this temperature. The C–H absorption bands gradually decreased in its intensity and finally disappeared when heating the samples from 473 to 623 K. The thermal decomposition of the methyl tin groups will be further discussed later in this paper.

3.2. Characterizations of the grafted species

3.2.1. IR spectroscopy of pyridine adsorption

The grafting –SnMe$_3$ to acid hydroxyls of zeolite were supported by IR study of adsorption pyridine on the modified and unmodified sample. Pyridine, a basic molecule which could combine with both the Brönsted acid sites and Lewis acid sites of the solid surface, was commonly used as a probe molecule to characterize the acidity of a solid catalyst. A pyridine molecule coordinated on a Brönsted acid site can be simply distinguished from that coordinated on a Lewis acid site by IR since the bands at 1545 and 1490 cm^{-1} were corresponding to the C–C stretching vibrations of the pyridine adsorbed on Brönsted acid sites, Brönsted + Lewis acid sites respectively, while the band at 1450 cm^{-1} was related to adsorption of pyridine molecules on Lewis acid sites
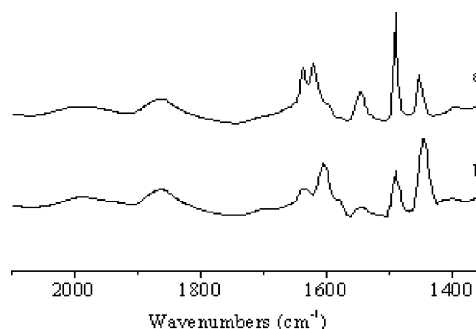

Fig. 2. Infrared spectra of pyridine adsorbed on zeolite (at room temperature 3 h) and evacuation (at 423 K 10^{-3} Pa). (a) Hβ; (b) the modified Hβ by SnMe$_4$.

[25]. Fig. 2 showed that the intensities of both 1545 and 1490 cm^{-1} bands become much weaker and that of band at 1450 cm^{-1} become much stronger after Hβ zeolite was modified. The decrease in the intensities for bands 1545 and 1490 cm^{-1} observed on the modified sample may be due to the consumption of the Brönsted acid sites on Hβ zeolite when it reacted with SnMe$_4$, while the increase in the intensity for band 1450 cm^{-1} was possibly related to an enhancement of Lewis acidity caused by the inductive effect of SnMe$_3$ group as an electron donor.

3.2.2. UV–Vis DRS

The DRS spectrum of the modified sample was obviously different from that of the unmodified one (Fig. 3). The former showed a strong band at 205 nm, which was a characteristic band of tetra-coordinate tin atom [26], while the latter had no absorption in the range from 200 to 600 nm. It suggested that the tin atoms in the grafted species existed as a well-defined tetra-coordinate state.

3.2.3. MAS NMR

The ^{13}C CP-MAS NMR of the grafted sample showed only a strong sharp peak at $\delta = 2.7$ ppm, suggesting that all carbon atoms were chemically equivalent
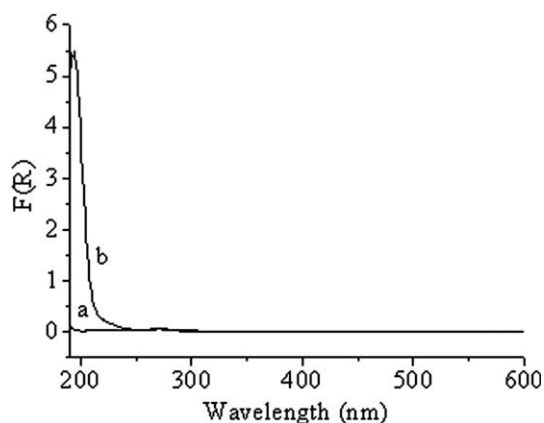

Fig. 3. UV–Visible diffuse reflectance spectra of Hβ zeolite after and before reaction with SnMe$_4$ (a) Hβ; (b) reaction with SnMe$_4$.

and corresponding to –CH$_3$. The ^{119}Sn MAS NMR of the modified sample showed only a strong peak at $\delta = 130$ ppm and indicated only one type of organotin species grafted onto the surface. The chemical shift is similar to that previously reported for the grafted product from the reaction between tetramethyltin and silica surface [22]. It was confirmed that the grafting reactions of tetramethyltin with Hβ zeolite leaded to the single grafted species –SnMe$_3$.

