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Preparation and catalytic properties of a bimetallic Sn–Pt complex in the supercages of NaY zeolite by use of surface organometallic chemistry

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The grafting reaction of $SnMe_4$ on the surface of Pt/NaY zeolite was investigated in a 1.6×10^4 Pa hydrogen atmosphere. The chemical compositions, structure and properties of the resulting solid were characterized by *in situ* FTIR, ICP, XRD, XPS, temperature programmed decomposition and nitrogen adsorption. The results show that Pt atoms of Pt/NaY zeolite react with tetramethyltin to form a bimetallic Me_3Sn–Pt surface species in the presence of hydrogen at 353 K. The reaction does not destroy the zeolite framework, while its surface properties are changed. The BET surface area and the pore volume of the zeolite decrease significantly. The CO chemisorption results and the XPS results show that the electronic properties of the modified Pt atoms on the surface of NaY zeolite are altered remarkably by the inductive effect of electron between Pt and methyl groups. The grafted product has excellent selective hydrogenation of furfural to furfuryl alcohol. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: surface organometallic chemistry; tetramethyltin; NaY zeolite; grafting reaction; furfural hydrogenation

INTRODUCTION

Furfuryl alcohol is an important intermediate for the polymer industry. It is used mainly for the production of furan resin, phenolic resin and furfuryl resin. At present, furfuryl alcohol is prepared mainly by the catalytic hydrogenation of furfural in gaseous or liquid phase.[1–4] A commercial process is the liquid phase hydrogenation of furfural over Cu–Cr catalyst. However, the toxicity, high energy consumption and moderate activity of this catalyst provide a challenge to develop a new high-efficiency catalyst without chromium. Recently, a few works concerning the gaseous phase hydrogenation of furfural over carbon-supported copper,[1,5] Raney nickel,[6] nickel amorphous alloys,[7–9] mixed copper–zinc oxides doped with Al, Mn and Fe[10] and homogeneous complexes of Rh, Ru and Pt[11] have been published, but the selectivity of these catalysts still does not reach commercial requirements. Therefore, the development of highly selective catalysts is currently a crucial goal.

Platinum is a known hydrogenation catalyst. However, platinum can usually catalyze deep hydrogenation and activate undesired side and consecutive reactions. Very recently, Kije'nski[12] reported that platinum deposited on supports (SiO_2, γ-Al_2O_3, MgO, TiO_2) covered with a transition metal oxide monolayer (TiO_2, V_2O_5, ZrO_2) had high selectivity for furfural hydrogenation to furfuryl alcohol at temperatures from 423 to 573 K. The difference between the electronegativity of Pt and that of the transitional metal resulted in a strong polarization of the catalyst surface, which was considered to be the reason for the high selectivity. Herein, we attempt to alter the electronic properties of surface Pt atoms to enhance the selectivity of hydrogenation via formation of a bimetallic Sn–Pt complex in the channel pores of zeolites. This concept has been demonstrated by the

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selective hydrogenation of crotonaldehyde to an unsaturable alcohol over a Pt–SiO_2 catalyst modified by organotin complex.[13,14] Our previous results also indicated that the modified HY zeolite by tetraalkyltin exhibited better size selectivity in the absorption of hydrocarbons, and the surface properties changed.[15–17]

In this study, a well-defined surface Sn–Pt bimetallic complex in NaY zeolite was prepared through surface organometallic chemistry (SOMC). The structure of the surface species was characterized by XRD, CO-TPD, *in situ* FTIR and XPS. The selective hydrogenation of furfural as a model reaction was used to examine the catalytic properties of the surface complex. It was found that the catalyst showed better performance in comparison with the parent Pt/NaY. This study will provide a theoretical basis for designing at molecular level a catalyst for highly selective hydrogenation of furfural.

EXPERIMENTAL

Materials

NH_4Y zeolite was obtained from Aldrich (Si : Al = 5.0). Tetramethyltin ($SnMe_4$, 99.5%) was purchased from Aldrich. $H_2PtCl_6 \cdot 6H_2O$ (AR grade) was purchased from Shanghai Chem. Co.

