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Reduction of platinum dispersed on dealuminated beta zeolite

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Abstract

The Si/Al ratio of a commercial HB-25 beta zeolite sample was increased by treatment of dealumination and silicon-insertion. Platinum ions were subsequently dispersed onto the starting and the treated samples through impregnation of aqueous $Pt(NH_3)_4(NO_3)_2$. Chemical environments of dispersed platinum were characterized by temperature-programmed reduction (TPR) technique. The obtained TPR traces varied with extents of dealumination. Nevertheless, three major signals, in reduction temperature regions around -50, 80 and 480°C were distinguished from these TPR traces and characterized as reductions of platinum oxides dispersed on the external surface of zeolite (Pt^eO), platinum oxides occluded in channels (Pt^oO_x), and Pt–(–O–Si≡)$_y$ complexes coordinated to external surface or defects of zeolite, respectively. From the variation in the contribution of the 480°C peak in TPR traces, a formation of Si–OH silanol function groups on the zeolite surface during the dealumination treatment and a elimination of these groups during the silicon-insertion treatment are indicated.

Keywords: TPR; Platinum oxide; Beta zeolite; Dealumination

1. Introduction

Pores in the beta and the KL zeolites are straight channels of 12-member ring. The KL zeolite has a Si/Al atomic ratio around 3.0 and unidimentional channels of 0.71 nm in diameter [1]. The beta zeolite is a three dimentionally interconnected channel system which has a high Si/Al ratio (>10) and an extensively faulted structure [2,3]. Both zeolites are widely used in industrial processes after impregnation with Pt. The Pt/KL catalyst exhibits a good selectivity for the aromatization of *n*-hexane [4,5], while the Pt/beta catalyst is an active bifunctional catalyst towards reforming and isomerization reactions [6,7].

The acidic strength of aluminum sites in a zeolite generally increases with its Si/Al ratio. The Si/Al ratio of a zeolite can be increased by treatments of either dealumination with inorganic acid (HNO_3 or HCl solution) [8], or silicon-insertion with $(NH_4)_2SiF_6$ [9]. During the acid treatment, aluminum ions are leached out and defective vacancies as well as terminal Si–OH groups are consequently formed on the framework of zeolite. The resulted defects and

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Table 1
Some literatures about TPR of Pt/zeolites

Sample	T_r (°C)	Pt species	Ref. [precursor]
Pt/Y	100	Pt^{2+} in supercage	[10] [$Pt(NH_3)_4(NO_3)_2$]
	250	Pt^{4+} in sodalite cage or hexagonal prism	[11] [$Pt(NH_3)_4Cl_2$]
Pt/ZSM-5	250	Pt^{4+} in channels	[11] [$Pt(NH_3)_4Cl_2$]
Pt/KL	r.t.	PtO on external surface	[11,12] [$Pt(NH_3)_4Cl_2$]
	80	PtO in channels	
	150	Pt^{2+} in channels	
	250	Pt^{4+} in channels	

terminal Si–OH groups may be partially removed by an additional treatment of silicon-insertion.

The temperature-programmed reduction (TPR) technique has been used successfully in literature (see Table 1) to characterize environments of Pt species supported on Y, ZSM-5 and L zeolites according to their reduction temperature (T_r) [10,12]. Sachtler et al. [10] and Foger and Jaeger [11] found that, platinum ions in the supercage of Y zeolite were reduced at a lower temperature ($T_r = 100$°C) than those in the sodalite cage or in the hexagonal prism ($T_r = 250$°C). Recently, four different Pt species, i.e., PtO deposited on external surface ($T_r < 25$°C), PtO occluded in channels ($T_r = 80$°C), Pt^{2+} coordinated to the framework ($T_r = 150$°C) as well as a coordinated Pt^{4+} species ($T_r = 250$°C) were further distinguished from Pt/KL zeolite samples [11,12].

In this work, platinum ions dispersed on beta zeolite are characterized by TPR. We want to report that defect sites formed during dealumination of the zeolite have a profound effect on the reduction of impregnated platinum.

