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Superbasic sodium stannate as catalyst for dehydrogenation, Michael addition and transesterification reactions

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ABSTRACT

It has been shown that sodium stannate with superbasic sites generated on its surface can be obtained through simple thermal treatment of sodium stannate hydrate in pure N_2. In this study, we analyzed the as-prepared materials using powder X-ray diffraction, X-ray photoelectron spectroscopy, and N_2 physisorption methods. The superbasic sites were characterized by techniques of Hammett indicators and temperature-programmed desorption using CO_2 as adsorbate. It was shown that after undergoing calcination at 623 K, there are ample superbasic sites on sodium stannate: up to 0.254 mmol/g. The superbasicity of the materials was further confirmed by employing the 1-hexene as well as cyclohexa-1,4-diene double bond isomerization reactions. The superbasicity is attributed to the higher electron-donating ability of surface O^{2-}. The sodium stannate samples showed excellent catalytic efficiency towards selected reactions, namely the dehydrogenation of propa-2-nol, Michael addition of electron-deficient olefins, and transesterification of cyclic carbonate with methanol. It was observed that with rise of heat-treatment temperature from 573 to 623 K, both superbasicity and catalytic activity increased, reaching a maximum at 623 K, and then declined. It is deduced that catalytic efficiency is closely related to superbasicity of the sodium stannate catalysts.

1. Introduction

Solid superbases are materials possessing basic sites with strength H_- higher than 26 [1]. The preparation and application of these materials have been studied with interest because they catalyze reactions for the production of fine chemicals under mild conditions with reduced waste [2–8]. However, since most of the known superbases are sensitive to oxygen and/or CO_2, they are complicated to prepare and cannot be applied in chemical industry in a convenient manner [1,9–12]. For the development of base-catalyzed processes that are eco-friendly, a new kind of superbases has to be designed.

Recently, we reported in a communication the *in situ* generation of a solid superbase through direct thermal treatment of sodium stannate hydrate under nitrogen at 623 K. The superbase showed good catalytic efficiency towards the anti-Markovnikov addition of N–H and O–H bonds across the C=C bonds of electron-deficient olefins [13]. In the present study, different techniques (e.g., XRD, XPS, BET, CO_2-TPD) were employed to characterize the materials. In order to further confirm their superbasicity, we studied the superbase materials by probe reactions, viz. double bond isomerization of 1-hexene and cyclohexa-1,4-diene. It has been reported that the probe reactions of olefins isomerization can be used for the discrimination of strong basic and acidic sites [3–6]. Moreover, the catalytic application of the superbases was extended to (i) dehydrogenation of propa-2-nol, (ii) Michael addition of electron-deficient olefins, and (iii) transesterification of cyclic carbonate with methanol. Additionally, we conducted an in-depth discussion on the relationship between superbasicity and catalytic activity which is crucial for application of the superbase material in the field of catalysis.

2. Experiment

2.1. Chemicals and reagents

The reagents and chemicals (analytic grade unless stated otherwise) were obtained from Kemiou Chemical Reagent Company (Tianjin, China) and Tianjin Damao Chemical Reagent Co., Ltd. We purchased 1-hexene and cyclohexa-1,4-diene from Adamas-Beta reagent Ltd. and J&K Chemical Ltd., respectively; they were dehydrated using 3 Å molecular sieves at room temperature before use. Cyclohexane was dried by sodium under reflux. Sodium stannate

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(chemically pure) was produced by Beijing Hongxing Chemical Plant.

2.2. Catalysts preparation

To prepare the catalyst, sodium stannate hydrate was *in situ* treated (using a tube furnace) at a selected temperature in the 573–873 K range for 2 h in a N_2 flow (99.99% purity, Changsha Gas Co., China). The samples are indicated hereinafter as Sample(X) where X stands for the temperature for thermal treatment. For example, the sample treated at 623 K is denoted as Sample(623).

