

Note

# Reactivities of tetraalkyltin complexes toward Pt/HY zeolite

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## Abstract

Tetraalkyltin complexes, SnR<sub>4</sub> (R = Me, Et, Pr, Bu) could react with Pt/HY at 193, 243, 273 and 333 K, respectively. The reactions occurred on the surface of the zeolite and the organotin grafted zeolites were characterized in detail. The framework and the microporous structure of the grafted Pt/HY zeolites were retained. However, the modified zeolites showed better size selectivity in the absorption of hydrocarbons.

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## 1. Introduction

Surface organometallic chemistry (SOMC) with the purposes to study the organometallic groups grafted on the surface and to prepare the catalytic and adsorbent materials with well-defined structure and peculiar capability [1,2] is a relatively new field of chemistry [3,4]. 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 composition. With well-defined crystallographic structures and abundant surface hydroxyl groups, the zeolites make good support for the study of SOMC. Zeolites have been extensively used as adsorbents, catalysts and supports of catalysts in the chemical industry due to their special and modifiable structures and properties. Our previous work have found that the grafting of organotin and organogermanium by SOMC on the surface of HY [5,6], MCM-41 [7], ZSM-5 [8] and H $\beta$  [9] zeolites can led to a significant modification in their adsorption properties and catalytic selectivities [5,6,10]. In this paper, the grafting reactions

between tetraalkyltin complexes and Pt/HY zeolites were systematically investigated. The goal of this study is to provide some useful information in understanding the elementary steps of the reactivities of the Pt/HY zeolite. We hope that the introduction of Pt could create new active sites by incorporating both Pt and organotin species into the zeolite and we can develop new surface-bound catalysts with well-defined structure and better performance.

## 2. Experimental

The HY zeolite was prepared by the NH<sub>4</sub>Y zeolite (Aldrich). The NH<sub>4</sub>Y zeolite was calcined at 793 K under flowing oxygen for 10 h and subsequently treated under vacuum at 693 K for 3 h. The Pt/HY zeolite was prepared by the wetness impregnation method. The HY zeolite was immersed in the appropriate amount of an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> · 6H<sub>2</sub>O (AR grade) at room temperature for 24 h. The resulting powder was dried at 393 K for 12 h, followed by calcination at 773 K. Then the powder was calcinated under a flow of H<sub>2</sub> to reduce the impregnated Pt(IV) to Pt(0). The grafting reactions of tetraalkyltin (Aldrich) on Pt/HY zeolites were performed in a glassware equipment connected to a vacuum line by a method reported previously [5]. The evolved gases were

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analyzed by GC–MS (HP-5973) and GC (Agilent 6890). The IR spectra during the treatments were recorded on a Nicolet Nexus 670 FT-IR Spectrometer. The DRS spectra were obtained on a Varian Carry 500. Spectrometer. The chemical compositions were analyzed by Vario EL III elemental analyzer (EA), inductively coupled plasma spectroscopy (ICP). The BET surface area was detected by N<sub>2</sub> 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 an 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% H<sub>2</sub>/Ar for TPR) was 30 mL min<sup>-1</sup> and the heating rate is 5 K min<sup>-1</sup>. The TG curves of the resulting solid products were obtained in nitrogen atmosphere at a heating rate of 5 K min<sup>-1</sup> on a PE TGA7 analyzer.

### 3. Results and discussion

#### 3.1. Grafting reactions of SnR<sub>4</sub> (R = Me, Et, Pr and Bu) on Pt/HY zeolite

When tetraalkyltin were contacted with Pt/HY zeolites, the alkyl C–H vibration adsorption bands could be observed clearly and alkane evolved immediately. In the meantime, the intensity of the supercage hydroxyl groups at 3669 cm<sup>-1</sup> decreased, while no change on the intensities of other hydroxyl groups were observed and suggested that SnR<sub>4</sub> could only react with the supercages hydroxyl of the Pt/HY zeolite [11,12]. The amount of the evolved alkanes increased gradually with the reaction time. However, the reactivities were different for the four organotins and SnMe<sub>4</sub>, SnEt<sub>4</sub>, SnPr<sub>4</sub> and SnBu<sub>4</sub> could react with the Pt/HY zeolite at 193, 243, 273 and 333 K, respectively. The quantitative analysis of the evolved gas indicated that when 1 g Pt/HY (1 wt.%Pt) zeolite was reacted with excess SnR<sub>4</sub> (R = Me, Et, Pr and Bu) at 353 K for 24 h, about 1.61 mmol of methane, 1.32 mmol of ethane, 1.03 mmol of propane and 0.84 mmol of butane could be obtained respectively. The less alkane evolved compared to that from the reaction between HY zeolites and the corresponding tetraalkyltin could be attributed to the less organotin grafted on the Pt/HY and was a result of the decrease of the pore volume of the zeolite after the loading of Pt. The results also indicated that the reactions between SnR<sub>4</sub> and Pt/HY occurred on the surface hydroxyl, but not on the surface of the Pt center.