2. Experimental

2.1. Dealumination of beta zeolite

The commercial (PQ Corporation) HB-25 beta zeolite (Si/Al atomic ratio = 11) was used as the starting zeolite sample in this work. This sample was dealuminated by stirring in a 1 M HNO_3 solution at room temperature for 3 days. The aluminum-leached sample was subsequently filtrated, washed with deionized water, dried overnight at 110°C, calcined in air at 540°C for 5 h and named as HB-N.

2.2. Insertion of silicon

Part of the HB-N sample prepared was further treated with a silicon-insertion agent. In this insertion, 15 ml of a 0.3 M aqueous $(N\text{-}H_4)_2SiF_6$ solution was added dropwise into 5 g of the HB-N sample suspended in an aqueous solution of ammonium acetate (50 ml, 2 M) at a temperature of 90°C. After filtration, washing, drying and calcination treatments, the resulted sample was stored as HB-NS.

Calcined HB-N and HB-NS maintained their beta structure according to XRD characterizations.

2.3. Platinum impregnation

Supported platinum samples were prepared by the incipient-wetness impregnation of HB, HB-N and HB-NS zeolites with a 0.023 M $Pt(NH_3)_4(NO_3)_2$ aqueous solution. After an overnight drying at 110°C, the impregnated samples were calcined at 400°C for 3 h and named as Pt/HB, Pt/HB-N, Pt/HB-NS, respectively.

2.4. Preparation of Pt/SiO_2

Two kinds of Pt/SiO_2 samples were prepared for this study. One was prepared by impregnating Carbosil M-5 powders (S.A. = 200 $m^2\ g^{-1}$) with an aqueous $PtCl_4$ solution. The other was prepared through sol–gel method by mixing $Pt(NH_3)_4(NO_3)_2$ (in 1 N NaOH) with $Si(OC_2H_5)_4$ in (EtOH/NaOH). After evaporation at 110°C, the obtained solid samples were calcined at 500°C for 4 h and named as Pt/SiO_2(i) and Pt/SiO_2(g).

2.5. ICP measurements

After a 2 h dehydration at 200°C, part of each prepared sample was dissolved in a mixed solution of HF and aqua regia at 120°C for composition determinations. The bulk Si/Al ratios were determined by a Jarrell-Ash, ICAP 9000 ICP/AES. Loadings of platinum impregnated on the zeolite samples were analyzed by a Kontron, S-35 ICP/MS.

2.6. ^{29}Si MAS NMR characterization

^{29}Si MAS NMR spectra for all of the beta zeolites used were obtained from a Brucker MSL-200 spectrometer at an operating frequency of 39.73 MHz. A 3000 Hz magic angle spinning was performed during the signal collection. Reported chemical shifts were related to a standard of $Si(CH_3)_4$.

2.7. TPR measurements

TPR studies were performed in an apparatus described in a previous report [13]. A 30 ml min^{-1} flow of 10 vol.% H_2 in Ar was used as the reductive gas. The rate of hydrogen consumption was monitored by a thermal conductivity detector on raising the sample temperature from −80 to 700°C at a constant rate of 7°C min^{-1}.

2.8. X-ray absorption spectroscopy

X-ray absorption spectra were recorded at the wiggler beamline S-5B of Synchrotron Radiation Research Center, Taiwan. The monochromator employs double Si(111) crystals for energy scanning. Powdered sample was pressed into a stainless steel holder and measured at liquid nitrogen temperature. A transmission mode was selected in which the intensities of incident and transmitted beams were measured using gas ionization chambers. Three scans were averaged to increase the signal-to-noise ratio. The computer software for data analysis was implemented in UWXAFS 3.0 package [14] in which the phase shift and backscattering amplitude of the photoelectron wave were theoretically calculated by using FEFF 6 code [15,16].