2.3. Catalyst evaluation

Dehydrogenation of propa-2-nol ($(CH_3)_2CHOH \rightarrow (CH_3)_2C{=}O + H_2$) was carried out at 573 K in a fixed-bed reactor (400 mm length and 10 mm diameter) connected to a nitrogen line and a gas chromatograph. The sodium stannate hydrate sample was pressed, crushed and sieved into 40–60 mesh particles before being loaded (0.5 g) into the fixed-bed reactor. Before the reaction, the catalyst was kept at a selected temperature (e.g., 623 K) for 2 h in a N_2 flow (15 ml min^{-1}). Then the temperature was changed to a designated temperature for a particular reaction. The feed of propa-2-nol was introduced into the closed reactor through a syringe pump with liquid hourly space velocity (LHSV) of 2.0 ml h^{-1} in the same N_2 flow rate of 15 ml min^{-1}. The products were analyzed by a gas chromatograph (GC) equipped with a 50 m OV-101 capillary column and FID.

Anti-Markovnikov Michael addition (monoaddition: $C_6H_{10}O + CH_2{=}CH{-}CN \rightarrow C_6H_9(O)CH_2CH_2CN$; bisaddition: $NCCH_2CN + CH_2{=}CH{-}CN \rightarrow (NC)_2C(CH_2CH_2CN)_2$) was performed in a glass batch reactor equipped with a magnetic stirrer. Cyclohexanone (5 mmol), acrylonitrile (5 mmol) and catalyst (0.025 g) were added and the mixture was stirred at room temperature for 1 h. In the case of using malononitrile and acrylonitrile as reactants, the molar amount of the malononitrile was 4 mmol while that of acrylonitrile was 10 mmol. After the reaction, the catalyst was separated from the mixture by centrifugation, and the reaction mixture was analyzed using an Agilent Technologies 7820 GC equipped with a FID and HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). The conversion of cyclohexanone and malononitrile was determined by the use of biphenyl as internal standard. Transesterification of propylene carbonate with methanol ($C_4H_6O_3 + CH_3OH \rightarrow CH_3OC(O)OCH_3 + CH_3CHOHCH_2OH$) to produce DMC was carried out at 353 K using 0.01 mmol propylene carbonate, 0.10 mol of methanol and 100 mg catalyst at a glass batch reactor equipped with condenser and a magnetic stirrer. The analysis of the products was similar to that of anti-Markovnikov Michael addition.

2.4. Catalyst characterization

Powder X-ray diffraction experiment (XRD) was conducted on a Rigaku Automatic Diffractometer (Rigaku D-MAX) with monochromatized Cu Kα radiation (λ = 0.15406 nm). X-ray photoelectron spectroscopic (XPS) measurements were carried out on a Leybold Heraeus-Shengyang SKL-12 electron spectrometer fitted with a VG CLAM 4 MCD electron energy analyzer. Mg Kα X-ray radiation ($h\nu$ = 1253.6 eV) was generated at 15 mA and 10 kV. Na 1s, C 1s, O 1s, and Sn 3d peaks were recorded in intervals of 0.1 eV, and binding energy was corrected taking the C 1s binding energy of adventitious carbon to be 284.8 eV. The residual gas pressure of spectrometer chamber was ca. 2×10^{-7} Pa during data acquisition. The specific surface areas of catalysts were determined by BET method based on nitrogen adsorption–desorption isotherms (at 77 K) collected over a Beckman (SA 3100) surface area analyzer.

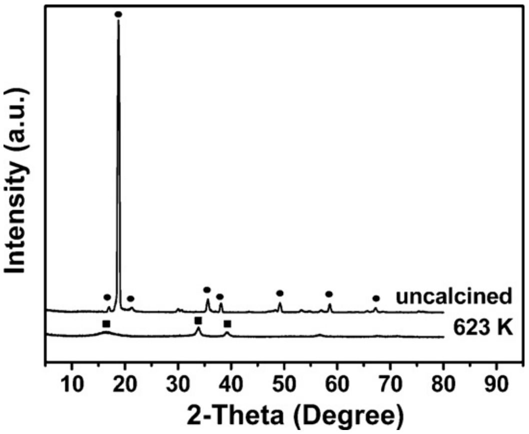

Fig. 1. XRD patterns of sodium stannate hydrate and Sample(623): (●) $Na_2SnO_3{\cdot}3H_2O$ and (■) anhydrous Na_2SnO_3.

