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Study of the grafting reaction of $SnMe_4$ on the surface of ZSM-5 zeolite

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The grafting reaction of tetramethyltin on the surface of ZSM-5 zeolite (Si : Al = 55.0) was studied under vacuum conditions, and the chemical compositions, structure and properties of the resulting solid were characterized by *in situ* FTIR, ICP, XRD, XPS, UV–vis DRS, temperature programmed decomposition (TPD) and N_2 adsorption. The results show that the reaction occurs on the surface of ZSM-5 zeolite at 223 K without destroying the zeolite framework. The BET surface area and the pore volume of the zeolite decrease and the surface properties change; however, the microporous structure is retained during the reaction and post treatment. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: surface organometallic chemistry; tetramethyltin; ZSM-5 zeolite; grafting reaction

INTRODUCTION

Zeolite ZSM-5, a medium-pore zeolite with a two-dimensional pore structure, contains two intersecting channel systems. One channel is sinusoidal and runs parallel to the *a*-axis of the orthorhombic unit cell. The other channel is straight, and parallel to the *b*-axis.[1,2] The elliptical 10-membered ring openings controlling the channels have an effective diameter of ca. 0.56 nm, less than that of Y and β zeolite. This novel and unique structure differs remarkably from the familiar large-pore faujasite Y and β zeolite with a three-dimensional pore structure. Owing to the unique channels, the strong acidity and the modifiable framework, ZSM-5 zeolite has been used successfully as a catalyst for cracking *n*-hexane, xylene isomerization, ethylbenzene dealkylation and hydrocarbon formation from methanol etc.[3]

The modification of zeolite extends its application field. At present, besides typical ion-exchange methods and isomorphous substitution, some new modified techniques, such as surface organometallic chemistry (SOMC), have been used to modify zeolites and molecular sieves. One of the main objectives of surface organometallic chemistry is to construct single-site catalysts with well-defined structure and composition via quantitative grafting of organometallic compounds to the surface of inorganic solids.[4] This strategy provides a novel route for the immobilization of catalysts, and has been used successfully to prepare zeolites and molecular sieves containing highly dispersed and well-defined titanium and iron active centers.[5–7] Previous results[8–10] show that the grafting only modifies the surface of zeolites without destroying the zeolite framework, and retaining the microporous structure. Modified zeolites can be still used as catalysts. However, the structural differences between zeolites lead possibly to differences in reactivities with tetramethyltin. In order to understand the reactive nature, in this study, the grafting of tetramethyltin to the surface of ZSM-5 zeolite and the resulting surface species were investigated by *in situ* Infrared spectra (IR), X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), UV-visible diffuse reflectance spectroscopy (UV-vis/DRS), Temperature Programmed Decomposition (TPD) and N_2 adsorption. The differences in reactivities of tetramethyltin with zeolites HZSM-5, HY, Hβ and MCM-41 are discussed in combination with previous results. This study may provide information of use as part of a foundation for the design of catalysts.

EXPERIMENTAL

Materials

ZSM-5 zeolite used for these experiments was purchased from Aldrich and had a Si : Al ratio equal to 55.0. Tetramethyltin ($SnMe_4$, 99.5%) was purchased from Aldrich.

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Preparation of $(Me)_3Sn$-ZSM-5 zeolite

An amount of ZSM-5 zeolite was enclosed in a self-made glass equipment connected to a vacuum line and treated under dynamic vacuum (10^{-3} Pa) at 673 K for 3 h. After cooling to room temperature, a large excess of liquid tetramethyltin was introduced to the reaction system with a syringe via a septum. A liquid nitrogen trap was used to condense the tetramethyltin vapour. The trap was removed and the reactor heated to 333 K for 5 h to ensure a complete reaction. The evolved gases were analyzed by gas chromatography (GC). Unreacted $SnMe_4$ was removed using dynamic vacuum (10^{-3} Pa) for 3 h at this temperature and the solid was transferred under pure nitrogen into a small ampoule.