3.2.4. XPS

XPS full range survey spectra of the modified sample showed obviously the Sn3d, C1s, Si2p, Si2s and O1s peaks.(Fig. 4), indicating the existence of tin, carbon, silica and oxygen on the surface of the grafted sample. The binding energies of Sn3d3/2 and Sn3d5/2 were 500.90 and 492.80 eV, respectively (Fig. 5). The difference between them was 8.10 eV, indicating that tin exists in the form of Sn^{2+} and Sn^{4+}, but not in the form of Sn^0 [27,28].

3.3. Properties of the grafted sample

3.3.1. Texture of the grafted sample

Comparison of the XRD patterns of Hβ and the modified Hβ sample (Fig. 6) showed their structures are essentially the same, which suggesting no change of the framework structure after the grafting reaction
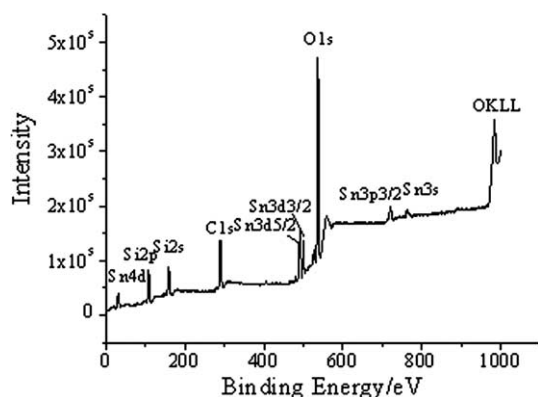
[17]. However, adsorption capacity, BET surface area, micropore volume and total pore volume of the zeolite were modified due to the grafting of organotin group on its surface of the channel. The nitrogen adsorption isotherms (Fig. 7) and the texture parameters (Table 1) showed that the Hβ retained the microporous characteristics after the modification.

3.3.2. Thermal decomposition of the grafted sample

The results of TPD carried out in a flow of He were shown in Fig. 8. The decomposition of SnMe$_3$/Hβ and the polymerization of the gaseous products occurred in the temperature ranged from 400 to 800 K. The discharges of CH$_4$, CH$_3$, CH$_2$, and C$_2$H$_4$ can also be detected in this temperature range. Since the ratio of the area of the peak centred at 473 K and that centred at

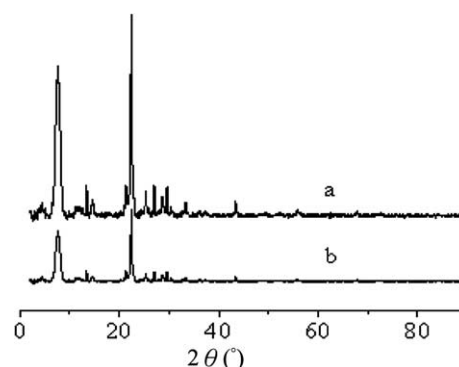Fig. 6. XRD profile of Hβ zeolite before (a) and after (b) modification.

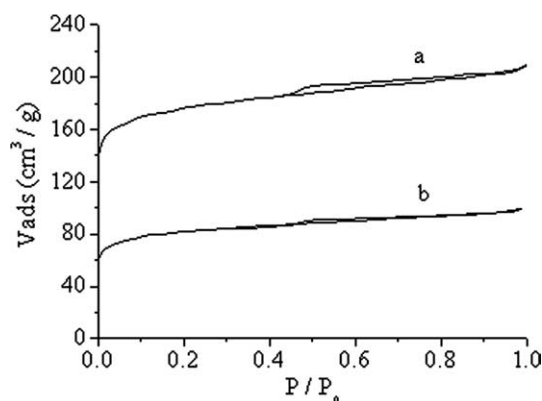Fig. 4. XPS survey scan spectra of SnMe$_3$/Hβ.