3. Results and discussion

3.1. Composition of Pt / beta samples

The analyzed Si/Al ratios of the starting (HB-25), dealuminated (HB-N) and Si-inserted (HB-NS) beta zeolites are seen in Table 2 to increase from 11 of the HB-25 to 90 of the HB-N and 127 of the HB-NS. Over 80% of Al atoms was removed from the starting beta zeolite by the dealumination treatment. Besides the expected silicon insertion, part of the aluminum ions remained in the HB-N sample was additionally removed in the Si-insertion treatment

Table 2
Compositions and TPR results of Pt samples prepared in this study

	ICP/AES		TPR (area %)				
	Si/Al ratio	Pt (wt.%)	−50°C	80°C	250°C	480°C	N_H/N_{Pt}
Pt/SiO_2(i)	∝	0.81	100	–	–	–	0.8
Pt/HB	11	0.39	35.1	3.8	3.0	58.1	2.0
Pt/HB-N	90	0.35	11.3	–	2.9	85.7	2.9
Pt/HB-NS	127	0.34	84.4	–	–	15.6	1.2
Pt/SiO_2(g)	∝	0.47	–	–	–	100	3.8

[9]. The platinum content in the three platinum impregnated samples was shown to be around 0.35 wt.% according to measurements by ICP/MS (Table 2).

3.2. ^{29}Si MAS NMR

Fig. 1 shows the ^{29}Si MAS NMR spectra of three beta zeolites used in this report. A major peak at ~ -110 ppm and a shoulder peak at -105 ppm were found in trace a from the fresh beta zeolite. They can be assigned to Si (0 Al) and Si (1 Al), respectively [17]. After acid treatment, the Si (1 Al) shoulder peak disappeared (trace b). In its replacement, a minor peak at -102 ppm appeared. This peak has been assigned by Corma et al. [18] to silicon atoms bonded to a hydroxyl group. Conceivably, the broad peak around -102 ppm is assigned to SiOH groups of hydroxyl nests

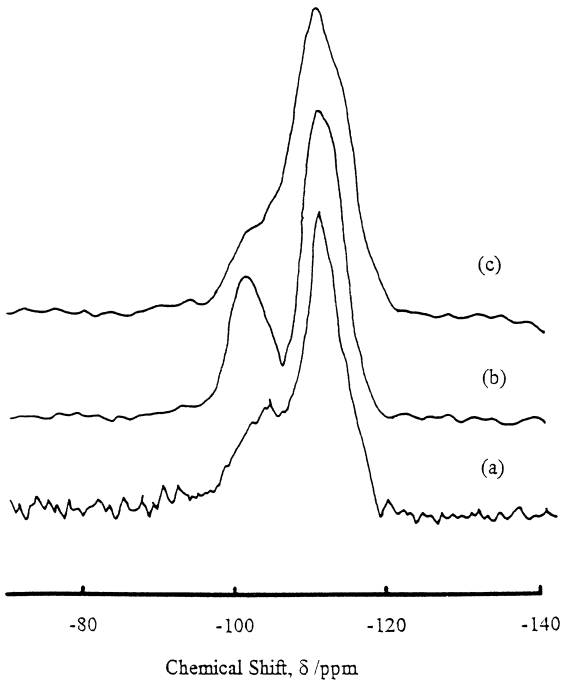


Fig. 1. ^{29}Si MAS NMR of (a) HB-25; (b) HB-N; (c) HB-NS.

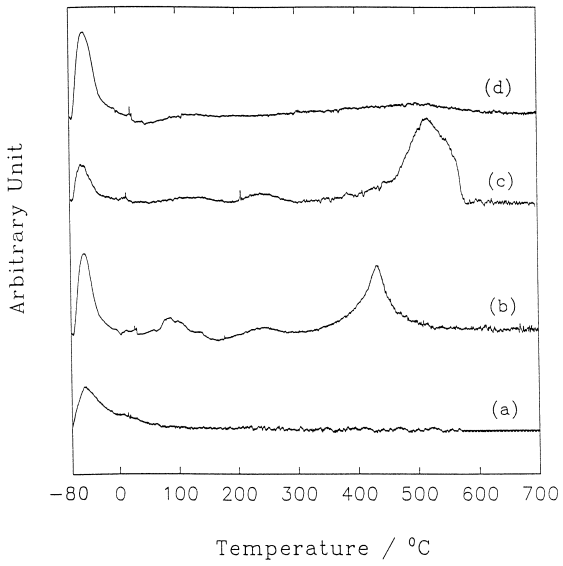
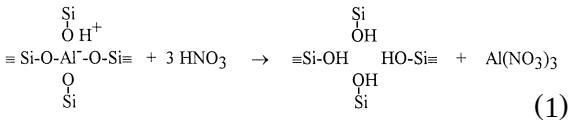