The grafting reaction was also monitored by *in situ* infrared spectroscopy. A 20–30 mg aliquot of ZSM-5 zeolite was pressed into a self-supporting wafer (diameter 18 mm) and loaded in a self-made IR cell with CaF_2 windows. The same treatment as above was performed and the IR spectra during treatment recorded on a Nicolet Nexus 670 FTIR spectrometer.

Characterization

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

The content of tin in the resulting solid was determined by 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).

XRD patterns were obtained using a Brucker Advance D8 X-ray powder diffractometer with Cu–K_α radiation (40 kV, 40 mA) at a scan speed of 0.2 in increments of $0.02°2\theta$.

N_2-physisorption (77 K) studies were carried out using an OMNISORP 100CX gas adsorb analyzer. A 0.10–0.15 g aliquot of sample was treated first under dynamic vacuum (10^{-6} Torr) at 333 K for 3 h.

The diffuse reflectance UV–vis spectra were recorded on a Varian Cary-500 spectrometer equipped with a diffuse-reflectance accessory. The spectra were collected at 200–500 nm referenced to $BaSO_4$.

Temperature-programmed decomposition (TPD) experiments were performed on an Autochem 2910 automatic catalyst characterization system equipped with an Omnistar GSD30103 mass spectrograph. The sample loading was 0.2 g. The flow rate of the supporting gas (He for TPD and 10% H_2–Ar for TPR) was 30 ml min^{-1} and the heating rate was 5 K min^{-1}.

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, 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.

RESULTS AND DISCUSSION

Grafting reactions of $SnMe_4$ on HZSM-5 zeolite

The FTIR spectra of HZSM-5 zeolite in the region 4000–2400 cm^{-1} is shown in Fig. 1. After treatment under vacuum at 673 K for 3 h, the zeolite shows three adsorption bands at 3727, 3667 and 3610 cm^{-1} [Fig. 1(a)], which can be assigned to terminal silanol OH groups, bridging OH [Si–(OH)–Al groups having strong Brönsted acidity] and OH connected to extra framework Al, respectively.[11–13] When tetramethyltin is contacted with HZSM-5 zeolite at 223 K, both *in situ* IR and GC analyses reveal that methane is the only gaseous product. This indicates that grafting can occur at this temperature, but this temperature is higher than those reported for grafting $SnMe_4$ to HY zeolite (193 K)[8] and Hβ

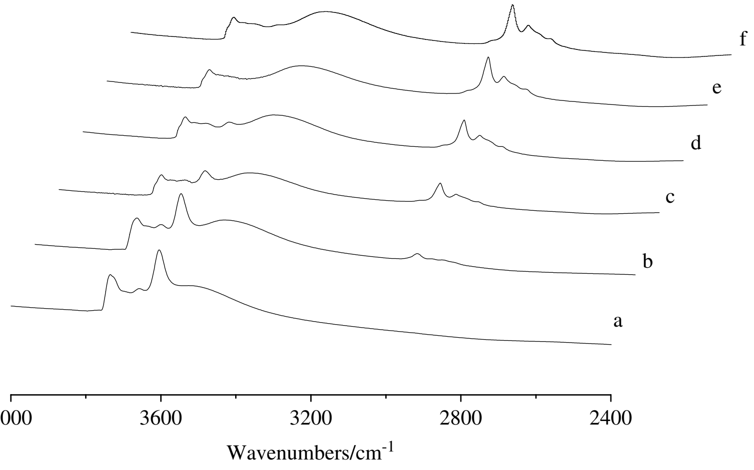

Figure 1. IR spectra of HZSM-5 before and after reaction with $SnMe_4$. (a) HZSM-5 dehydroxylated at 673 K. (b) HZSM-5 after reaction with $SnMe_4$ at 333 K for 1 h. (c) at 333 K for 10 h. (d) at 333 K for 20 h (e) at 333 K for 24 h. (f) at 333 K for 30 h.

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(183 K),[9] and is lower than those reported for grafting $SnMe_4$ on silica (298 K)[14] and MCM-41 (343 K).[10] It suggests that the channel structure and acidity of zeolites may have important effects on the grafting reaction.