Fig. 7. Nitrogen adsorption isotherms at 77 K (a) Hβ; (b) reaction with SnMe$_4$.

Fig. 5. XPS Sn3d narrow scan spectra of SnMe$_3$/Hβ.

Table 1
BET surface area, micropore volume (V_u) and total pore volume (V_t) of modified and unmodified Hβ zeolites

Sample	BET (m^2 g^{-1})	V_t (cm^3 g^{-1})	V_u (cm^3 g^{-1})
Hβ	574	0.295	0.321
SnMe$_3$/Hβ	268	0.134	0.152

673 K is ca. 1:2 (Fig. 8), the decomposition of SnMe₃/Hβ may occur in two following steps and is basically in agreement with the results obtained from IR spectra.

400–573 K $SnR_3/H\beta \rightarrow SnR_2/H\beta + RH$

573–800 K $SnR_2/H\beta \rightarrow Sn/H\beta + 2RH$
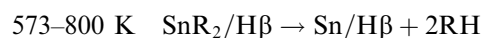
The peak centered at 423 K was related to the adsorption of the physically adsorbed water, while the peak at 798 K resulted from the condensation of hydroxyl groups [23].
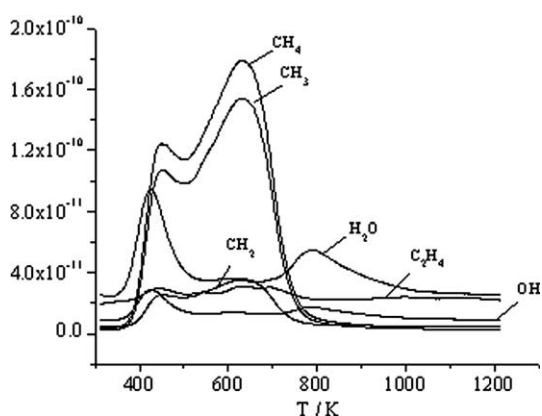
H₂–TPR plot of SnMe₃/Hβ (Fig. 9) was similar to the TPD plot in the kinds of gas products and the temperatures in which the gas products evolved, except that water peaks were observed at 950 and 1073 K. The difference may be attributed to the reductions of the trimethyltin species grafted on the surface [29,30].

