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Grafting $SnCl_4$ catalyst as a novel solid acid for the synthesis of 3-methylbut-3-en-1-ol

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ABSTRACT

Grafting $SnCl_4$ on inorganic support as a novel solid acid catalyst was used to catalyze the Prins condensation reaction of isobutene with formaldehyde to produce 3-methylbut-3-en-1-ol (MBOH). Three supports of SiO_2, $SiO_2–Al_2O_3$ and γ-Al_2O_3 were used to prepare the catalysts, and the structure and acid property of the tin chloride species formed over different supports was investigated. It was found that the $SnCl_4$ grafted on SiO_2 exhibited high activity and selectivity at a low reaction temperature of 100 °C, with formaldehyde conversion of 55% and MBOH selectivity of 92%. The superior performance of $SnCl_x–SiO_2$ catalyst was attributed to its low electron density of tin nucleus and strong Lewis acidity.

1. Introduction

3-Methylbut-3-en-1-ol (MBOH) is an important chemical intermediate for producing organic compounds such as paints, pesticides and citral aldehyde [1,2]. MBOH is available to be produced by Prins condensation reaction of isobutene with formaldehyde under anhydrous conditions in the presence of $SnCl_4$, $ZnCl_2$, or $SiCl_4$ as the catalyst [3]. However, these homogeneous catalysts pose considerable problems such as toxicity, potential danger in handling, disposal problems due to large amount of acidic effluents, and difficulties in product isolation [4]. Thus, many efforts have been concentrated on some solid catalysts for an environmentally friendly manufacture of MBOH. Dumitriu [5,6] studied the catalytic performance of isobutylene with formaldehyde to isoprene over a series of zeolites (HY, USY, H-ZSM-5, H-Boralite, H-B-MCM-41) at 300 °C in a pulse microreactor. It has been pointed out that the acid strength of the catalyst is the most important factor affecting the product selectivity, and the zeolite has been employed as potential substitutes for Prins condensation. However, the high reaction temperature and pressure conditions are needed for a feasible commercial process. In 2001, a novel reusable Lewis acid catalyst of $SnCl_4$ anchored on tetraalkylammonium chloride functionalized MCM-41 was developed [7]. The conversion of formaldehyde and the selectivity to MBOH over the tin chloride immobilized on organic functionalized MCM-41 at 60 °C after 2 h were about 76 and 94%, respectively. Owing to the high catalytic activity and mild reaction conditions, it has attracted much attention.

In the present work, we initiate our investigation on the catalyst preparation of grafting $SnCl_4$ on different supports by using a simple procedure. The aim is to study the effect of support on the tin chloride structure and on the catalytic performance of the catalysts for the condensation of isobutene with formaldehyde. The relationship between the structure of tin chloride species and its catalytic activity was discussed.

2. Experimental

2.1. Catalyst preparation

Three kinds of commercially available supports made in China were used in the present study. Silica gel was produced by the Branch of Qingdao Haiyang Chemical Plant Co. Silica–alumina and alumina were provided by the Fushun Research Institute of Petroleum and Petrochemicals. The graft process of $SnCl_4$ on silica gel was carried out as follows: the starting silica gel before use was dehydrated at 300 °C for 3 h. 4.46 g of a solution of anhydrous $SnCl_4$ in 30 ml ethanol was added to 10 g of silica gel followed by stirring overnight at 78 °C. After the above treatment, the material was exhaustively washed with ethanol and dried under vacuum. The

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catalysts of grafting $SnCl_4$ on silica–alumina and alumina supports were also prepared by the same method.

2.2. Catalyst characterization

The BET surface areas and the pore properties of supports and catalysts were measured by nitrogen physisorption on a ASAP 2010 instrument at 77 K. The chloride content of the catalysts was determined by using inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 2000DV). ^{119}Sn Mössbauer spectra of the catalysts and a standard SnO_2 were recorded by a conventional Mössbauer spectrometer (Topologic, Japan) working in a constant acceleration mode in transmission geometry. A $Ca^{119}SnO_3$ Mössbauer source was used to supply the gamma rays for the measurements. The velocity calibration was performed by α-Fe and standard $CaSnO_3$ measurements. The spectra were fitted with appropriate superpositions of Lorentzian lines using the MossWinn computer program [8]. Fourier transform infrared (FTIR) spectra of the catalysts chemically adsorbed pyridine were collected on an EQUINOX55 FTIR spectrometer. The catalysts were smashed to 200 mesh and used as thin wafer (8 mg/cm^2). Firstly, the catalyst wafer was placed in the measurement cell and pretreated at 150 °C under vacuum for 2 h, cooled down to room temperature, followed by exposure to pyridine at this temperature for 30 min; secondly, the sample was evacuated at 150 °C under vacuum (10^{-5} Torr) for 1 h to remove physically adsorbed pyridine; finally, the spectra were separately recorded at 150 °C.