The thermolysis of the organotin grafted Pt/HY was carried out in a static vacuum at 673 K for 3 h and the gas evolution was studied by GC. For tetramethyltin and tetraethyltin grafted zeolites, the produced alkane during the thermolysis were about three times of those evolved during the grafted reactions, while less than three times for tetrapropyltin and tetrabutyltin grafted zeolites. How-

ever, for the latter, a little amount of propylene and butylene were detected and indicated propane and butane were cracked on the acid center and Pt atom. The combination of GC and the elemental analysis indicated that the organotin grafted on the Pt/HY zeolite surface was –SnR<sub>3</sub> (see Fig. 1).

#### 3.2. Coordination state of the grafted species

The DRS spectra of the modified samples were obviously different from that of the unmodified Pt/HY (Fig. 2). The former showed a strong band at ca. 205 nm, which was a characteristic band of tetra-coordinated SnO<sub>4</sub> [13–15], while the latter had no absorption in the range of 200–600 nm. It suggested that Sn in the grafted species existed in a well-defined tetra-coordinated state. It is reasonable to observe that the position of the band for different organotin grafted zeolites existed in the following order: SnMe<sub>3</sub> > SnEt<sub>3</sub> > SnPr<sub>3</sub> > SnBu<sub>3</sub> since the ability of the electron donation increased with the size of the alkyl group.

Fig. 3 displays the reduction profiles obtained by TPR. Two reduction peaks were observed on the H<sub>2</sub>-TPR plot of SnR<sub>3</sub>/Pt/HY. The lower temperature peak was attributed to the reduction of Sn<sup>4+</sup>–Sn<sup>2+</sup>, while the higher one may be due to the reductions of Sn<sup>2+</sup>–Sn<sup>0</sup> and Sn<sup>4+</sup>–Sn<sup>0</sup> [16,17]. This indicated that the tin existed as Sn (IV) in the grafted species. Fig. 3 also showed that the intensities of the reduction peaks decreased with the size of the alkyl groups. This result was consistent with the GC analysis and indicated that less alkyltin was grafted on the surface of Pt/HY for larger organotin complexes.

#### 3.3. Structure and properties of the grafted sample

The nitrogen adsorption and desorption isotherms (Fig. 4) and the texture parameters (Table 1) showed that the microporous structure of Pt/HY was retained after the modification. However, the adsorption capacity, BET surface area, micropore volume and total pore volume of

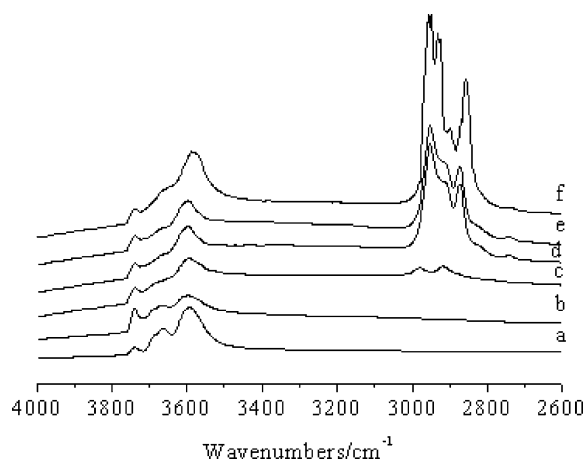


Fig. 1. IR spectra of HY (a) Pt/HY and (b) SnR<sub>3</sub>/Pt/HY (R = Me (c); Et (d); Pr (e) and Bu (f)).

