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1. Introduction

Increasing concerns about global climate change and depletion of fossil fuel resources have promoted the development of producing industrial chemicals and fuels from natural resources. Carboxylic acids are a family of important platform chemicals that can be produced by biological and chemical pretreatments of biomass. In recent years, the catalytic reduction of carboxylic acid has attracted a lot of attention since it offers a simple and direct route to synthesize aldehydes, alcohols and esters.1-3 Hydrogenation of mono- and multifunctional carboxylic acids can make alcohols and polyols, respectively, which can be used as fuels, solvents and

A well fabricated PtSn/SiO₂ catalyst with enhanced synergy between Pt and Sn for acetic acid hydrogenation to ethanol⁺

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This work reported a well-fabricated PtSn/SiO₂ catalyst prepared by a modified two-step sol-gel (MTSG) method. The adoption of strong electrostatic adsorption (SEA) and sol-gel (SG) method could give both a significantly high Pt dispersion and a large amount of Lewis acid sites. The homogenous distribution of Sn species could not only provide more opportunity for the Pt precursor to disperse on the support by forming Pt-(O-Sn \equiv) $_{v}^{2-y}$ analogous species, but also enhance the synergy between Pt and Sn species. Consequently, an excellent activity was achieved in the hydrogenation of acetic acid (AcOH) with a conversion of 100% and ethanol (EtOH) selectivity of 93%. Investigations on the effect of Sn/Pt molar ratio showed that the dispersion of Pt decreases obviously with the increasing Sn/Pt ratio due to the geometric or electronic effects caused by SnO_x species. A balancing effect between Pt active sites and Lewis acid sites was found to be responsible for the superior catalytic performance in AcOH hydrogenation. Moreover, a parallel reaction path model was proposed for the hydrogenation of AcOH over PtSn/SiO₂ catalyst, in which ethanol and ethyl acetate (AcOEt) are formed competitively through the adsorbed ethoxy intermediate.

> monomers for polymer production.⁴ Among the numerous carboxylic acid hydrogenation processes, hydrogenation of AcOH into ethanol is of great interest. AcOH is the simplest carboxylic acid so it is used as a good model to investigate C-C bond and C-O or C=O bond activation. Meanwhile, ethanol is an attractive product that has been widely used as a fuel additive, solvent and antiseptic.5,6

> AcOH hydrogenation has been studied since the 1990's. It was found that the direct catalytic hydrogenation of AcOH requires the presence of both metal and metal oxide phases.7 Further researches showed that the adsorption of AcOH on the oxide phases plays a major role in determining the hydroconversion kinetics and the role of metal is to provide mobile, activated hydrogen atoms. However, the mechanism of AcOH hydrogenation is still on debate. Two types of mechanism involving Mars-Van Krevelen mechanism and Langmuir-Hinshelwood mechanism have been proposed. The difference between the two mechanisms is the definition of active site for AcOH activation. The former attributes the active sites to the surface vacancies, while in the later it is assigned to the Lewis acid sites/metal cations on the catalyst surface.1,2,8,9

> Recently, bimetallic supported noble-based catalysts such as Pt-Sn, Pt-Fe, Ru-Fe, Pd-Re etc., are reported to be effective for AcOH hydrogenation.7,9-12 Among these catalysts, PtSn supported bimetallic catalyst acquires a lot of attention since it exhibits good activation for the hydrogenation of AcOH to ethanol. Nevertheless, most of the PtSn catalysts are generally prepared by impregnation (IM) method nowadays, which is

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[†] Electronic supplementary information (ESI) available: Fig. S1 shows the N2 adsorption-desorption isotherms and pore size distribution of reduced catalysts. Fig. S2 displays the HAADF-STEM and EDX elemental-mapping images of the reduced PtSn1.6/SiO2-MTSG catalyst. Fig. S3 shows the TEM images of reduced PtSnx/SiO2-MTSG catalysts. Fig. S4 represents the deconvolution of the fit about FTIR spectra of chemisorbed pyridine on reduced catalysts. Fig. S5 displays the hydrogenation performance of AcOH over PtSn1.6/SiO2-MTSG catalyst as a function of WHSV(AcOH). Table S1 shows the fitted results of H2-TPR experiments of catalysts. Table S2 displays the integral quantity of Lewis acid sites of reduced catalysts. Table S3 illustrates the hydrogenation performance of AcOH over PtSn1.6/SiO2-MTSG catalysts. See DOI: 10.1039/c6ra09199g

quite limited to control the structural parameters. Consequently, the hydrogenation process still suffers from a variety of issues such as lower ethanol selectivity, harsh reaction conditions and high catalyst costs.^{12,13}