Preparation of the Pt/NaY zeolite

NH_4Y zeolite was calcined at 793 K under flowing oxygen for 10 h to completely transform it into HY zeolite. NaY zeolite was prepared by the treatment of HY zeolite with a dilute solution of NaOH at 353 K for 2 h. The resulting solid was dried in air overnight at 373 K, and calcined at 773 K for 2 h. Then the NaY zeolite was immersed in the appropriate amount of an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (AR grade) at room temperature for 24 h. The resulting powder was dried in air overnight at 383 K, and then incessantly heated in tube furnace with a ramping of 1 K min^{-1} to 473, 573, 623 and 673 K and maintained at each temperature for 0.5 h. Subsequently, the temperature increased from 673 to 773 K. After holding for 4 h, the sample was flushed with N_2 and reduced under H_2 for 5 h at this temperature. When the temperature decreased to room temperature, the sample was transferred into a desiccator filled with He. The as-prepared Pt/NaY zeolite was used as a starting material for preparing organotin-grafted samples.

Preparation of $(Me)_3Sn$–Pt/NaY

The amount of Pt/NaY zeolite was enclosed in home-made glass equipment and treated under dynamic vacuum (0.133 Pa) at 673 K for 3 h. After cooling to room temperature, the reactor was filled with 1.6×10^4 Pa of hydrogen. Subsequently, an amount of liquid tetramethyltin was introduced to the reaction system with a syringe via a septum. The reactor was kept at the temperature 373 K for 24 h to ensure a complete reaction. The evolved gases were analyzed by gas phase chromatogram (GC). Elimination of hydrogen and unreacted $SnMe_4$ was achieved by treatment under vacuum at this temperature for 1 h.

The reaction was also monitored by *in situ* infrared spectroscopy. A 20–30 mg aliquot of Pt/NaY zeolite was pressed as a disk (diameter 18 mm) and used to redo the experiment under the same conditions as above.

Physico-chemical characterization

The evolved gases were analyzed using an Agilent 6890 GC equipped with an FID detector. The chromatography used a HP-PLOT Al_2O_3 capillary column. The supporting gas was He.

The content of tin in the resulting solid was determined by Inductively Coupled Plasma (ICP) after the sample was dissolved completely using diluted hydrochloric acid and a small amount of hydrofluoric acid. The ICP measurements were carried out using a model ICPQ-100. The content of carbon in the resulting solid was analyzed using a Vario EL III elemental analyzer (EA).

X-ray diffraction (XRD) measurements were performed with a Brucker Advance D8 X-ray power diffractometer with Cu-K_α radiation (40 kV, 40 mA) at a scan speed of 0.2 in increments of 0.0–2.2θ.

In situ infrared spectra were recorded on a Nicolet Nexus 670 FTIR Spectrometer. The BET surface area was detected by N_2 adsorption with an OMNISORP 100CX gas adsorb analyzer.

XPS spectra were recorded on a PHI-5300/ESCA Spectrometer (Al/Mg dianode, 0.8 eV energy resolution, 45° angle resolution and 80 kCPS sensitivity). The base pressure was maintained at 2.0×10^{-7} Pa during XPS analysis (energy 3.0 kV, current 25 mA). Powder samples were mounted on sample stubs with conductive carbon tape. The sputtering was operated at 30 kV, 25 mA and 4 nm min^{-1}, and argon ion bombardment was used. The analyzed area was 8×8 mm^2. The C 1s line (284.6 eV) was used as the reference to calculate the binding energies (BE).

Experiments of temperature-programmed CO desorption (CO-TPD) was performed on an Autochem 2910 automatic catalyst characterization system. The loading amount of the sample was 0.2000 g. The flow rate of the supporting gas (He for TPD) was 30 ml min^{-1} and the heating rate was 5 K min^{-1}.

Catalytic activity tests

The catalytic tests were performed in a home made glass reactor (i.d. 18 mm) with a thermocouple under atmosphere pressure. Catalyst was packed into the reactor and pretreated with hydrogen from room temperature to 423 K at a heating rate of 5 K min^{-1}. The furfural liquid was added into the hydrogen steam using a peristaltic pump. The reactant mixture was passed through the reactor. The reaction products were cooled and analyzed using a gas chromatograph (Agilent 6890 GC) equipped with an FID detector. The chromatograph used an HP-FFAP