After reacting for 1 h at 333 K, as shown in Fig. 1(b), a methyl (C–H) absorption band is observed clearly in the range 3000–2900 cm^{-1}, and the intensities of both OH absorption bands at 3660 and 3610 cm^{-1} decrease gradually with increasing reaction time, along with increasing C–H vibration absorption band, while the band at 3727 cm^{-1} does not change. This indicates that the reaction of $SnMe_4$ with HZSM-5 occurs mainly on the bridge OH and the extra framework Al–OH. After reacting for 24 h, the lack of changes in the absorption bands [Fig. 1(e, f)] suggests a complete reaction between surface hydroxyls and $SnMe_4$.

The reaction of $SnMe_4$ with deuterated ZSM-5 zeolite was examined to confirm grafting under the same conditions. As is shown in Fig. 2, HZSM-5 is exchanged by D_2O for 3 h to form D-ZSM-5. Three OH bands at 3660, 3727 and 3610 cm^{-1} decrease significantly, while three new bands appear at 2760, 2730 and 2670 cm^{-1}, which are assigned to Si–OD, Al–OD and Si–(OD)–Al, respectively [Fig. 3(b)].[15,16] After exchanging for 5 h, 95% of hydroxyls are deuterated [Fig. 3(c)].

When $SnMe_4$ is introduced to react with DZSM-5 under the above conditions, the vibration absorption bands of C–H in the range 3000–2900 cm^{-1} are observed clearly as well. GC-MS analysis shows that gas products consist of 95% CH_3D and a small amount of CH_4. This is due to the incomplete deuteration of HZSM-5 zeolite. With increasing reaction time, the Al-OD and Si–(OD)–Al bands decrease, accompanied

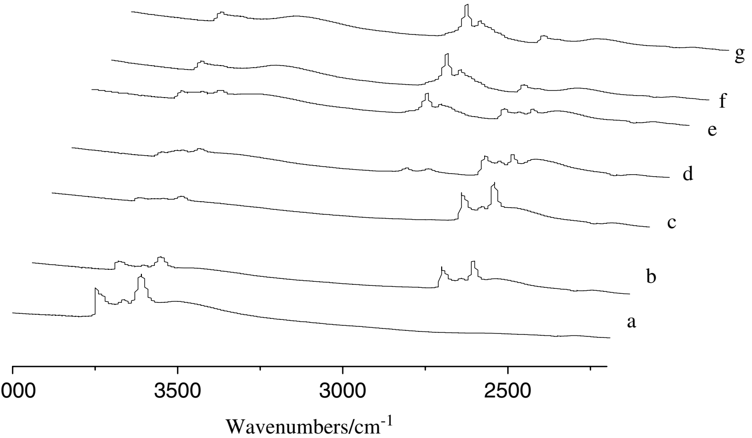


Figure 2. Infrared spectra of ZSM-5 (deuterated) before and after reaction with $SnMe_4$. (a) ZSM-5 dehydroxylated at 673 K for 3 h. (b) ZSM-5 (OD exchanged) 3 h. (c) ZSM-5 (OD exchanged) 5 h. (d) ZSM-5 reacted with $SnMe_4$ at 333 K for 2 h and evacuated at 333 K for 1 h. (e) at 333 K reacted 10 h and evacuated for 2 h. (f) at 333 K reacted 24 h and evacuated for 2 h. (g) at 333 K reacted 30 h and evacuated for 2 h.

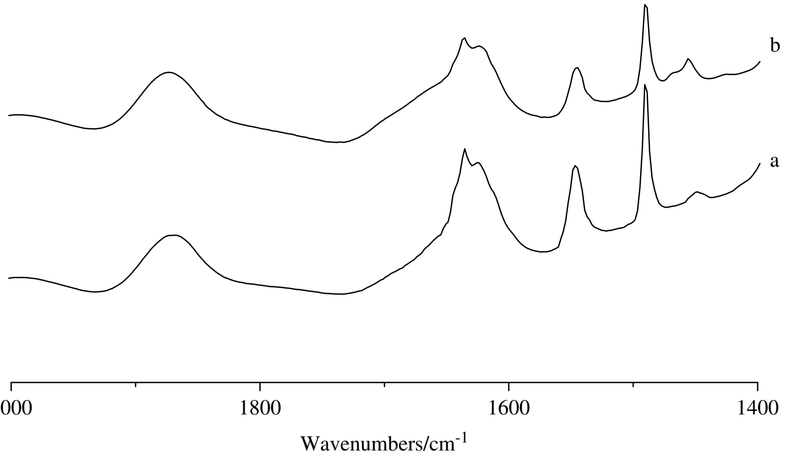
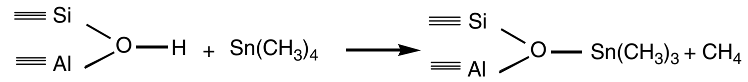