CO_2 temperature-programmed desorption (CO_2-TPD) investigation was conducted on a Micromeritics 2920 apparatus using a thermal conductivity detector (TCD). The basicity of sodium stannate samples was also determined by Hammett indicators method as detailed in [13]. The probe reactions employed were the isomerizations of 1-hexene into 2-hexene ($CH_3(CH_2)_3CH{=}CH_2 \rightarrow CH_3CH{=}CH(CH_2)_2CH_3$ (*cis*/*trans*-2-hexene)) and cyclohexa-1,4-diene into cyclohexa-1,3-diene ($(CH{=}CH)(CH_2)_2(CH{=}CH) \rightarrow (CH{=}CH)_2(CH_2)_2$). The isomerization reactions were carried out at 523 K with LHSV being 0.4 ml h^{-1} following the same procedure of propa-2-nol dehydrogenation previously described in Section 2.3. The reaction products were analyzed by a GC equipped with a FID and 50 m OV-101 capillary column. The olefin conversion and the selectivity to isomerized products were calculated according to Eqs. (1) and (2):

$$\text{Conversion}_{\text{olefin}}\,(\%) = \frac{\text{olefin}\,\%\,\text{in field} - \text{olefin}\,\%\,\text{in products}}{\text{olefin}\,\%\,\text{in field}} \times 100 \tag{1}$$

$$\text{Selectivity}_{C_xH_y}\,(\%) = \frac{C_xH_y\,\%\,\text{in products}}{\sum C_xH_y\,\%\,\text{in products}} \times 100 \tag{2}$$

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD

Fig. 1 shows the XRD patterns of sodium stannate hydrate and Sample(623). The XRD pattern of the former shows a sharp peak at 2θ = 18.7° and four small peaks at 2θ = 16.9, 35.7, 21.4, 38.0, 49.2 and 58.6°; they are attributable to $Na_2SnO_3{\cdot}3H_2O$ according to the standard JCPDS (01-1115) card. After thermal treatment at 623 K, the peaks of $Na_2SnO_3{\cdot}3H_2O$ vanished, and peaks at 2θ = 16.2°, 37.4° and 39.3° ascribable to anhydrous Na_2SnO_3 (JCPDS 30-1252) appear. Thus, Sample(623) is anhydrous Na_2SnO_3.

3.1.2. XPS

The XPS spectrum of Sample(623) is depicted in Fig. 2; one can see signals of the C, O, Sn and Na elements. Furthermore, according to the Sn 3d spectrum showing spin–orbit doublet at 487.2 (3d5/2) and 495.8 eV (3d3/2) (inset of Fig. 2), the chemical state of Sn can be assigned to Sn(IV) [14]. Using the related sensitivity factors, it was found that the chemical formula of the sample with thermal treatment can be expressed as Na_2SnO_3. The result is in accord with that of XRD, further confirming that the heated sample is Na_2SnO_3.

In addition, it has been pointed out that the binding energy of O 1s peaks in XPS study can provide direct evidence of surface basicity

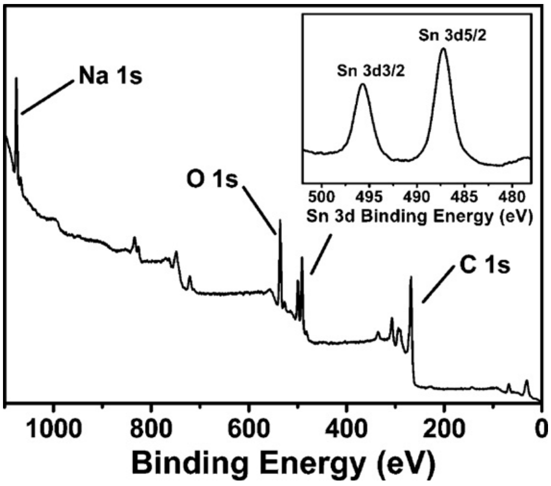

Fig. 2. XPS spectrum of Sample(623) (inset: Sn 3d peaks).