PtSn bimetallic catalysts have been widely used in many catalytic processes. Various ways of preparing PtSn bimetallic catalyst have been developed to tailor the electronic and geometric structures for different applications.¹⁴⁻¹⁶ Up to now, supported PtSn bimetallic catalysts could be prepared by coreduction method, co-precipitation method, sol-gel (SG) method, hydrothermal approach, carbonyl route, and a controlled surface reaction method.13,17,18 SG method has been reported to be one of the promising technologies to prepare PtSn catalysts with well-defined physical properties. It increased the homogeneity and purity of the solid, with better microstructural control of the support, well-defined pore size distribution, and higher thermal stability of the catalysts. Two types of sol-gel methods have been reported in preparing PtSn/Al₂O₃ catalyst for *n*-heptane reforming.¹⁹ One is the one-step sol-gel (OSG) method, which starts from both the support and metal precursors and then go all way to the final catalysts in one batch. The other is two-step sol-gel (TSG) method, where platinum is uploaded by IM method after tin is introduced into alumina support by SG method. Both of them could give catalysts with higher activity and stability.

On another hand, high dispersion of metal nanoparticles is thought to be crucial in the design of supported noble metal catalysts, in order to achieve high performance and minimize the cost. It was reported that Pt-based catalysts prepared by strong electrostatic adsorption (SEA) method exhibited higher dispersion of Pt than those prepared by IM method.²⁰ By controlling the pH value of the impregnation solution, the hydroxyl groups that bonding on oxide surface become protonated or deprotonated, thus become positively charged below a characteristic pH value or negatively charged above the characteristic pH value. Therefore, the metal complex could deposit onto the support surface by SEA method, resulting in a relative higher metal dispersion.²¹⁻²³

Herein, we use a modified two-step sol-gel (MTSG) method for the synthesis of highly dispersed and homogeneously distributed PtSn catalyst, in which Sn/SiO₂ was firstly synthesized by SG method and then Pt was uploaded by SEA method sequentially. The effects of the synthesis methods on the surface structure and catalytic properties of AcOH hydrogenation were studied. It shows that this MTSG strategy could enhance both the catalytic activity and selectivity for the hydrogenation of AcOH into ethanol, due to the enhanced synergy between Pt and Sn species. Moreover, the influence of Sn/Pt molar ratio was investigated and a reaction model for the formation of ethanol and AcOEt was proposed.

2. Experimental

2.1. Catalyst preparation

 Sn/SiO_2 (denoted as Sn/SiO_2 -SG) and SiO_2 in this study were prepared by SG method with $Si(OC_2H_5)_4$ (TEOS, 99.5%, Sinopharm Chemical Reagent Co., Ltd) and $SnCl_2 \cdot 2H_2O$ (98%, Sinopharm Chemical Reagent Co., Ltd) precursor with variable Sn content from 0 to 5 wt%. The molar ratio of TEOS : C_2H_5 -OH : H_2O was 1 : 3.85 : 10.20. TEOS was mixed with ethanol and an alcoholic solution of SnCl₂·2H₂O. After that, deionized water was added dropwise into the solution with vigorously stirring at room temperature. The pH of the solution was kept to be *ca.* 4 during the water dropping process. After that, the clear sol was allowed to gel in air for 48 h. Subsequently, the obtained gel was aged for 24 h at 60 °C. The resulting solids were filtered, washed with ethanol until negative chloride test, and then dried in oven at 105 °C. The obtained xerogel was then calcined in air at 500 °C for 4 h. For comparison, Sn precursor was also uploaded by IM method with controlled concentration of SnCl₂ solution (1% wt/wt Sn loading), and the acquired substrate was denoted as Sn/SiO₂-IM.