Figure 3. Infrared spectra of adsorbed pyridine on zeolite (at room temperature for 3 h) and evacuation (at 423 K, 10^{-3} Pa). (a) ZSM-5. (b) the modified ZSM-5 by $SnMe_4$.



Scheme 1. The reaction of $SnMe_4$ with the hydroxyls of HZSM-5 zeolite.

by increases in the vibration absorption bands of methyl [Fig. 3(d–g)]. GC analysis shows that, when the reaction is continued for 24 h at 333 K, the amount of CH_3D reaches a maximum, supporting the conclusion that $SnMe_4$ can react with the surface hydroxyls of HZSM-5 at this temperature.

In order to accurately analyze the reaction products, 500 mg of HZSM-5 zeolite and excess $SnMe_4$ were used to redo this experiment under the same conditions. Chemical analysis of the resulting solid after removal of the physisorbed species gives a C : Sn mole ratio of 2.92 (%C = 0.50 wt%, %Sn = 1.70 wt%). The above results suggest that $SnMe_4$ reacts with the Brönsted acid OH and Al–OH of HZSM-5 to form (Al–O–Si) $SnMe_3$ (Scheme 1) surface species. The reaction is as shown in Scheme 1. It is analogous to the grafting reactions occurring on silica[14] and HY zeolite.[8]

The grafting of —$SnMe_3$ to acid hydroxyls of HZSM-5 zeolite is also supported by IR studies on pyridine absorption on the modified and unmodified samples (Fig. 3). After HZSM-5 zeolite adsorbs pyridine [Fig. 3(a)], three characteristic absorption bands, corresponding to the C–C stretching vibrations of pyridine adsorbing on Brönsted acid sites, Brönsted + Lewis acid sites and Lewis acid sites, appear at 1545, 1490 and 1455 cm^{-1}, respectively.[17] The intensities of the 1545 and 1490 cm^{-1} bands become much weaker after HZSM-5 zeolite is modified. The intensity of the 1545 cm^{-1} band decreases by 60%, indicating that the grafting reaction occurs on the Brönsted acid sites of HZSM-5.

The increase in the intensity for band 1455 cm^{-1} is related possibly to an enhancement of Lewis acidity caused by the inductive effect of $SnMe_3$ group as an electron donor. The above results differ considerably from those of HY zeolite as a support. The decreasing intensity of the 1545 cm^{-1} band was beyond 95% after HY zeolite was modified, showing that the majority of the supercage acid OHs react with $SnMe_4$.[8] The small main channels (0.56 nm) of HZSM-5 zeolite, which are less than the supercage window (0.74 nm) of HY zeolite and the 12-membered ring openings (0.62 nm) of Hβ, are responsible mainly for this difference because a small amount of $SnMe_4$ can enter the channels to react with surface acid hydroxyls.

Structure and properties of the grafted sample

Comparison of the XRD patterns of HZSM-5 and the modified HZSM-5 sample (Fig. 4) shows that their structures are essentially the same, which suggests that the grafting reaction does not destroy the framework structure, and the grafting reaction occurs only on the surface of zeolite. The texture parameters (Table 1) show that the modified HZSM-5 zeolite still retains the microporous characteristics. BET surface area, micropore volume and total pore volume of zeolite only decrease by 9.51, 9.30 and 16.49%, respectively, suggesting that a small amount of organotin species is grafted on the surface of the channel. The DRS spectrum of the modified sample appears to have a stronger absorption band at 230 nm (Fig. 5), which arises from the ≡SiO–$SnMe_3$ surface species, showing that Sn atoms grafted on surface exist in a tetra-coordinated state.[18–20] However, in comparison with DRS spectra of the modified HY and Hβzeolites,[8,9] the band shifts towards the longer wavelength region.