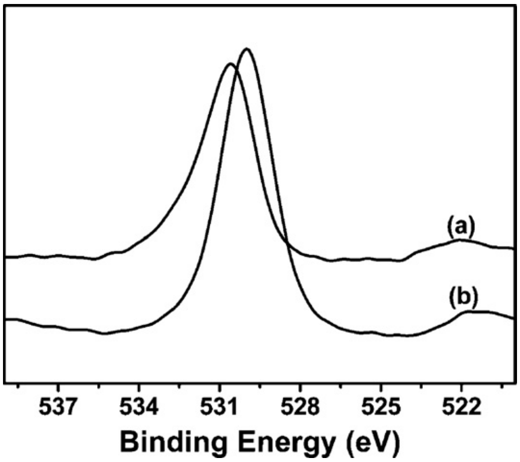

Fig. 3. O 1s spectrum of (a) sodium stannate hydrate and (b) Sample(623).

of metal oxides [15]. Fig. 3 shows the O 1s peaks of $Na_2SnO_3{\cdot}3H_2O$ and Sample(623). It is known that the electron-donating ability of electron pairs of a metal oxide is related to O 1s binding energy: a lower O 1s binding energy implies higher ability of donating the electron pairs. The O 1s binding energy of $Na_2SnO_3{\cdot}3H_2O$ is ca. 531.0 eV whereas that of Sample(623) is 530.0 eV. The lowering of binding energy from ca. 531.0 to 530.0 eV can be considered as an enhancement of surface basicity [16]. It is reasonable to deduce that the enhanced basicity (including superbasicity) of Sample(623) is a result of the higher electron-donating ability of surface O^{2-} [17,18]. In other words, the surface O^{2-} ions of Sample(623) can function as active basic sites.

3.1.3. Basicity characterization

In order to confirm the surface superbasicity of the calcined Na_2SnO_3, Hammett indicators and CO_2-TPD approaches were employed. Moreover, the superbasicity of these materials were probed by 1-hexene as well as cyclohexa-1,4-diene double bond isomerization reactions.

3.1.3.1. Hammett indicators method. The base strength (H_-) and amount of basic sites of samples were measured using the Hammett indicators method (Table 1). One can see that sodium stannate hydrate shows weak basicity ($9.3 \le H_- < 15.0$). After heating sodium stannate hydrate at temperatures ranging from 573 to 873 K, the as-obtained samples exhibit basic strength in the $26.5 \le H_- < 33.0$ range. As defined by Tanabe, materials with a basic strength higher than 26 can be regarded as superbasic [1]. In other words, every Sample(X) is a solid superbase. However, they are different in the amount of superbasic sites with the one heated at 623 K showing the highest amount (0.254 mmol/g). Based on the results, it is reasonable to deduce that sodium stannate with superbasic sites on its surface can be directly generated from sodium stannate hydrate through a simple step of thermal treatment.

Table 1
Basicity measurements of Sample(X) catalysts.

Treatment temperature (K)	Base strength[a] (H_-)	Amount of superbasic sites[a] (mmol/g)
–	$9.3 \le H_- < 15.0$	0
573	$26.5 \le H_- < 33.0$	0.067
623	$26.5 \le H_- < 33.0$	0.254
673	$26.5 \le H_- < 33.0$	0.175
773	$26.5 \le H_- < 33.0$	0.152
873	$26.5 \le H_- < 33.0$	0.054

[a] Experiment process as detailed in [13].