2.3. Catalytic activity measurements

The Prins condensation reaction of isobutene with formaldehyde was carried out in a magnetically stirred autoclave at 100 °C. Paraformaldehyde (1.5 g), isobutene (8.4 g) and fresh catalyst were loaded in the reactor containing 15 ml of dioxane (solvent) and then stirred for 3 h. Samples of the reaction mixture were analyzed by a gas chromatographic analyzer (Agilent-6890 N) equipped with a HP-5 capillary column (length: 30 m; diameter: 0.53 mm; thickness of the film: 0.15 μm) and a flame ionization detector (FID).

3. Results and discussion

3.1. Structure of tin chloride grafted on different supports

The BET surface area, pore diameter and the loadings of tin chloride of the catalysts are presented in Table 1. Compared with the pure supports, three grafting $SnCl_4$ catalysts show the decreasing pore diameter and surface area, which is primarily due to the penetration of $SnCl_4$ into the pores of support. Based on the results of Cl/Sn atomic ratio listed in Table 1 and the immobilization model of $AlCl_3$ on silica gel reported by others [9,10], we propose that the graft mechanism of $SnCl_4$ on support surface is possibly via the reaction of $SnCl_4$ with the surface hydroxyl groups of the support accompanied by HCl release. The loaded chloride species on catalyst surface is available to be expressed as $–SnO_{4-x}Cl_x$ herein below. From Table 1, it can be seen that with the support order of SiO_2, $SiO_2–Al_2O_3$ and Al_2O_3, both the Sn and Cl loadings are increased, and the atomic ratio of Cl/Sn is enhanced simultaneously. It is noted that the property of support influences the chloride loading and its structure. Usually, the atomic ratio of chlorine to metal can be used to deduce the chemical configuration of grafted chloride on the support [10]. So, for the catalyst of $SnCl_x–Al_2O_3$, the value of Cl/Sn is 3.06, which is very close to 3, indicating that the most possible composition of Sn species is $–SnOCl_3$. For the catalyst of $SnCl_x–SiO_2$, the value of Cl/Sn ratio of is 2.46, which is smaller than that of $SnCl_x–Al_2O_3$, indicating that the composition of tin species in this catalyst is not only $–SnOCl_3$ but also $–SnO_2Cl_2$.