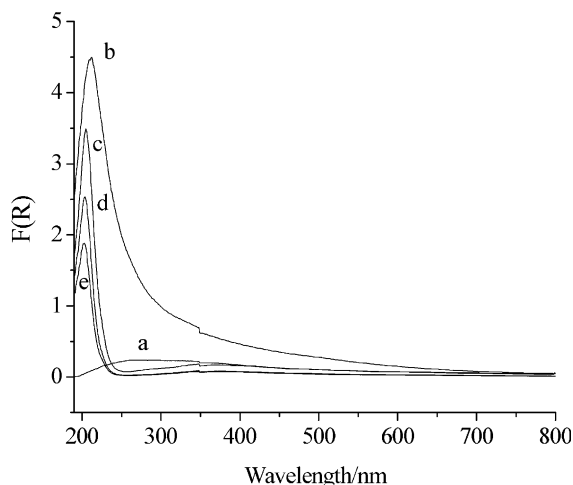


Fig. 2. DRS spectra of Pt/HY zeolite (a) and SnR<sub>3</sub>/Pt/HY (R = Me (b); Et (c); Pr (d) and Bu (e)).

the zeolite were modified due to the grafting of organotin group on its surface of the channel.

The change of the pore volume of the modified samples was reflected in their abilities in the adsorption of hydrocarbons. The adsorption capacities for *n*-hexane, *n*-heptane, *iso*-octane, benzene, toluene, ethylbenzene, cumene (determined by the pulse method) for Pt/HY before and after graft are shown in Fig. 5. In general, a decrease in the adsorption capacity for the hydrocarbons was observed due to the presence of the organotin fragments. This decrease was the result of the following two effects [18]: a decrease in the pore volume and a slower diffusion of the hydrocarbons through the channels of the modified zeolite. Besides this, a better shape-form-selectivity for larger hydrocarbons, like *iso*-octane, cumene was also observed. After graft reaction, *iso*-octane and cumene could no longer enter the pore system of SnR<sub>3</sub>/Pt/HY.

### 3.4. Thermal stability of the grafted samples

Thermal stability is an important character of catalysts and adsorbents in consideration of their applications in

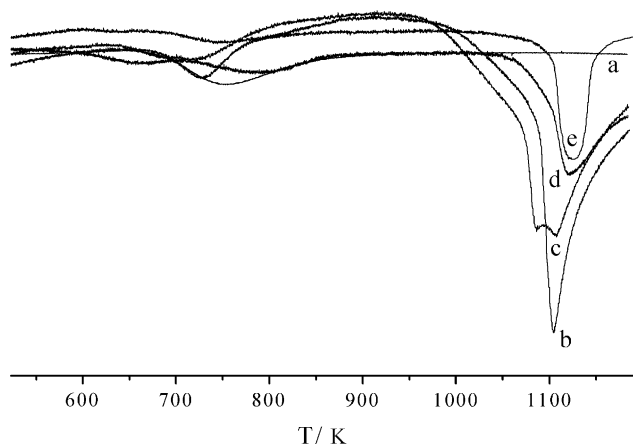


Fig. 3. TPR plots of Pt/HY (a) and SnR<sub>3</sub>/Pt/HY (a) (R = Me (b); Et (c); Pr (d) and Bu (e)).

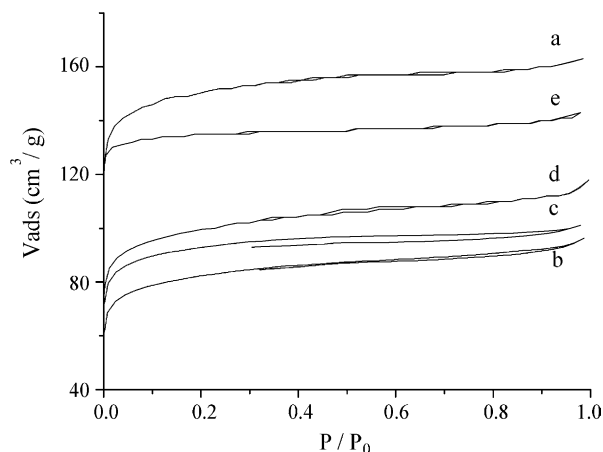


Fig. 4. N<sub>2</sub> adsorption and desorption isotherms at 77 K of Pt/HY (a) and SnR<sub>3</sub>/Pt/HY (R = Me (b); Et (c); Pr (d) and Bu (e)).