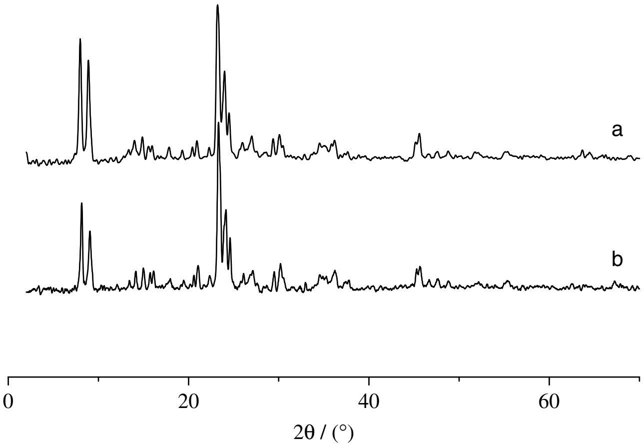


Figure 4. XRD profile of ZSM-5 zeolite before (a) and after (b) modification with $SnMe_4$.

Table 1. BET surface area micropore volume (*Vu*) and total porevolume (*Vt*) of HZSM-5 zeolite modified or unmodified by reactionwith tetraalkyl tin

Sample	BET ($m^2\,g^{-1}$)	*Vt* ($cm^3\,g^{-1}$)	*Vu* ($cm^3\,g^{-1}$)
HZSM-5	334	0.172	0.188
$SnMe_3$/HZSM-5	305	0.156	0.157

XPS characterization of the grafted sample

XPS full range survey spectrum of the modified sample obviously shows the Sn3d, C1s, Si2p, Si2s and O1s peaks (Fig. 6), indicating the existence of tin, carbon, silicon and oxygen on the surface of the grafted sample. The binding energies of $Sn3d_{3/2}$ and $Sn3d_{5/2}$ are 500.90 and 492.30 eV, respectively (Fig. 7). The difference between both values is equal to 8.60 eV, indicating that tin exists in the form of Sn^{4+}, but not in the form of Sn^0.[21,22]

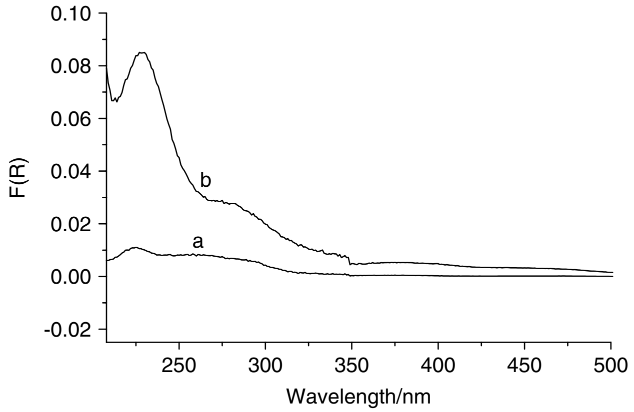


Figure 5. UV–visible diffuse reflectance spectra of ZSM-5 zeolite after and before reaction with $SnMe_4$ (a) ZSM-5 (b) reaction with $SnMe_4$.

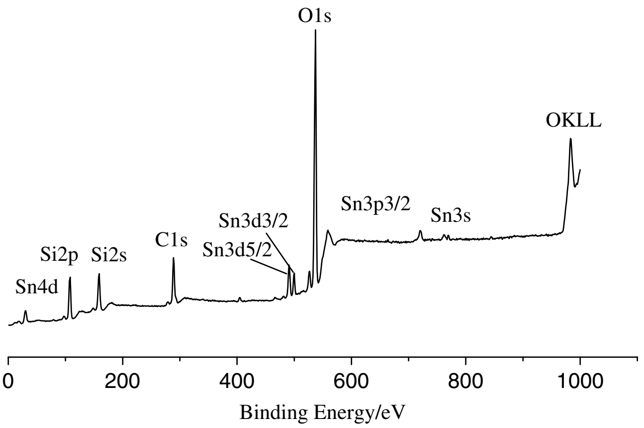


Figure 6. XPS survey scan spectra of $SnMe_3$/ZSM-5.