Supported Pt catalysts were obtained by depositing the metal precursor onto the support surface by SEA method. Platinum(II) tetra-ammine chloride ($[Pt(NH_3)_4]Cl_2$, 99%, Sinopharm Chemical Reagent Co., Ltd) was used as the metal precursor. The SiO₂ or Sn/SiO₂-SG support was firstly suspended in NH₄OH solution (aq., pH = 10.6) under stirring for 0.5 h. The solution of [Pt(NH₃)₄]Cl₂ was then added with controlled concentration to obtain 1% wt/wt Pt loading on the support. The suspension was kept under stirring for 10 h and then was separated by filtration under vacuum. The solid was rinsed with water, and then was dried at 105 °C for 5 h. These catalysts were named as PtSnx/ SiO_2 -MTSG and x represents for the theoretical Sn/Pt molar ratio. For comparison, other two types of PtSn/SiO₂ catalysts were also prepared. One was obtained by loading Pt onto Sn/ SiO₂-IM by SEA method, which was denoted as PtSn1.6/SiO₂-MIM. The other was prepared by impregnation of $[Pt(NH_3)_4]Cl_2$ onto Sn/SiO₂-SG, and was denoted as PtSn1.6/SiO₂-TSG.

2.2. Catalyst testing

The hydrogenation performances of the catalysts were carried out in a stainless steel tubular fixed bed reactor. Catalysts (0.8 g, ca. 2 mL, 40-60 mesh) were placed in the center of the reactor, and both sides of the catalyst bed were packed with quarts powder (20-40 mesh). The catalysts were firstly reduced in situ in flowing hydrogen (99.999%, 100 mL min $^{-1})$ at 300 $^\circ C$ for 4 h. After that, AcOH (99.5%) was pumped into the reactor system using a constant-flow pump and vaporized through a preheater maintained at 200 °C. The hydrogenation products in liquidphase were analyzed by BEIFEN 3420A gas chromatograph equipped with an HP-INNOWAX (30 m \times 0.25 mm \times 0.25 μ m) capillary column and a flame ionization detector (FID). Giving that neglected C_2H_6 , CH_4 , CO and CO_2 were detected in the effluent gas stream, AcOH conversion was determined from a carbon balance based on the analysis of compounds detected in the liquid phase, and product selectivity was based on the carbon-containing products, which excluded the amount of water formed. Only the selectivity of ethanol and AcOEt were presented here because other hydrogenation products like aldehyde could be neglected in the selected reaction conditions.

The turn over frequency (TOF) of the reaction was measured under the conditions (270 °C, 2.6 MPa, $H_2/HOAc$ (mol mol⁻¹) =

20) where AcOH conversion was 60–70%. The TOF_{Pt} value was based on exposed Pt atoms, indicating the moles of AcOH converted per hour by per mole of exposed Pt atoms at the catalyst surface.

2.3. Catalyst characterization

Textual properties of the catalysts were measured using a Micromeritics Tristar 3000 analyzer by nitrogen adsorption at the boiling temperature of liquid nitrogen. The specific surface areas were calculated from the isotherms using the BET method. Platinum and tin contents were determined by ICP-OES (VISTA-MPX, Varian) and were expressed in metal weight percent. The size distribution of metal particles was determined by transmission electron microscopy (TEM) on a FEI Tecnai G2 F20 transmission electron microscope at 200 kV. The sample powder was dispersed in ethanol by sonication, and then drops of the suspension were applied onto a copper grid-supported transparent carbon foil and dried in air.

The *in situ* DRIFTs experiments were carried out on a Thermo Scientific Nicolet 6700 spectrometer (32 scans, 4 cm⁻¹), equipped with a Harrick Scientific DRIFT cell and a mercury-cadmium-telluride (MCT) detector cooled by liquid N₂. All the samples were pretreated at 100 °C under Ar (30 mL min⁻¹) for 1 h, and then FTIR spectra was collected using KBr as background spectrum.

Temperature-programmed reduction (H₂-TPR) tests were carried out on a Micromeritics AutoChem 2920 TPD/TPR apparatus using *ca.* 0.15 g of catalyst. The catalyst was prior treated at 200 °C for 2 h in flowing He. A flow rate of 30 mL min⁻¹ of 10 vol% H₂/Ar was used for the reduction with the temperature range from 50 °C to 900 °C at a rate of 10 °C min⁻¹. A thermal conductivity detector (TCD) was employed to determine the amount of hydrogen consumed.