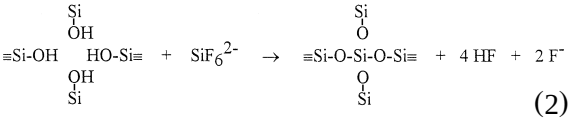
Fig. 2. TPR diagrams of (a) Pt/SiO_2(i); (b) Pt/HB; (c) Pt/HB-N; (d) Pt/HB-NS.

formed during the following dealumination reaction [19]:



(1)

The peak at -102 ppm diminished after silicon insertion (HB-NS sample) (trace c). Evidently, most of the SiOH groups on HB-N sample was removed by the following reaction:



(2)

3.3. TPR of Pt / beta samples

Fig. 2 shows the TPR traces of four Pt samples prepared. These traces are composed of four reduction peaks, with $T_r = -50$, 80, 250 and around 480°C, respectively. Their relative areas in these traces are also listed in Table 2.

The Pt/SiO_2(i) sample was prepared by impregnating a Pt complex onto the Carbosil M-5 support. This support is composed of highly

sintered silica grains (with diameters ~ 30 nm) which do not contain any internal pore. The Pt species dispersed on the surface of these grains was reduced (in trace a of Fig. 2) exclusively at −50°C [11]. Accordingly, the Pt species reduced at −50°C in traces b, c and d of Pt/beta samples can also be assigned to Pt oxides deposited on the external surface of beta zeolite (Pt^eO). The remaining three peaks, with $T_r = 80$, 250 and around 480°C , respectively, must have resulted from Pt species either occluded into the zeolite channels or coordinated to the surface of zeolites.

Recently, Sachtler et al. [12] characterized the Pt/KL samples by TPR. Besides the PtO on external surface, they found three other platinum species, i.e., PtO occluded in channels ($T_r = 80$°C), Pt^{2+} ($T_r = 150$°C) and Pt^{4+} ($T_r = 250$°C) ions, respectively. Two of these peaks with $T_r = 80$ and 150°C are also observed in the trace b of Fig. 2 from the Pt/HB sample. However, the total contribution of these three peaks ($< 10\%$) in trace b is much smaller than those found in the Pt/KL samples ($> 80\%$ in total). The difference in contribution probably resulted from the difference in Si/Al ratio between the HB (Si/Al ~ 11) and KL (Si/Al ~ 3) zeolites.

The 430°C peak is a major peak in trace b of Pt/HB sample. This peak was observed in the Pt/KL and Pt/KB samples of Perez-Pariente et al. [20] and Zhang et al. [21]. In their reports, the peak with $T_r = 430$°C was assigned to Pt^{2+} ions in some hidden sites. However, Treacy and Newsam [3] proposed that beta zeolite is a highly intergrown hybrid of two distinctive but closely related polymorphs (A and B) and contains a large population of stacking faults and terminal SiOH (silanol) groups. Accordingly, part of platinum complex ions on Pt/beta samples may coordinate to the silanol (≡Si–OH) sites during impregnation to form Pt–(O–Si≡)$_y^{2-y}$:

$$Pt(NH_3)_4^{2+} + y\,HO\text{–}Si\equiv \rightarrow Pt\text{–}(O\text{–}Si\equiv)_y^{2-y} + 4NH_4^+ . \quad (3)$$

The observed 430°C peak is therefore attributed to a reduction of Pt–(O–Si≡)$_y^{2-y}$ species formed in reaction 3.