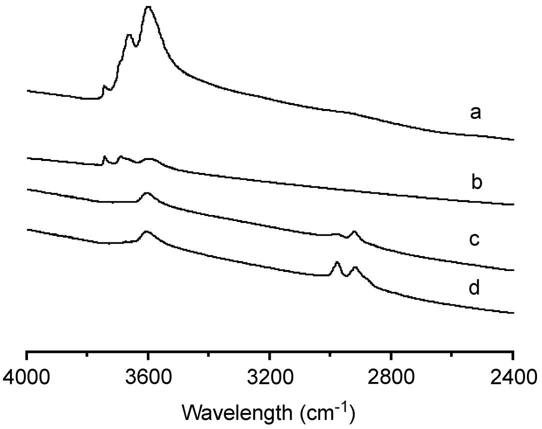

Figure 1. IR spectra of Pt/NaY zeolite before and after reaction with $SnMe_4$. (a) HY zeolite dehydroxylated at 673 K; (b) Pt/NaY dehydroxylated at 673 K; (c) Pt/NaY after reaction with $SnMe_4$ at 353 K for 24 h under vacuum; (d) (c) at 1.6×10^4 Pa H_2 and 353 K for 24 h.

(crosslinked, 25 m × 0.32 μm film thickness) capillary column. The supporting gas was He.

RESULTS AND DISCUSSION

The reactivity of $SnMe_4$ on Pt/NaY zeolite

The FTIR spectra of HY zeolite in the range of 4000–2400 cm^{-1} is shown in Fig. 1. After treatment under dynamic vacuum at 673 K for 3 h, zeolite showed three vibration adsorption bands at 3744, 3669 and 3600 cm^{-1}, which could be assigned to external non-acidic silanol groups, supercage acidic hydroxyl groups and inaccessible other acidic hydroxyl groups [Fig. 1(a)],[18] respectively. However, both supercage acidic hydroxyls at 3669 cm^{-1} and acidic hydroxyls at 3600 cm^{-1} in Pt/NaY zeolite are largely decreased [Fig. 1(b)], indicating that a majority of acidic hydroxyls are eliminated by –OH. When $SnMe_4$ is contacted with Pt/NaY zeolite at 353 K, and kept at this temperature for 24 h under vacuum conditions, supercage acidic hydroxyl groups disappear completely, and C–H stretching vibration adsorptions of methyl and methylene appear at 2800–3000 cm^{-1} [Fig. 1(d)]. Gas chromatography analysis revealed that per gram Pt/NaY zeolite (2% of Pt) reacting with excess of $SnMe_4$ under the same conditions as above resulted in 0.11 mmol of MeH. It indicated that $SnMe_4$ reacted with remanent supercage acid hydroxyls at this temperature.[15] After the unreacted $SnMe_4$ and gaseous products are removed, 1.6×10^4 Pa of hydrogen and excess $SnMe_4$ are introduced into the reaction system at 353 K, and held for 24 h at this temperature in the hydrogen atmosphere, the band intensity at 2800–3000 cm^{-1} clearly increased [Fig. 1(e)], while the acidic hydroxyls at 3600 cm^{-1} did not change. In the meantime, 0.10 mmol of MeH was obtained. This indicates that $SnMe_4$ reacts with absorbed hydrogen,[19] thereby the second grafting reaction occurs on the surface Pt atoms of Pt/NaY zeolite.

$$\mathrm{Pt\ H_{ads} + SnMe_4 \longrightarrow Pt\text{-}SnMe_3 + MeH} \qquad (1)$$

Some evident change could be observed from the IR spectrum of CO chemisorption at 293 K (Fig. 2). For the parent Pt/NaY zeolite [Fig. 2(a)], its IR spectrum in the range 1750–2200 cm^{-1} was composed of two IR bands, one, which was assignable to the Pt–CO linear vibrator, appeared at 2060 cm^{-1}; the other, which was attributed to bridged CO species, occurred at 1870 cm^{-1}.[20–24] However, after the second grafting reaction, the bridged CO band at 1870 cm^{-1} disappeared. This indicates indirectly that a majority of Pt atoms react with $SnMe_4$ to form bimetallic Pt–Sn organometallic complexes, while those unreacted Pt atoms on the surface of NaY zeolite may be highly isolated. In the meantime, the band at 2060 cm^{-1} shifts to low wavenumbers due to the increasing electron feedback from metal to CO molecules, and its absorption intensity clearly decreases. These change suggest that the electronic properties of Pt atoms on surface of NaY zeolite are altered by the introduction of tetramethyltin.