The metal dispersion of the catalysts was determined according to literature¹² by pulsed hydrogen titration of oxygen pre-covered sites using a Micromeritics 2920 TPD/TPR apparatus. Prior to the analysis, catalysts (0.15 g) were reduced in flowing 10 vol% H_2/Ar at 300 °C for 2 h, followed by purging with He to remove any physical adsorbed hydrogen. After cooling to 50 °C in flowing He, the catalysts were exposed to 10 vol% O_2/He for 0.5 h followed by purging with Ar. Titration with pulses of 10 vol% H_2/Ar was then employed until no further H_2 uptake occurred.

The *in situ* FTIR of chemisorbed CO on reduced catalysts were collected on a Nicolet 6700 (32 scans, 4 cm⁻¹) spectrometer using a stainless steel cell connected to a gas dosing and evacuation system. The sample powders were prior reduced at 300 °C in H₂ for 4 h and then cooled to room temperature. After that, the powder was pressed into a self-supporting disk (*ca.* 20 mg) under the pressure of 8 MPa and then was introduced into the IR cell. The disk was re-reduced in 10 vol% H₂/Ar at 300 °C for 0.5 h and then cooled to 30 °C under a high-purity He flow for collecting the background spectrum. Afterward, the sample was exposed to the flow of CO at 30 °C for 0.5 h. FTIR spectra were collected after purging He for 0.5 h and referenced to the background spectrum of reduced catalysts. For normalization,

the intensity of the spectrum was enlarged by the same multiple as the disk weight used to be enlarged to 1 g.

Fourier transform infrared (FTIR) spectra of pyridine adsorption were also collected on a Thermo Scientific Nicolet 6700 (32 scans, 4 cm⁻¹). The pretreatment for the sample was same as that for CO adsorption. After the pretreatment, the disk was re-reduced in 10 vol% H₂–Ar at 300 °C for 0.5 h and then was evacuated under reduced pressure at the same temperature. After cooling to 50 °C, the samples were saturated with pyridine vapor for 0.5 h and then evacuated at 150 °C for 0.5 h, respectively. Spectra were recorded at the evacuation temperature in the range of 4000–650 cm⁻¹. The amount of the Lewis acid sites in samples was calculated by peak deconvolution of characteristic band at *ca.* 1450 cm⁻¹.²⁴

X-ray photoelectron spectrometer (XPS) was carried out on a Thermo ESCALAB 250Xi system, using a monochromatic Al-K α (1486.6 eV) source operating at 10.8 mA × 15 kV and a pass energy of 50 eV under an operating pressure of 7.1 × 10⁻⁵/7.1 × 10⁻⁷ Pa. The energy resolution is 1 eV. Catalysts were mounted on a special-designed holders. After reduction *in situ* in the rapid sampling chamber and pre-treatment chamber, samples were transferred into analysis chamber by vacuumed gradually. Possible deviations caused by electric charge on the samples were corrected through taking the Si 2p line as an internal standard at 103.4 eV. Peak fitting was achieved using XPSPeak 41 software.

3. Results and discussion

3.1. PtSn/SiO₂ synthesized by MTSG method

3.1.1. Catalytic testing. Table 2 shows the hydrogenation performance of monometallic Pt/SiO2-MTSG and Sn/SiO2-SG catalysts as well as bimetallic PtSn catalysts prepared by different methods. All the bimetallic PtSn catalysts exhibit remarkable higher catalytic performance than the monometallic catalysts, indicating that the hydrogenation of AcOH is catalyzed by the synergy between Pt and Sn species.12,13 It also shows that the catalyst prepared by MTSG method has the highest catalytic performance. Conversion of AcOH over PtSn1.6/SiO₂-MTSG could reach up to 98.3% and the selectivity of ethanol is 91.8%. PtSn1.6/SiO2-MIM presents a lower AcOH conversion and a similar ethanol selectivity. However, for PtSn1.6/SiO₂-TSG catalyst, both AcOH conversion and ethanol selectivity decrease dramatically. As mentioned above, SG method could give uniform distribution of tin throughout silicon matrix.19 Thus, the homogeneous distribution of Sn could be one of the important reasons for the excellent catalytic activity of catalyst prepared by MTSG method. Another possible reason may be the higher dispersion of Pt, resulting from the SEA method instead of commonly used IM method. It is noteworthy that the deteriorative selectivity of ethanol for the PtSn1.6/SiO₂-TSG could be ascribed to the less Pt active sites, induced by the IM method. Considering the adsorption of AcOH is the rate control step, it could be concluded that the hydrogenation activity of PtSn catalyst could be determined by the amount of surface active Sn species.9 While the selectivity of ethanol has close relationship with the amount of surface