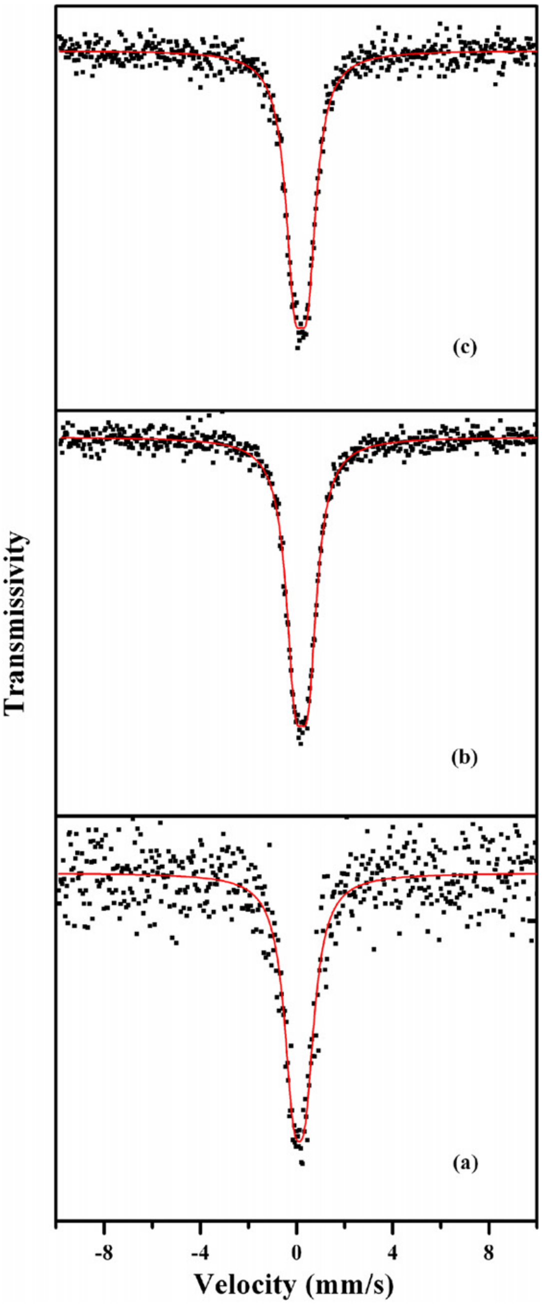

Fig. 1. ^{119}Sn Mössbauer spectra of the grafting $SnCl_4$ catalysts at room temperature: (a) $SnCl_x–SiO_2$, (b) $SnCl_x–SiO_2–Al_2O_3$, and (c) $SnCl_x–Al_2O_3$.

In order to identify the coordination environment and valence state of tin species in the catalyst surface, ^{119}Sn Mössbauer spectra of the three prepared catalysts (see Fig. 1) are measured at room temperature. It is found that the ^{119}Sn Mössbauer spectra of all the grafting $SnCl_4$ catalysts can be fitted with a single narrow quadrupole doublet. The Mössbauer parameters are listed in Table 2. For comparison, the Mössbauer results of both standard SnO_2 measured here and bulk $SnCl_4$ reported by Burger et al. [11] are also included in Table 2. The IS values of the three catalysts are estimated in the range of −0.01 to 0.09 mm/s relative to $CaSnO_3$, which are clearly lower than that of bulk $SnCl_4$ (0.72 mm/s) and larger than that of the standard SnO_2 (−0.04 mm/s). It indicates that some new tin species are formed on the catalyst surface, and the electron density of the tin nucleus is lower than that of bulk $SnCl_4$ and higher than that of

Table 1
Physico-chemical properties of the supports and grafting $SnCl_4$ catalysts.

Catalyst	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Pore diameter (nm)	Sn^{4+} loading (mmol g-cat^{-1})	Cl^- loading (mmol g-cat^{-1})	Cl/Sn of atomic ratio
$SnCl_x$–SiO_2	269	0.83	9.48	0.37	0.91	2.46
$SnCl_x$–SiO_2–Al_2O_3	230	0.59	9.85	0.39	1.07	2.78
$SnCl_x$–Al_2O_3	245	0.59	7.70	0.47	1.44	3.06
SiO_2	344	0.93	10.81	–	–	–
SiO_2–Al_2O_3	261	0.65	10.80	–	–	–
Al_2O_3	292	0.66	9.43	–	–	–

Table 2
^{119}Sn Mössbauer parameters at 293 K.

Catalyst	Position	IS[b] (mm/s)	QS (mm/s)	LW (mm/s)
SnO_2	Bulk	−0.04	0.58	1.23
$SnCl_x$–SiO_2	Surface bound	−0.01	0.50	0.97
$SnCl_x$–SiO_2–Al_2O_3	Surface bound	0.07	0.55	0.90
$SnCl_x$–Al_2O_3	Surface bound	0.09	0.55	0.91
$SnCl_4$[a]	Bulk	0.72	–	–

[a] This data were obtained by Burger et al. [11].

[b] The IS values were referred to the $CaSnO_3$ standard absorber.

standard SnO_2. As we know, the catalyst support can influence the properties of the supported active centre due to its interaction [12]. The IS values listed in Table 2 increase in the sequence as $SnO_2 < SnCl_x$–$SiO_2 < SnCl_x$–SiO_2–$Al_2O_3 < SnCl_x$–$Al_2O_3 < SnCl_4$, that means the electron density of the tin nucleus decreases with the trend of $SnCl_4 > SnCl_x$–$Al_2O_3 > SnCl_x$–SiO_2–$Al_2O_3 > SnCl_x$–$SiO_2 > SnO_2$, and this variability of IS values should be ascribed to the replacement of the Cl atom by more electronegative O atom [13]. The higher IS value of $SnCl_x$–Al_2O_3 indicates that the grafting tin chloride species on Al_2O_3 surface contains more Cl atoms. It is consistent with the results of Cl/Sn atomic ratio measured by ICP method (Table 1).

Based on the ICP, Mössbauer data and the previous studies about immobilization of $AlCl_3$ on silica gel [10,14], the possible structure of tin chloride grafted on SiO_2 and Al_2O_3 are proposed as shown in Fig. 2.