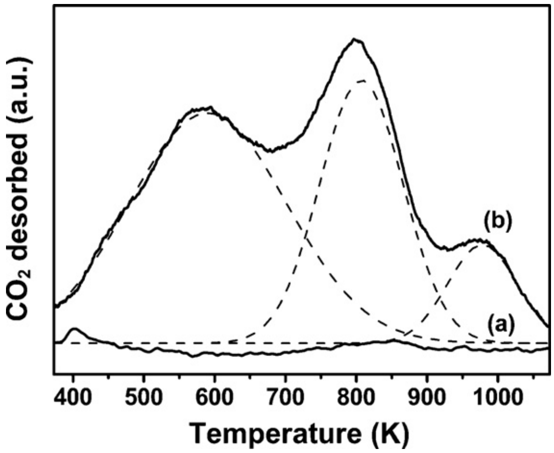

Fig. 4. CO_2-TPD profiles of (a) sodium stannate hydrate and (b) Sample(623).

3.1.3.2. CO_2-TPD. The CO_2-TPD results of sodium stannate hydrate and Sample(623) are depicted in Fig. 4. It is clear from Fig. 4 that the former shows poor CO_2 adsorption, displaying only low-intensity signals at around 403 and 853 K. Over Sample(623), intense desorption peaks are observed at ca. 573, 803, and 973 K. The CO_2 desorption at 973 K can be considered as a clear indication of superbasicity [4]. The results confirm the presence of superbasic sites on Sample(623), in good agreement with the results of Hammett indicators method (Table 1).

The basicity distribution of Sample(623) according to the CO_2-TPD results and those of Hammett indicator-Benzoic acid titration (as described in [13]) are listed in Table 2. According to the data of titration, Sample(623) possesses weak (7.2–15.0), strong (15.0–26.5) and super (26.5–33.0) basic sites, in amounts of 1.317, 1.225 and 0.254 mmol/g, respectively, giving a total of 2.796 mmol/g. In the CO_2-TPD investigation, desorbed peaks at 573, 803 and 973 K indicate weak, strong and super basic sites, respectively. The amounts of these basic sites were calculated by the integral method based on the area of the corresponding desorption peaks; they are 1.286, 1.025 and 0.243 mmol/g, respectively (Table 2). It is apparent that the distributions of base strength obtained based on the results of Hammett indicators and CO_2-TPD methods are in good agreement with each other (Table 2).

3.1.3.3. Double bond isomerization of 1-hexene and cyclohexa-1,4-diene. The probe reactions are applied to characterize basic sites that are different in strength [1,3–6]. Isomerization of 1-hexene and

Table 2
Basicity distribution of Sample(623) measured by Hammett indicators method and CO_2-TPD.

Method	Base strength H_- distribution (mmol/g)			
	7.2–15.0 (weak)	15.0–26.5 (strong)	26.5–33.0 (super strong)	Total basicity
Hammett indicators method[a]	1.317	1.225	0.254	2.796
CO_2-TPD	1.276	1.035	0.243	2.554

[a] Experiment process as detailed in [13].