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metallic Pt species. However, further experiments and characterizations are necessary to reveal the explanation for the effects of these preparation methods.

3.1.2. Catalyst characterization

3.1.2.1. TEM. Fig. 1 shows TEM images of the reduced Pt/ SiO₂-MTSG and PtSn/SiO₂ catalysts prepared by different methods. All the catalysts prepared by SEA method exhibit small particles homogeneously distributing on the silica support, similar to the report that monolayer adsorption of Pt complexes by SEA method can lead to small raft-like metal particles.^{22,23} The average diameter of metal particles is about 1.4-1.8 nm. However, the catalyst prepared by impregnation of $[Pt(NH_3)_4]Cl_2$ (PtSn1.6/SiO₂-TSG) gives much larger particles with a wide particle size distribution. According to the literature, the ionic interaction between $[Pt(NH_3)_4]^{2+}$ and the surface hydroxyl group of SiO₂ could be responsible for the high dispersion of Pt over SiO2 surface.22,23 Thus, considering the similar surface properties of SnO_x (x < 2) and SiO_2 , it could be speculated that the interaction between $[Pt(NH_3)_4]^{2+}$ and the surface hydroxyl provided by oxide tin could also exist. Therefore, Pt-(O-Sn \equiv)_y^{2-y} analogous species could be formed on the catalyst surface.^{25,26} Consequently, the interaction between Pt and Sn species could be enhanced when Pt is uploaded by SEA method. However, such interaction should be weakened when Pt is uploaded by IM method because of the lack of such interaction between Pt and Sn species.

3.1.2.2. FTIR. The FTIR spectra of SiO₂ and Pt/SiO₂-MTSG are shown in Fig. 2. FTIR spectra in OH stretching region suggests that both SiO₂ and Pt/SiO₂-MTSG contained isolated external silanol groups (3743 cm⁻¹), free internal silanol groups (3732 cm⁻¹), and delocalized hydrogen-bonded groups (3510 cm⁻¹) of lattice defects.²⁷ Meanwhile, compared to the FTIR spectra of SiO₂, Pt/SiO₂-MTSG shows a significant decrease in



Fig. 1 TEM images of the reduced catalysts. (A) Pt/SiO_2-MTSG , (B) $PtSn1.6/SiO_2-MTSG$, (C) $PtSn1.6/SiO_2-MIM$, (D) $PtSn1.6/SiO_2-TSG$.



Fig. 2 FTIR spectra of hydroxyl groups of SiO₂ and Pt/SiO₂-MTSG.

silanol groups (3510 cm⁻¹ and 3743 cm⁻¹), suggesting consumption of silanol groups in the strong electrostatic adsorption process. It was speculated that $Pt-(O-Si\equiv)_y^{2-y}$ analogous species might be formed by the interaction between $[Pt(NH_4)_3]^{2+}$ and SiOH groups.^{28,29}

3.1.2.3. HAADF-STEM. Fig. S2[†] shows the HAADF-STEM images of reduced PtSn1.6/SiO₂-MTSG catalyst. Small discrete particles are observed on the surface of the support, further demonstrating the homogenous distribution of Pt and Sn species (Fig. S2A and B[†]). The distribution of Pt and Sn species was determined by EDX elemental-mapping analysis (shown in Fig. S2C and D[†]). It shows that most of the nanoparticles contain both Pt and Sn elements, indicating that MTSG method could provide more possibility for the close contact between Pt and Sn atoms.³⁰

3.1.2.4. Temperature-programmed reduction (H_2 -TPR). The H_2 -TPR profiles of the monometallic Pt/SiO₂-MTSG and Sn/SiO₂-SG catalysts along with PtSn/SiO₂ bimetallic catalysts are shown in Fig. 3. Two reduction peaks centered at around 206 °C and



Fig. 3 H₂-TPR profiles of Sn/SiO₂-SG, Pt and PtSn/SiO₂ catalysts.