3.2. Acidity characterization of catalysts

The pyridine-FTIR spectra of $SnCl_x$–SiO_2, $SnCl_x$–SiO_2–Al_2O_3 and $SnCl_x$–Al_2O_3 recorded at 150 °C are shown in Fig. 3. It is known that the band at 1546 cm^{-1} is attributed to Brönsted acid sites, the band at 1454 cm^{-1} is assigned to Lewis acid sites and the band at 1496 cm^{-1} is assigned to a combination signal associated with both Brönsted and Lewis acid sites [15]. From Fig. 3 it can be seen that Lewis acid sites are the predominant acid species on the three grafting $SnCl_4$ catalysts.

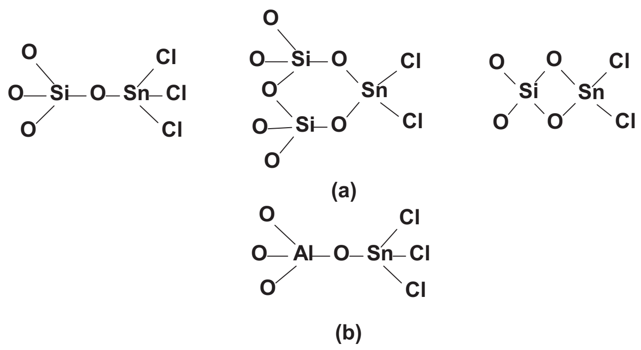

Fig. 2. Proposed the structures of grafting tin chloride species over the SiO_2 (a) and Al_2O_3 (b) supports.

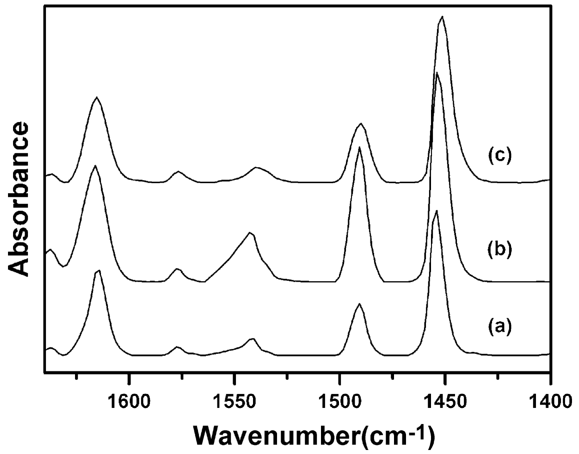

Fig. 3. Pyridine-FTIR spectra of (a) $SnCl_x$–SiO_2, (b) $SnCl_x$–SiO_2–Al_2O_3, and (c) $SnCl_x$–Al_2O_3.

Table 3
Infrared shift data for pyridine adsorbed onto the grafting $SnCl_4$ catalysts.

Catalyst	Shift of Lewis band[a] (cm^{-1})
$SnCl_x$–SiO_2	16.4
$SnCl_x$–SiO_2–Al_2O_3	15.0
$SnCl_x$–Al_2O_3	13.4

[a] The free pyridine band occurs at 1438.5 cm^{-1}.

A summary of the infrared shift data for pyridine adsorbed onto the catalysts is presented in Table 3. The largest peak shift was obtained over $SnCl_x$–SiO_2, while the lowest one was found over $SnCl_x$–Al_2O_3 catalyst. The inductive effect from the donation of the nitrogen lone pair of the pyridine to a vacant orbital on a Lewis acid increases the pπ–pπ interaction between the nitrogen and ring carbons, leading to an increase in the bending mode frequency as the strength of the Lewis acid increases [16]. So, the largest infrared shift of pyridine in $SnCl_x$–SiO_2 can be ascribed to its strongest Lewis acidity, and the order of the acidity strength of above three catalysts is as follows: $SnCl_x$–$SiO_2 > SnCl_x$–SiO_2–$Al_2O_3 > SnCl_x$–Al_2O_3. This furtherly confirmed the structures of tin chloride grafted on different supports as proposed in Fig. 2.

3.3. Catalytic performance

The catalytic properties of catalysts were evaluated in terms of formaldehyde conversion, products selectivity and MBOH yield. As shown in Table 4, the highest formaldehyde conversion of 55% and MBOH yield of 54% were obtained over the catalyst of $SnCl_x$–SiO_2, while the lowest condensation reaction activity was found over $SnCl_x$–Al_2O_3. This activity tendency of catalysts is associated with their acid strengths and electron density of tin nucleus, which means that both the strong Lewis acidity and relatively low electron density of tin nucleus are beneficial to the Prins condensation of formaldehyde with isobutene for the grafting

Table 4
Comparison of the catalyst performances in the Prins condensation of isobutene with formaldehyde.