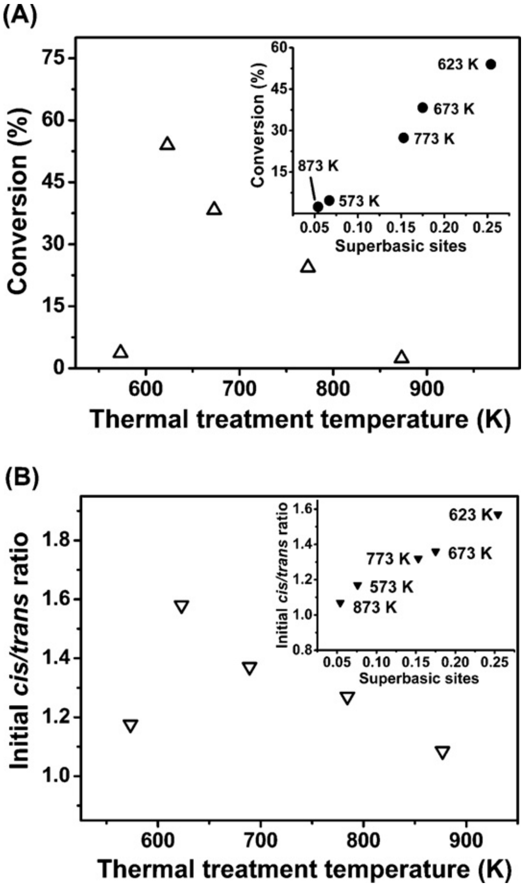

Fig. 5. Activity of Sample(X) catalysts as a function of thermal treatment temperature (X) in double bond isomerization of 1-hexene. (A): Initial conversion of 1-hexene (inset: a plot of initial 1-hexene conversion versus superbasicity); (B) initial *cis*/*trans* ratios of 2-hexene (inset: a plot of initial *cis*/*trans* ratios of 2-hexene versus superbasicity). Reaction conditions: temperature, 523 K; LHSV, 0.4 ml h^{-1}; N_2 flow rate, 15 ml min^{-1}.

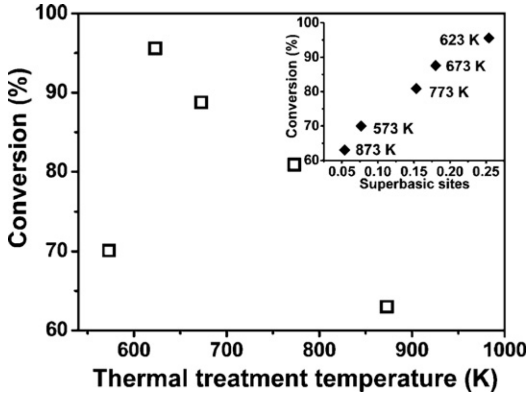

Fig. 6. Activity of Sample(X) catalysts as a function of thermal treatment temperature (X) in double bond isomerization of cyclohexa-1,4-diene (inset: a plot of initial conversion of cyclohexa-1,4-diene versus superbasicity). Reaction conditions: temperature, 523 K; LHSV, 0.4 ml h^{-1}; N_2 flow rate, 15 ml min^{-1}.

cyclohexa-1,4-diene was employed in this study for this purpose. The isomerization of olefins has been applied to probe solid bases of strong basicity [3–6]. The reaction is initiated by the abstraction of allylic H by basic sites to generate *cis* and *trans* forms of allyl anion in which the former is more stable than the latter. Therefore, *cis* is predominantly formed in the initial stage of the reaction [19]. A high *cis*/*trans* ratio is a characteristic feature of isomerization catalyzed by catalysts of strong or super basicity.

Fig. 5 shows the conversion of 1-hexene and initial *cis*/*trans* ratios of 2-hexene over Sample(X). A rise in treatment temperature (X) from 573 to 623 K would result in increase of 1-hexene conversion and *cis*/*trans* ratio, and the highest *cis*/*trans* ratio (1.58) was observed over Sample(623). Further rise in X would result in sharp decline in catalytic activity, and Sample(873) only showed low activity. For Sample(923), no activity was detected even when the reaction temperature was elevated to 623 K.

The reported activity for 1-hexene isomerization was usually low [19–21]. In the case of double bond migration of cyclohexa-1,4-diene, the effect of X on catalytic activity is similar to that of 1-hexene isomerization but much clearer (Fig. 6). With an increase in X, the activity for double bond isomerization of cyclohexa-1,4-diene first increased, reaching a maximum at 623 K, and then decreased. The results imply the existence of superbasic sites [3–6], consistent with the results of CO_2-TPD and Hammett indicators methods. Similar results were obtained over KF/alumina, a solid catalyst of strong base, as described by Kabashima et al. [9].