During the dealumination treatment, the number of terminal Si–OH groups on beta zeolite should be increased due to a formation of Si–OH nests [22,23], through reaction 1. Platinum ions impregnated onto the HB-N sample therefore had a better chance to coordinate with the hydroxyl nests to form Pt–(O–Si≡)$_y^{2-y}$. This expectation is indeed confirmed by a dominant 530°C peak in trace c of Fig. 2. A large N_H/N_{Pt} ratio (2.9) shows that most of Pt ions in the nest has been oxidized into 4 + oxidation state during the calcination pretreatment. The notable variation in T_r (from 430°C to 530°C) probably resulted from differences in the stoichiometry of y of reaction 3 and/or in the oxidation state (n, 4 + or 2 +) of Pt ions.

Most of the hydroxyl nests on HB-N should be eliminated during the Si-insertion treatment (reaction 2). In agreement to our expectation, the peak of Pt–(O–Si≡)$_y^{n-y}$ suddenly became diminished in trace d for the Pt/HB-NS sample.

3.4. TPR of Pt / SiO_2(g)

In order to prove that the structure of Pt species reduced around 480°C is Pt–(O–Si≡)$_y^{n-y}$, we specially prepared a Pt/SiO_2(g) sample from gelating a Pt solution [$Pt(NH_3)_4(NO_3)_2$] in the basic tetraethyl orthosilicate solution. In this basic solution, $Si(OC_2H_5)_4$ would react with NaOH to form SiOH groups:

$$Si(OC_2H_5)_4 + 4NaOH \rightarrow Si(OH)_4 + 4NaOC_2H_5. \quad (4)$$

The SiOH groups formed should subsequently coordinate to Pt ions (reaction 3) to form Pt–(O–Si≡)$_y^{4-y}$ complexes during the gelation and the calcination treatment. These Pt species were found reduced around 550°C in trace a of Fig. 3. Accordingly, the reduction peak between 400 and 550°C in Pt/beta zeolite samples can in-

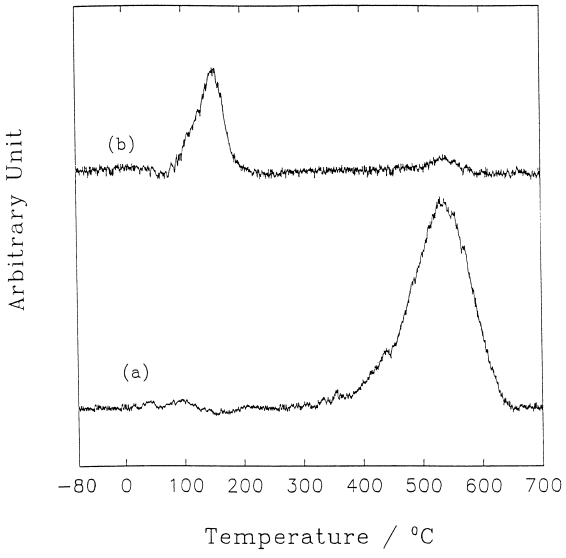


Fig. 3. TPR diagrams of $Pt/SiO_2(g)$: (a) fresh sample; (b) sample (a) reoxidized at 500 °C.

deed be assigned to the reduction of Pt–(O–Si≡)$_y^{4-y}$ species:

$$Pt\text{–}(O\text{–}Si\equiv)_y^{4-y} + y/2H_2 \rightarrow Pt^o + y\equiv Si\text{–}OH. \quad (5)$$

The oxidation state of Pt ions in this species is in 4+ because the stoichoimetry (N_H/N_{Pt}) observed was 3.8 (Table 2).