Table 1  
BET surface area and microporous volume of Pt/HY zeolite modified and unmodified by reaction with tetraalkyltin

Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	V <sub>u</sub> (cm <sup>3</sup> g <sup>-1</sup> )
Pt/HY	546.31	0.28
SnMe <sub>3</sub> /Pt/HY	259.85	0.13
SnEt <sub>3</sub> /Pt/HY	303.96	0.15
SnPr <sub>3</sub> /Pt/HY	327.47	0.16
SnBu <sub>3</sub> /Pt/HY	354.30	0.18

high temperature. Fig. 6 shows the TG curves of the grafted complexes obtained in nitrogen atmosphere at a heating rate of 5 K min<sup>-1</sup>. For Pt/HY, only one weight loss which corresponds to water desorption was observed. For organotin grafted Pt/HY zeolites, two stages of weight loss were observed.

The first weight loss at a temperature lower than 423 K was due to the desorption of water while the second one in the temperature range of 473–773 K could be ascribed to

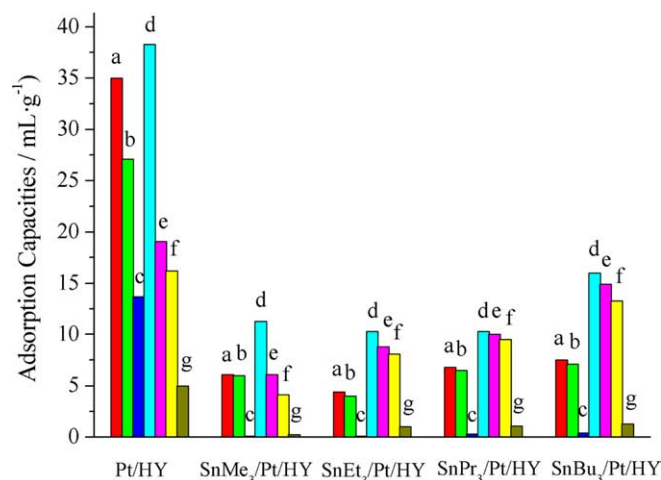


Fig. 5. Pulse adsorption capacities of hydrocarbons on Pt/HY and SnR<sub>3</sub>/Pt/HY (R = Me, Et, Pr, Bu). (a) *n*-Hexane, (b) *n*-heptane, (c) *iso*-octane, (d) benzene, (e) toluene, (f) ethylbenzene, (g) cumene.

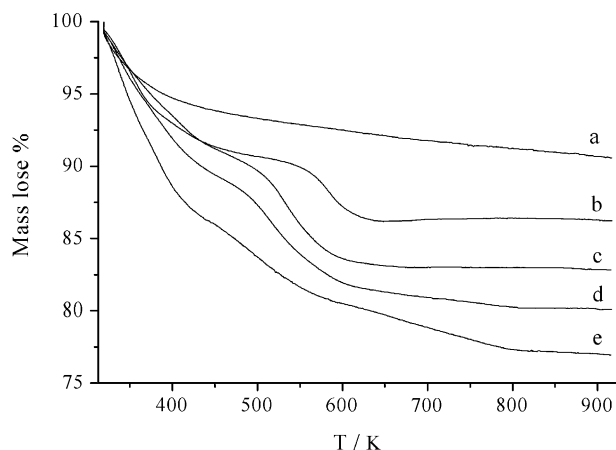


Fig. 6. TG plot of Pt/HY and modified Pt/HY with SnR<sub>4</sub>. (a) Pt/HY, (b) SnMe<sub>3</sub>/Pt/HY, (c) SnEt<sub>3</sub>/Pt/HY, (d) SnPr<sub>3</sub>/Pt/HY, (e) SnBu<sub>3</sub>/Pt/HY.

the decomposition of the grafted organotin. The weight loss for methyltin, ethyltin, propyltin and butyltin species were 13.78%, 17.18%, 19.88%, 22.04%, respectively, and were basically accorded with the weight of alkyltin groups grafted. To study the decomposition course of alkyltin groups grafted on the surface, temperature programmed decomposition (TPD) was carried out at a heating rate of 5 K min<sup>-1</sup> in a flow of He. The decomposition of SnR<sub>3</sub>/Pt/HY may be occurred in the following two steps [9]:



C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>8</sub> produced from the polymerization of ethane, propane and butane cracked on the acid center could be detected in the temperature range from 400 to 800 K. These are basically in agreement with the results obtained from GC analysis. However, the decomposition temperature was different for different organotins grafted on Pt/HY zeolite. The larger the alkyltin group, the lower the thermolysis temperatures were observed.

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