As seen in Tables 1 and 2, Sample(X) is similar in basic strength but different in the amount of superbasic sites, and Sample(623) is the highest in terms of the amount of superbasic sites. The insets of Figs. 5 and 6 show the relationship between activity and amount of superbasic sites of the catalysts. In the case of 1-hexene isomerization, both 1-hexene conversion and *cis*/*trans* ratio increased linearly with rise of superbasic sites. A similar trend can also be seen in the case of double bond isomerization of cyclohexa-1,4-diene. Thus, the activity of Sample(X) correlated with the basic strength as well as the amount of superbasic sites: the more the amount of superbasic sites or the stronger the base strength, the higher the catalytic activity. It is obvious that 623 K is the optimal treatment temperature to obtain superbasic sites for catalytic efficiency. Thus, Sample(623) was chosen for further investigation.

3.1.4. N_2 adsorption/desorption isotherm

The N_2 adsorption/desorption isotherm of Sample(623) is typical of type-IV isotherm, showing little uptake at high partial pressure (Fig. 7). According to the hysteresis loop, Sample(623) is mesoporous in nature [4]. According to SEM pictures (not shown here), the mesopores of the material are generated between the particles rather than inside the particles. Generally, the pores of such a dimension would allow easy diffusion of small reactants into the catalyst [1]. The specific surface area of Sample(623) is 32.5 m^2 g^{-1}, and the low specific surface area implies that the surface density of basic and superbasic sites is high. With basic and superbasic sites located on the external surface as well as on the surface of mesoporous channels, Sample(623) is suitable for base-catalyzed reactions.

Table 3
Acetone yield in the decomposition of 2-propanol and DMC yield in the transesterification of PC with methanol over Sample(623) at different reaction times.

Decomposition of 2-propanol[a]		Transesterification[b]	
Reaction time (h)	Acetone yield (%)	Reaction time (h)	DMC yield (%)
0.25	88.8	1	53.2
0.75	73.7	3	64.5
1.5	75.9	5	72.6
2.25	71.5	7	73.0
3.0	7.6	9	71.8
3.75	6.2	11	72.3

[a] Reaction conditions: temperature, 573 K; LHSV, 2.0 ml h^{-1}; N_2 flow rate, 15 ml min^{-1}.

[b] Reaction conditions: catalyst, 100 mg; propylene carbonate, 0.01 mmol; methanol, 0.10 mol; reaction temperature, 353 K.

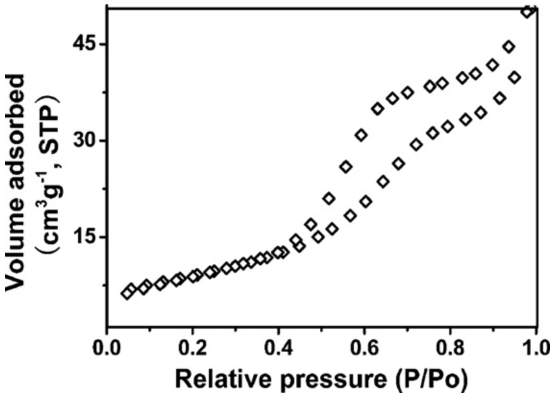

Fig. 7 N_2. adsorption/desorption isotherm of Sample(623).

3.2. Catalytic applications

In a recent communication, we reported the high catalytic activity of Na_2SnO_3 for the anti-Markovnikov hydroamination and hydroalkoxylation of electron-deficient olefins with nucleophiles [13]. In this study, we applied the catalyst to (i) dehydrogenation of propa-2-nol, (ii) Michael addition of electron-deficient olefins, and (iii) transesterification of propylene carbonate with methanol.