Table 1 Physical properties of supported PtSn/SiO₂ catalysts

Catalyst	Loading ^a (wt%)							
	Pt	Sn	$S_{\rm BET} \left({ m m}^2 { m g}^{-1} ight)$	D _{pore} (nm)	$V_{\rm pore} ({\rm cm}^3 {\rm g}^{-1})$	D^{b} (nm)	Pt dispersion ^c (%)	
Sn/SiO ₂ -SG	_	0.87	975	2.91	0.40	_	_	
Pt/SiO ₂ -MTSG	0.89	_	451	2.98	0.19	1.42	70.1	
PtSn1.6/SiO2-MTSG	0.87	0.89	492	3.86	0.49	1.46	55.6	
PtSn1.6/SiO ₂ -MIM	0.90	0.81	538	3.22	0.35	1.84	47.9	
PtSn1.6/SiO2-TSG	0.86	0.89	582	2.81	0.18	4.16	30.2	
PtSn1.0/SiO2-MTSG	0.89	0.62	395	4.01	0.38	1.43	61.9	
PtSn3.3/SiO2-MTSG	0.89	1.64	449	3.30	0.30	1.70	34.4	
PtSn8.2/SiO ₂ -MTSG	0.88	4.29	483	3.31	0.33	1.98	17.6	

366 °C are observed over Pt/SiO₂-MTSG catalyst. According to the literature, the peak in the lower temperature is attributed to the reduction of Pt having a weak interaction with the support. The other at higher temperature corresponds to the reduction of Pt– $(O-Si\equiv)_y^{2-y}$ species.³¹ In the case of Sn/SiO₂-SG catalyst, the reduction profile is characterized by a broad peak with a maximal temperature (T_M) at 503 °C, and the reduction peak begins at 300 °C and ends at 700 °C, which is due to the reduction of SnO₂ species.¹⁴

H₂-TPR profiles of the PtSn/SiO₂ catalysts display features related to the preparation methods. Comparing with the Pt/ SiO₂-MTSG catalyst, PtSn1.6/SiO₂-MTSG catalyst presents a overlapped reduction peak at 282 °C, which could be attributed to the co-reduction of Pt species with weak interaction with the support and Pt-(O-Sn \equiv) y^{2-y} analogous species. A tiny reduction peak at 430 °C could be ascribed to the reduction of SnO2.14 For the PtSn1.6/SiO2-MIM catalyst, two reduction peaks are centered at 272 °C and 360 °C, the former could be assigned to the co-reduction of Pt and Sn species and the later could be the reduction of Pt-(O-Si \equiv) v^{2-y} species. Considering the nonuniform distribution of Sn over PtSn1.6/SiO2-MIM, the presence of Pt-(O-Si \equiv)_v^{2-y} species is reasonable. The catalyst (PtSn1.6/SiO₂-TSG) in which Pt precursor is uploaded by IM method exhibits three peaks, approximately at 91 °C, 193 °C and 420 °C. The peaks at 91 °C and 193 °C could be associated to the reduction of Pt precursor with no and weak interaction with the support respectively. The peak at 420 °C is attributed to the reduction of SnO₂. The reduction temperature of PtSn1.6/SiO₂-TSG is lower than that of PtSn1.6/SiO₂-MTSG, indicating that

Table 2	Hydrogenation	of AcOH	over supported	PtSn/SiO ₂	catalysts ^a

	-	Selectivity (%)		
Catalyst	Conv. (%)	EtOH	AcOEt	
Pt/SiO ₂ -MTSG	11.3	76.6	21.4	
Sn/SiO ₂ -SG	0.4	15.5	84.5	
PtSn1.6/SiO ₂ -MTSG	98.3	91.8	7.6	
PtSn1.6/SiO ₂ -MIM	78.4	90.0	9.2	
PtSn1.6/SiO ₂ -TSG	52.4	73.8	25.0	

 a Reaction conditions: 270 $^\circ \rm C$, 2.6 MPa, H_2/AcOH (mol ratio) = 20, WHSV_{(AcOH)} = 2.0 h^{-1}.

the strong interaction between Pt and Sn exists in the MTSG preparation process. Based on the TPR results, it could be proposed that Pt species in PtSn1.6/SiO₂-MTSG catalyst have the closest interaction with Sn species.