Structural characterization of the modified sample

Comparison of the XRD patterns of Pt/NaY and the modified Pt/NaY sample (Fig. 3) shows that their structures are essentially the same and the diffraction intensity changes slightly, which suggests that the grafting reaction does not destroy the framework structure and the reaction occurs only on the surface of zeolite. The texture parameters (Table 1) showed that the Pt/NaY zeolite retained the microporous characteristics after modification. BET surface area, micropore volume and total pore volume of the modified Pt/NaY zeolite

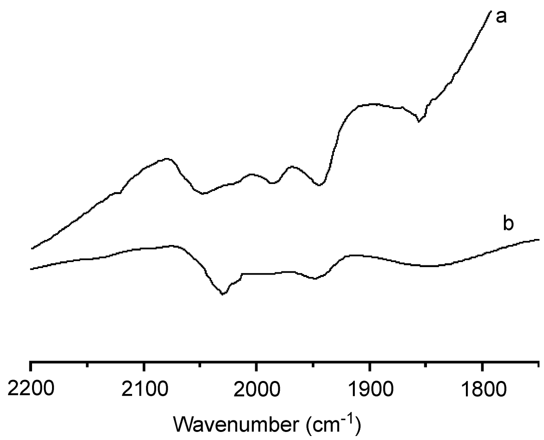

Figure 2. IR spectra of CO adsorbed on Pt/NaY zeolite (a) and the modified Pt/NaY (b).

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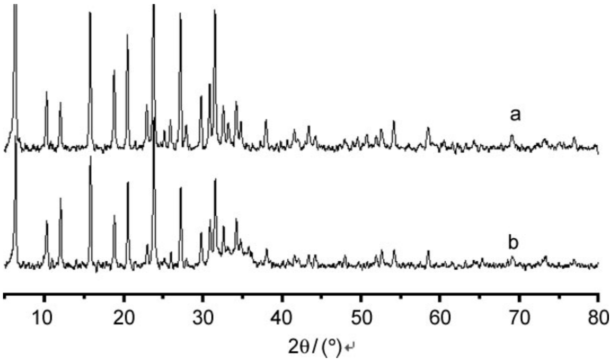

Figure 3. XRD spectra of Pt/NaY zeolite (a) and the modified sample (b).

Table 1. BET surface area micropore volume (V_u) and total pore volume (V_t) of Pt/NaY zeolite modified or unmodified by reactionwith tetraalkyltin

Sample	BET ($m^2\ g^{-1}$)	V_t($cm^3\ g^{-1}$)	V_u($cm^3\ g^{-1}$)
Pt/NaY	620	0.320	0.310
$SnMe_3$/Pt/NaY	317	0.173	0.164

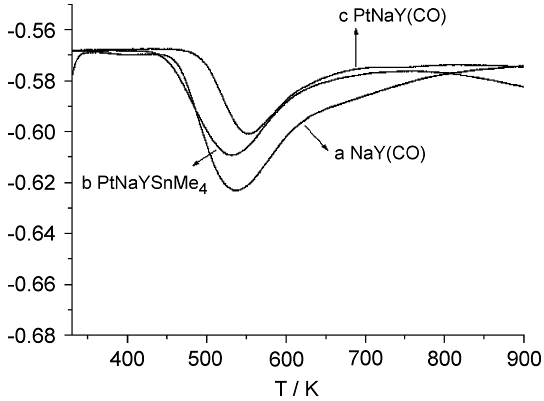

Figure 4. CO-TPD profiles of NaY zeolite before and after modification.

decreased remarkably, indicating that the surface properties of the Pt/NaY zeolite changed after the reaction.

CO-TPD and XPS characterization of the modified sample

Figure 4 presents TPD spectra of CO on NaY, Pt/NaY and Me_3Sn–Pt/NaY. The CO-TPD profiles of these samples consist of only a broad desorption peak in the 350–900 K region. Obviously, the higher temperature of CO desorption on Pt-modified NaY zeolite was obtained due to the strong adsorption between CO and Pt in comparison with the parent NaY zeolite. However, after the modification, the CO desorption temperature decreased because of the existence of organotin surface complex, and even the initial desorption temperature was lower than that of NaY. This indicates that the grafting reaction results in reducing surface adsorption capacity of Pt atoms, further confirming that the electronic properties of Pt atoms change after modification. The XPS analytic result on the Me_3Sn–Pt/NaY Sample also confirms this.