After the experiment of trace a, the reduced $Pt/SiO_2(g)$ sample was reoxidized at 500°C for a second TPR experiment. Trace b of Fig. 3 indicated that the reduction of the reoxidized platinum on $Pt/SiO_2(g)$ was shifted to 130°C. Probably, the Pt^o crystallites reduced in reaction 5 were incorporated in the bulk of SiO_2 support [24]. Therefore, the peak with $T_r = 130$°C in the trace b should be the reduction of Pt oxides burried in the SiO_2 matrix.

3.5. Extended X-ray absorption fine structure (EXAFS) of $Pt/SiO_2(g)$

After the background subtraction and normalization with respect to the edge jump step in the raw X-ray absorption spectra, the EXAFS function (χ) was obtained. Fig. 4 shows the k^3-weighted EXAFS function and its Fourier transform of the $Pt/SiO_2(g)$ sample. Computer-fitted results indicate that in average there are 3.5 nearest oxygen atoms surrounding each Pt atom

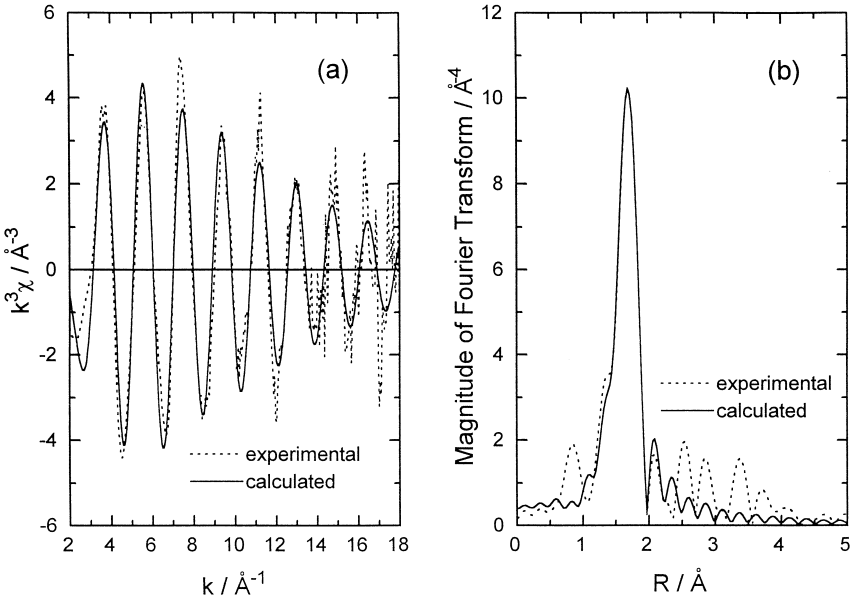


Fig. 4. (a) k^3-Weighted EXAFS function at Pt L_3-edge of $Pt/SiO_2(g)$; (b) Magnitude of Fourier transform (without phase correction).

with a Pt–O bond length of 2.02 Å [14]. Taking into account the uncertainty in estimating the coordination number from EXAFS data analysis of $\pm 15\%$. Pt ions should locate at the center of a local oxygen tetrahedron, similar to the situation that the Si center is substituted by Pt in a SiO_4 unit in gel structure. In view of the fact that the $Pt/SiO_2(g)$ sample exhibits no peak in XRD pattern due to the lack of long-range order, it becomes difficult to see the contribution in EXAFS from higher-shell neighbors surrounding the Pt center.

4. Conclusions

Four kinds of TPR peaks were observed in Fig. 2 and assigned to reductions of the Pt^eO ($T_r \sim -50$°C), the Pt^oO_x ($T_r = 80$°C), Pt^{4+} ions in zeolite channels ($T_r = 250$°C), and species of $Pt–(O–Si\equiv)_y^{n-y}$ in the defects of beta zeolite (T_r between 400 and 550°C), respectively. The distribution of platinum in these environments can be estimated from the area of these peaks in TPR traces. Besides, a generation of Si–OH functional groups during the dealumination treatment and an elimination of these groups during the Si-insertion treatment was confirmed by variations in area of a TPR peak with T_r around 480°C. Accordingly, TPR technique can be used to characterize effects of dealumination treatments on zeolite structure.

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