3.2.1. Dehydrogenation of propa-2-nol

Catalytic decomposition of propa-2-nol promoted by solid base catalysts is important for the production of acetone [3]. Strongly basic catalysts used to promote the decomposition of propa-2-nol usually enjoy supremacy such as being high in acetone selectivity and yield [22–25]. The industrial application of the procedure is extremely promising since the cost of propa-2-nol is much lower than that of acetone. The yield of acetone in the decomposition of propa-2-nol at 573 K over Sample(623) at different reaction times is shown in Table 3. The catalyst is highly active: acetone yield as high as 88.8% was obtained at 0.25 h. At reaction time of 2.25 h, the yield declined to 71.5% but acetone selectivity was above 97.0%. There was a big decline in yield when reaction time exceeded 2.5 h due to a big drop in propa-2-nol conversion (to 7.6%). Nonetheless, the catalytic efficiency is better than that reported in the literature [3], noted that in the present study the reaction temperature was lower and acetone selectivity and yield were much higher. It was observed that when reaction time exceeded 3.75 h, the color of the catalyst changed from white to gray, suggesting that the deactivation was a result of coking. Unlike the solid acid catalysts on which coke formation was fast [26], the superbase Na_2SnO_3 catalyst has better resistance towards coking. Moreover, a deactivated catalyst can be easily regenerated by calcination in air or O_2 flow, followed by thermal treatment in a flow of high-purity N_2. With such advantage, the catalyst has wide application in chemical industries because coke formation on catalysts in some high-temperature reactions can be retarded.

3.2.2. Michael addition

Michael addition is for C–C bond formation and is widely used in organic synthesis [27]. The reaction is commonly catalyzed by strong bases [28]. In the application of Na_2SnO_3 in the Michael addition of cyclohexanone to acrylonitrile, we observed monoaddition product. However, in the case of malononitrile, bis-addition product was obtained. We confirmed that proportionate yield of bis-addition product was obtained whether the molar amount of acrylonitrile used in the reaction was equal to or less than that of malononitrile. On the other hand, the use of excess cyclohexanone did not furnish any bis-addition product under similar reaction condition. In Michael addition, although mono-adduct was obtained with all conventional basic reagents [29–36], the generation of bis-adduct is not unprecedented. It was reported to be possible by Alvarez et al. in Michael addition of acrylonitrile to malononitrile over a solid ruthenium(II) complex [37]. Furthermore, the use of our superbase materials has the advantages of being short in reaction time (ca. 5 min) and relatively high in yield (99.2%) at room temperature and atmosphere pressure, demonstrating that the strong basic sites on Na_2SnO_3 are apt for this kind of base-catalyzed processes.

3.2.3. Transesterification of cyclic carbonate with methanol to produce DMC

Transesterification of ester with alcohol is important in the synthesis of fine chemicals, and this kind of reactions is commonly catalyzed by basic materials [38–40]. We used Sample(623) to catalyze the transesterification of propylene carbonate (PC) with methanol to produce dimethyl carbonate (DMC) and propylene glycol (PG). The results are shown in Table 3. A 72.6% yield of DMC was achieved after reaction time of 5 h under atmospheric pressure, higher than those recorded in the literature [41–44]. The DMC yield kept almost constant even the reaction was prolonged to 11 h, suggesting that the reaction was limited by thermodynamic equilibrium [45].

It was suggested that both moderately and strongly basic sites are active for the transesterification of cyclic carbonate with methanol to produce DMC [46,47]. In other words, the DMC yield depends on the total amounts of basic sites. It is interesting to point out that 1-alkoxy-2-propanol and 2-alkoxy-1-propanol were not detected as by-products in our study. According to the basicity distribution of Sample(623) displayed in Table 2, there are ample amount of sites that are strongly basic on the surface. It is plausible that the availability of these sites is a determining factor for high selectivity to DMC.

4. Conclusions

A solid superbase catalyst can be generated simply by thermal treatment of sodium stannate hydrate under a flow of pure N_2. There are ample superbasic sites (0.254 mmol/g) on the surface with strength in the $26.5 \leq H_- < 33.0$ range. Maximum superbasicity and catalytic efficiency were observed over the sample that was heated at 623 K. Moreover, there is a correlation between the superbasicity and catalytic activity in the selected base-catalyzed reactions: the higher the superbasicity and/or the more the superbasic sites, the better the catalytic activity. The thermal treatment of sodium stannate hydrate for the generation of superbasic sites can be performed *in situ* prior to reaction, making storage of superbasic materials not a concern. It is envisaged that this solid superbasic material will find wide applications in reactions that are catalyzed by basic materials.

Acknowledgments

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