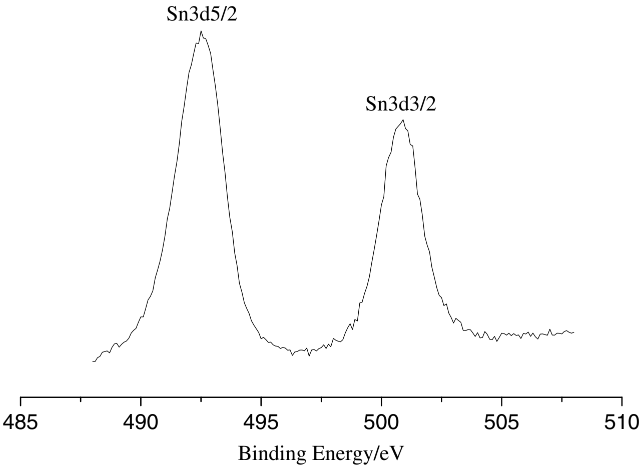


Figure 7. XPS Sn3d narrow scan spectra of $SnMe_3$/ZSM-5.

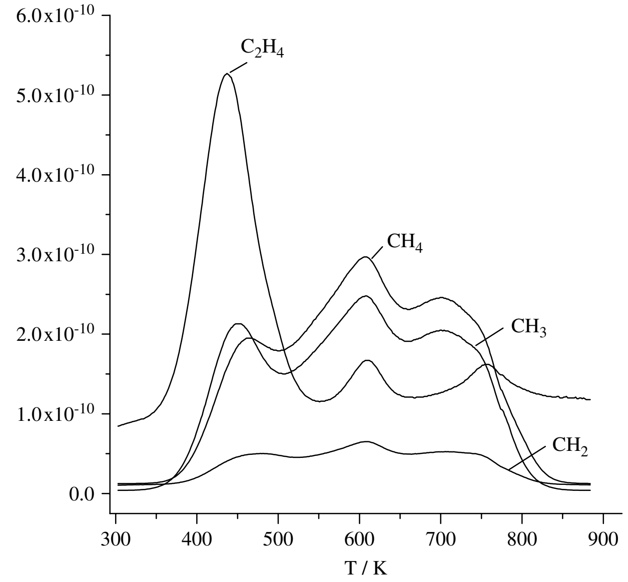


Figure 8. TPD-MS spectra of $SnMe_3$/ZSM-5.

The thermal stability of the grafted sample

The results of TPD carried out in flowing He are shown in Fig. 8. C_2H_4, CH_4, CH_3 and CH_2 are detected from 350 to 850 K, showing that decomposition of $SnMe_3$/ZSM-5 and polymerization of the gaseous products occur in this temperature range. Each TPD pattern shows three desorption peaks and the area ratios of the three peaks, such as CH_4, CH_3 and CH_2, are close to 1 : 1:1, indicating that decomposition of $SnMe_3$/ZSM-5 occurs in three steps. The decomposition of both $SnMe_3$/HY and $SnMe_3/H\beta$ occurs in two steps.[8,9] The decomposition onset temperatures are at 473 and 523 K, respectively, and are higher than for $SnMe_3$/ZSM-5. This suggests that the pore structure and acidity of zeolites play a crucial role in the thermal stability of the grafted species. The confined spaces of pore in ZSM-5 zeolite decrease the thermal stability of the $SnMe_3$ surface species. The mechanism of the stepwise decomposition of $SnMe_3$/ZSM-5 is similar to that of $SnMe_3/H\beta$.[9] It is noteworthy that the evolution of C_2H_4 is far greater than that of CH_4 at an onset decomposition temperature of 450 K. This possibly results from C–C coupling of methane catalyzed by ZSM-5 zeolite, which has been investigated in depth.