Catalyst[a]	Conversion of formaldehyde (%)	Selectivity[b] (%)		MBOH yield[c] (%)
		Isobutene oligomer	MBOH	
$SnCl_x–SiO_2$	55	6	92	54
$SnCl_x–SiO_2–Al_2O_3$	47	19	76	45
$SnCl_x–Al_2O_3$	21	11	84	20
SiO_2	0	0	0	0
$SiO_2–Al_2O_3$	24	24	61	15
Al_2O_3	11	3	88	10

[a] Catalysts containing 0.25 mmol of $SnCl_x$ species, the amount of bare supports were the same with its corresponding grafted $SnCl_4$ catalysts.
[b] Other products included 4,4-dimethyl-1,3-dioxane and 3-methylbut-2-en-1-ol.
[c] Yield was determined by using n-heptane as an internal standard.

$SnCl_4$ catalytic system. However, the MBOH selectivity decreases as the order of $SnCl_x–SiO_2 > SnCl_x–Al_2O_3 > SnCl_x–SiO_2–Al_2O_3$. In this reaction system, isobutene polymerization reaction can occur by the catalysis of tin chloride, accompanying with Prins condensation reaction. The high selectivity of isobutene oligomer over $SnCl_x–SiO_2–Al_2O_3$ catalyst should be related to $SiO_2–Al_2O_3$ support.

4. Conclusions

In conclusion, this study has demonstrated that grafting $SnCl_4$ catalyst has high catalytic activity and selectivity for Prins condensation of isobutene with formaldehyde to 3-methylbut-3-en-1-ol (MBOH), and the type of support greatly influences the structure of tin chloride species and the surface acidity of the catalyst. The species of $–SnO_2Cl_2$ with strong Lewis acidity could be identified over SiO_2 and $SiO_2–Al_2O_3$, while only $–SnOCl_3$ was found over Al_2O_3 surface. The strongest Lewis acidity of $SnCl_4$ grafted on SiO_2 and the lowest electron density of tin nucleus are considerable to be beneficial to the highest formaldehyde conversion and MBOH yield in the condensation of formaldehyde with isobutene. In short, the grafting $SnCl_4$ on inorganic support is a promising method for developing environmentally friendly alternative catalyst for the Prins condensation and thereby promoting the application of tin chloride based catalytic materials.

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References

[1] W. Rebafka, US Patent 4,310,709, 1982, Assigned to BASF Aktiengesellscharf.
[2] W.F. Hoelderich, Catal. Today 62 (2000) 115.
[3] E. Arundale, L.A. Mikelska, Chem. Rev. 51 (1952) 505.
[4] X. Hu, G.K. Chuah, S. Jaenicke, Appl. Catal. A: Gen. 217 (2001) 1.
[5] E. Dumitriu, D. Trong On, S. Kaliaguine, J. Catal. 170 (1997) 150.
[6] E. Dumitriu, V. Hulea, I. Fechete, C. Catrinescu, A. Auroux, J.-F. Lacaze, C. Guimon, Appl. Catal. A: Gen. 181 (1999) 15.
[7] T.M. Jyothi, M.L. Kaliya, M. Herskowitz, M.V. Landau, Chem. Commun. (2001) 992.
[8] Z. Klencsar, E. Kuzmann, A. Vertes, J. Radioanal. Nucl. Chem. 210 (1996) 105.
[9] R.S. Drago, S.C. Petrosius, C.W. Chronister, Inorg. Chem. 33 (1994) 367.
[10] S. Sato, G.E. Maciel, J. Mol. Catal. A: Chem. 101 (1995) 153.
[11] K. Burger, A. Vértes, I. Dékány, M. Szekeres, Z. Homonnay, Z.S. Nemes-Vetéssy, N. Buzás, Colloid. Polym. Sci. 275 (1997) 587.
[12] K. Burger, Spectrochim. Acta 43A (1987) 1105.
[13] R. Vivas-Reyes, F.D. Proft, M. Biesemans, R. Willem, P. Geerlings, J. Phys. Chem. A 106 (2002) 2753.
[14] T. Xu, N. Kob, R.S. Drago, J.B. Nicholas, J.F. Haw, J. Am. Chem. Soc. 119 (1997) 12231.
[15] A. Ghanbari-Siahkali, A. Philippou, A. Garforth, C.S. Cundy, M.W. Anderson, J. Dwyer, J. Mater. Chem. 11 (2001) 569.
[16] E.E. Getty, R.S. Drago, Inorg. Chem. 29 (1990) 1186.