3.1.2.5. H_2 -O₂ titration. Table 1 shows the dispersion of Pt particles in reduced Pt and PtSn catalysts. The dispersion of Pt in monometallic Pt/SiO₂-MTSG catalyst is 70.1%. For PtSn bimetallic catalysts, the dispersion of Pt particles decrease because of the geometric or electronic effect induced by Sn species.³² The dispersion of Pt in PtSn1.6/SiO₂-MTSG is slightly higher than that of PtSn1.6/SiO₂-MIM catalyst, which could be attributed to the different reduction temperature of Pt-(O-Sn \equiv)_y^{2-y} and Pt-(O-Si \equiv)_y^{2-y} species. Nevertheless, the dispersion of Pt particles in PtSn1.6/SiO₂-TSG is 30.2%, resulting from the aggregation of Pt particles. These results are consistent with the TEM images.

3.1.2.6. Pyridine-FTIR. It was claimed that metal-acid bifunctional sites are indispensable for the catalytic hydrogenation of carboxylic acid.33,34 Therefore, the infrared experiments of pyridine adsorption were carried out to detect the surface acidity of PtSn catalysts. The FTIR spectra of pyridine adsorbed on SiO₂ support, monometallic catalysts Sn/SiO₂-SG and Pt/SiO2-MTSG are shown in Fig. 4A. Two bands are observed at 1445 cm⁻¹ and 1596 cm⁻¹ over SiO₂, which are related to the adsorbed pyridine molecules bonded on the surface hydroxyl groups of silica through weak hydrogen bonds.35 In the case of Pt/SiO₂-MTSG catalyst, the FTIR spectrum is similar to that of SiO₂, suggesting that the presence of Pt would not modify the acid properties of SiO2. However, FTIR spectrum of Sn/SiO2-SG shows new bands at 1452 cm⁻¹, 1490 cm⁻¹, 1545 cm⁻¹, 1612 $\rm cm^{-1}$ and 1640 $\rm cm^{-1}$, indicating that Sn/SiO₂-SG possesses both Lewis and Brønsted acid sites.³⁶ According to literature reports, Lewis acid sites are provided by Sn²⁺ or unsaturated Sn⁴⁺ cations, while Brønsted acid sites are related to the surface hydroxyl groups bonded on Sn4+.34 FTIR spectra over PtSn/SiO2 catalysts are also shown in Fig. 4A. It is observed that the acidity of all the PtSn catalysts decreases comparing with the Sn/SiO₂-SG substrate, which could be due to the increasing reduction degree of oxide tin caused by H-spillover. Moreover, the amount of Lewis acid sites decreases in the order of PtSn1.6/SiO2-MIM < PtSn1.6/SiO₂-MTSG < PtSn1.6/SiO₂-TSG. Such phenomenon



Fig. 4 FTIR spectra of chemisorbed pyridine on reduced catalysts.

could also be attributed to the difference in dispersion of Pt and distribution of Sn species as well as the interaction between both species. For PtSn1.6/SiO₂-TSG catalyst, the Pt particle size is relatively larger than the other two catalysts. Therefore, the reduction of Sn species caused by H-spillover is limited, retaining the maximum Lewis acid sites. While the reason for the lowest Lewis acid sites over PtSn1.6/SiO₂-MIM could be its nonuniform distribution of Sn, though it presents similar Pt particle sizes as PtSn1.6/SiO₂-MTSG.