As is listed in Table 2, for Pt/NaY, the binding energy of Pt ($4f_{7/2}$) equals 71.50 eV. However, after $SnMe_4$ was grafted onto Pt atoms in Pt/NaY zeolite, the binding energy of Pt ($4f_{7/2}$) split into 71.20 and 74.68 eV.[25,26] This change in the binding energy confirms that $SnMe_4$ reacts with Pt atoms in Pt/NaY zeolite, and shows that two different Pt species exist in the supercages of NaY zeolite.[27] This is in agreement with the above IR results of CO chemisorption. The binding energies of $Sn3d_{3/2}$ and $Sn3d_{5/2}$ are 495.48 and 486.98 eV, respectively.[28,29] The difference between these values is 8.50 eV, indicating that tin exists in the form of Sn^{4+}, but not in the form of Sn^0.[30,31]

Catalytic activity for the hydrogenation of furfural

The above experimental results show that a bimetallic Me_3Sn–Pt surface complex in NaY zeolite can be successfully prepared by the grafting reaction of $SnMe_4$ with Pt atoms in the H_2 atmosphere. It is well known that methyl is an organic group with ample electrons. In principle, it can transfer electrons to Pt atom by the intermediate Sn atoms so as to increase the electron density around Pt atom, consequently weakening the absorption of Pt atom to hydrogen. Theoretically, the inductive effect of electrons between methyl and Pt inevitably impairs the hydrogenation ability of Pt to unsaturate hydrocarbons. Enhancement of the selectivity of hydrogenation of Pt may be realized.

In order to validate above theoretical deduction, as-synthesized bimetallic Me_3Sn–Pt/NaY was used to catalyze the hydrogenation of furfural to furfuryl alcohol. The primary experiment results are listed in Table 3. Despite there being no significant change in the conversion ratio of Furfural, it is worth noting that the selectivity of furfuryl alcohol was enhanced prominently in comparison with that of Pt/NaY zeolite. It can be seen from the above experimental results that, for as-synthesized bimetallic Me_3Sn–Pt/NaY, notwithstanding that some unreacted Pt atoms and Me_3Sn–O complexes exist in the supercage of NaY zeolite, surely the Me_3Sn–O complexes is not responsible for the reaction, and those unreacted Pt atoms also do not play a role

Table 2. XPS analysis of Pt/NaY and $SnMe_3$/Pt/NaY sample: binding energies (eV) of Pt ($4f_{7/2}$) and Sn $3d_{5/2}$, $Sn3d_{3/2}$) electrons

Sample	Pt $4f_{7/2}$		$Sn3d_{3/2}$	$Sn3d_{5/2}$
Pt/NaY	71. 50			
$SnMe_3$/Pt/NaY	71.20	74.68	495.48	486.98

Table 3. The yields Furfural hydrogenation over Pt/NaY and PtSn/NaY (p = 1 atm, T = 423 K, HLSV = 0.40 g/g_{cat}h, hydrogen/furfural=8 mol/mol)

Catalyst	Furfural conversion(%)	Furfuryl alcohol Selectivity(%)	Tetrahydrofuryl alcohol Selectivity(%)	other products Selectivity(%)
Pt/NaY	72.26	40.62	30.09	29.29
PtSn/NaY	70.97	66.50	8.49	25.01

in enhancing the selectivity since Pt atoms can catalyze deep furfural hydrogenation.[32] Indeed, a key factor is the surface Me_3Sn-Pt complexes. In addition, the stereo effect of methyl may be propitious to producing unsaturated alcohol (UOL).[33] Comprehensive evaluation of catalysis activity and optimization of the synthesis conditions will be further investigated in later work.

CONCLUSION

Pt atoms of Pt/NaY zeolite can react with tetramethyltin to form a bimetallic Me_3Sn-Pt surface species in the presence of hydrogen at 353 K. Per-gram Pt/NaY (2% of Pt) reacting with excessive of $SnMe_4$ at 353 K for 24 h results in 0.085 mmol Sn grafted on the surface of Pt atoms. After modification, the crystal structure of Pt/NaY zeolite is not destroyed, but the surface properties are changed. The BET surface area and the pore volume of zeolite decrease, while the microporous structure is retained. The CO chemisorption results and the XPS results show that the electronic properties of the modified Pt atoms on surface of NaY zeolite are altered remarkably by the inductive effect of electrons between Pt and methyl groups, consequently weakening the deep hydrogenation ability of Pt to furfural, and enhancing the selectivity of furfuryl alcohol. The bimetallic Me_3Sn-Pt surface species is responsible for the enhancement of the selectivity.

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