$$350\text{–}550\ \text{K}: \text{SnMe}_3/\text{ZSM-5} \longrightarrow \text{SnMe}_2/\text{ZSM-5} + \text{MeH} \quad (1)$$

$$553\text{–}603\ \text{K}: \text{SnMe}_2/\text{ZSM-5} \longrightarrow \text{SnMe}/\text{ZSM-5} + \text{MeH} \quad (2)$$

$$623\text{–}823\ \text{K}: \text{SnMe}/\text{ZSM-5} \longrightarrow \text{Sn}/\text{ZSM-5} + \text{MeH} \quad (3)$$

CONCLUSION

Hydroxyl groups on HZSM-5 zeolite can react with tetramethyltin to form a surface species (≡Si–O–Al≡) $SnMe_3$

on the surface of zeolite. Per-gram HZSM-5 zeolite reacting with excess $SnMe_4$ at 333 K for 24 h results in 0.146 mmol tetracoordinated tin grafted on the surface. Modification by $SnMe_4$ does not change the zeolite structure of HZSM-5, but its surface properties are altered. The BET surface area and the pore volume decrease, while the microporous structure is retained. The stepwise decomposition of $SnMe_3$/ZSM-5 occurs at 450, 600 and 710 K, respectively. It is completely different from those of $SnMe_3$/HY, $SnMe_3$/Hβ and $SnMe_3$/MCM-41.

Acknowledgments

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REFERENCES

1. Kokotailo GT, Lawton SL, Olson DH, Meier WM. *Nature* 1978; **272**: 437.
2. Pope CG. *J. Catal.* 1981; **72**: 174.
3. Chu CTW, Kuehl GH, Lago RM, Chang CD. *J.Catal.* 1985; **93**: 451.
4. Copéret C, Chabanas M, Arroman RPS, Basset JM. *Angew. Chem. Int. Edn* 2003; **42**(2): 156.
5. Wang XX, Lian WH, Fu. XZ, Basset JM, Lefebvre F. *J. Catal.* 2006; **238**: 13.
6. Maschmeyer T, Rey F, Sankar G, Thomas JM. *Nature* 1995; **378**: 159.
7. Nozaki C, Lugmair CG, Bell AT, Tilly TD. *J. Am. Chem. Soc.* 2002; **124**: 13194.
8. Zheng Y, Wang XX, Fu XZ, Wei KM. *Acta Chim. Sin.* 2004; **64**(5): 449.
9. Zheng Y, Wang XX, Li ZhH, Fu XZ, Wei KM. *J. Organomet. Chem.* 2005; **690**: 3187.
10. Zheng Y, Wang XX, Fu XZ, Wei KM. *Phys. Chin. Sin.* 2005; **21**(2): 149.
11. Brabec L, Nováková J, Kubelková L. *J. Mol. Catal.* 1994; **94**: 117.
12. Zhang JZ, Longa MA, Howe RF. *Catal. Today* 1998; **44**: 293.
13. Tynjälä P, Pakkanen TT. *J. Mol. Catal. A: Chem.* 1997; **122**: 159.
14. Ne'dez C, Theolier A, Lefebvre F, *et al. J. Am. Chem. Soc.* 1993; **115**: 722.
15. Kondo JN, Domen KJ, Wakabayashi F. *Micropor. Mesopor. Mater.* 1998; **21**: 429.
16. Kondo JN, Domen K. *J. Mol. Catal. A: Chem.* 2003; **199**: 27.
17. Mihályi RM, Beyer HK, Mavrodinova V, Minchev C, Neinska Y. *Micropor. Mesopor. Mater.* 1998; **24**: 143.
18. Mal NK, Ramaswamy VA. *J. Mol. Catal. A: Chem.* 1996; **105**: 149.
19. Chaudhari K, Das TK, Rajmohanan PR, Lazar K, Sivasanker S, Chandwadkar AJ. *J. Catal.* 1999; **183**: 281.
20. Dutoit DCM, Schneider M, Baiker A. *J. Catal.* 1995; **153**: 165.
21. Bernede JC, Marsillac S. *Mater. Res. Bull.* 1997; **32**(9): 1193.
22. Lee WH, Son HC, Moon HS, Kim YI, Sung SH, Kim JY, Lee JG, Park JW. *J. Power Sources* 2000; **89**: 102.

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