The mechanism of the stepwise decomposition of SnMe₃/Hβ to SnR₂/Hβ and Sn/Hβ is illustrated in Scheme 1. Firstly, a thermolytic reaction of SnMe₃/Hβ with a free hydroxyl groups (≡Al–OH–Si≡) leads to a bi-grafted complex (≡Al–O–Si≡)₂SnMe₂ with the
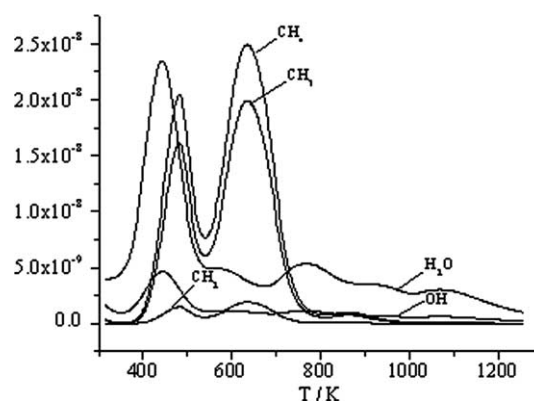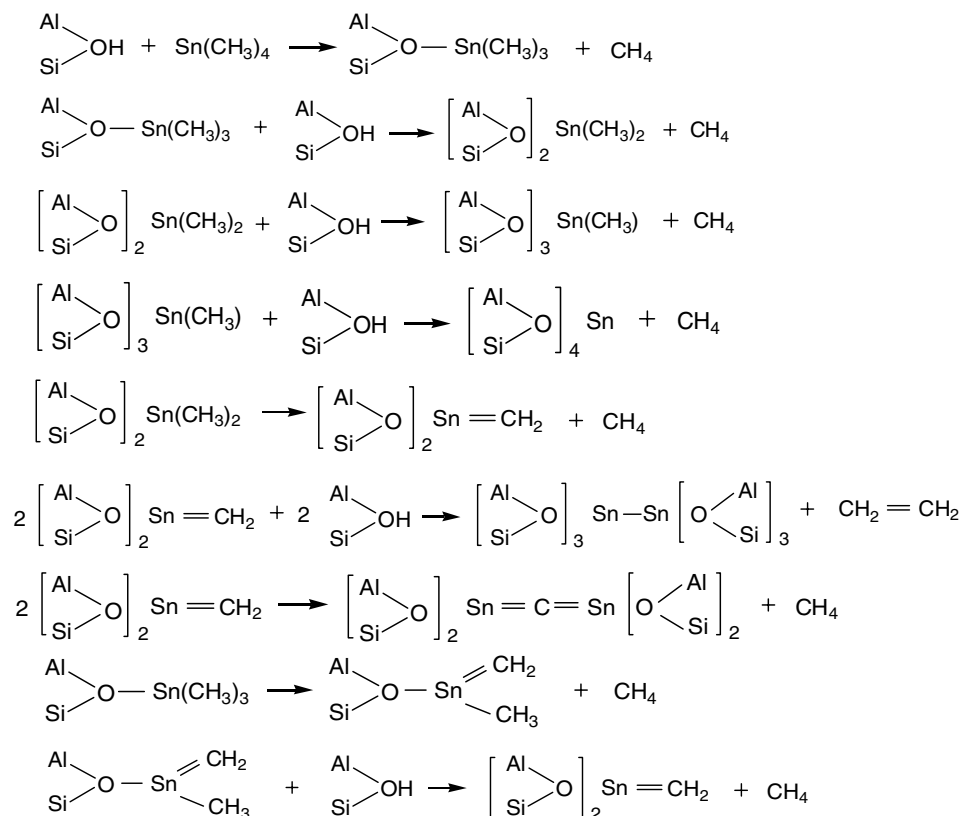

Fig. 8. TPD-MS spectra of SnMe₃/Hβ.

Fig. 9. TPR-MS spectra of SnMe₃/Hβ.

Scheme 1. The thermolytic mechanism of SnR₃/Hβ.

evolution of methane and ethene. Then further reactions between this complex and the free hydroxyl groups results in a tri-grafted complex $(\equiv Al{-}O{-}Si\equiv)_3SnMe$ and $(\equiv Al{-}O{-}Si\equiv)_4Sn$.

The thermolysis temperature of $SnMe_3$/MCM-41 was reported to be at about 723 K [23] which was higher than the thermolytic temperature of $SnMe_3$/Hβ. This result also suggested that the states of $-SnMe_3$ groups on the surface with strong acidity (Hβ zeolite) and weak acidity (MCM-41) could be different. The former one may have some ionic properties [31], while the latter one may be covalent. The thermolysis temperature and the decomposition products were quite similar in H_2 and He except that in H_2 environment tin was reduced.

4. Conclusion

Hydroxyl groups on Hβ zeolite can react with tetramethyltin to form a surface species $(\equiv Al{-}O{-}Si\equiv)SnMe_3$ on the surface of zeolite. Per-gram Hβ zeolite reacting with excess of tetramethyl tin at 323 K for 24 h resulted in 1.06 mmol tetracoordinated tin grafted on the surface. After modified by $SnMe_4$, the crystal structure of Hβ zeolite was not destroyed. The grafted species had an effect on the surface properties of Hβ zeolite. The BET surface area and the pore volume of zeolite decreased, while the microporous structure of the Hβ zeolite is retained after grafting reaction.

Acknowledgments

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