3.1.2.7. XPS. The surface chemical states and composition of PtSn catalysts were analyzed by XPS experiments after in situ reduction. As shown in Fig. 5, the Pt 4f spectra are described by two features. The dominant core-level feature is located at 71.3 eV, which is assigned to metallic Pt (Pt⁰). The other relatively broad feature is located at 72.7 eV, which could be attributed to PtO.35,37 According to the literature, the Sn core-level spectra in Sn/SiO₂-SG is described by two oxide states (Sn²⁺ and Sn⁴⁺), located at 486.6 eV and 487.9 eV.37 However, with the addition of Pt, a new feature assigned to metallic Sn shows up and the percentage of Sn²⁺ increases, suggesting the increasing reduction degree of oxide tin caused by H-spillover. Moreover, the percentage of metallic Sn, Sn²⁺ and Sn⁴⁺ (obtained by peak deconvolution) in the compared PtSn catalysts is totally different. In PtSn/SiO₂-MIM catalyst, the reduction degree of Sn is the highest. While in the case of PtSn/ SiO₂-TSG, majority of the Sn species are still in the Sn⁴⁺ state because of its poor dispersion of Pt. According to the different



Fig. 5 XPS spectra of the reduced catalysts. (A) Pt 4f spectra, (B) Sn 3d spectra.

reduction degree of Sn species, it is clear that the interaction between Pt and Sn species could be strengthened by SEA method and the distribution of Sn could be improved by SG method, which is consistent with the results of H_2 -TPR and pyridine-FTIR.

Based on these characterization results, it could be concluded that the MTSG method was an effective approach to fabricate the PtSn/SiO₂ catalyst with high dispersion of Pt particles. Besides, this method presented a larger amount of Lewis acid sites, which is crucial for AcOH adsorption.^{8,9,38-40} Moreover, the homogenous distribution of Sn species in the catalyst prepared by MTSG method can give abundant surface hydroxyl, providing more opportunity for Pt precursor to disperse on the support by forming Pt-(O-Sn \equiv)_y^{2-y} analogous species. Herein, the synergy between Pt and Sn species was enhanced over PtSn1.6/SiO₂-MTSG, so it exhibited excellent catalytic performance. Nevertheless, PtSn catalysts prepared by other methods either have low Pt dispersion or lack enough Lewis acid sites, thus resulting in poor catalytic activity and lower ethanol selectivity.

3.2. Effect of Sn/Pt molar ratio

The influence of Sn/Pt molar ratio on the catalytic performance over the PtSnx/SiO₂-MTSG (x = 1.0, 1.6, 3.3, 8.2) catalysts were investigated. As shown in Fig. 6, both AcOH conversion and

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Fig. 6 Effect of Sn/Pt molar ratio on the catalytic performance. Reaction conditions: 270 °C, 2.6 MPa, H₂/AcOH (mol mol⁻¹) = 20, WHSV_(AcOH) = 1 h⁻¹.

ethanol selectivity display a volcano trend with the increase of Sn/Pt ratio, and the optimal Sn/Pt ratio is found to be 1.6. When Sn/Pt ratio increases from 1.0 to 1.6, the conversion of AcOH increases from 74.2% to 99.7% with the selectivity of ethanol remaining at *ca.* 90%. The increase of AcOH conversion could be caused by the increase of active sites for AcOH adsorption. However, the conversion of AcOH and ethanol selectivity decreases significantly when Sn/Pt ratio is further increased from 1.6 to 8.2. In order to understand the effect of Sn/Pt ratio on the physicochemical properties of the catalysts, PtSn bime-tallic catalysts with different Sn/Pt ratio were also examined by TEM, CO-FTIR, pyridine-FTIR and H₂–O₂ titration.

Fig. S3[†] shows the TEM images and particle size distributions of bimetallic PtSn*x*/SiO₂-MTSG catalysts with various Sn/Pt ratio. It shows that the average particle sizes increase with the increase of Sn/Pt ratio. According to the H₂–O₂ titration results, the dispersion of Pt particles decreases from 61.9% to 17.6% with the increasing Sn/Pt ratio (listed in Table 1). It may be resulted from the geometric or electronic effect between Pt and Sn species.⁴¹ The decrease of Pt dispersion suggests that the hydrogen adsorption ability of PtSn catalysts decreases with the increasing Sn/Pt ratio.⁴²

CO-FTIR profiles of PtSnx/SiO₂-MTSG are shown in Fig. 7. The adsorbed CO on the Pt/SiO₂-MTSG catalyst clearly presents a sharp peak at 2067 cm⁻¹ with a shoulder peak at 2043 cm⁻¹, which corresponds to CO linearly bonded onto surface Pt atoms (CO_L, adsorbed atop of Pt atoms). The broad peak in the range of 1800–1900 cm⁻¹ is attributed to the bridge-bound CO (CO_B, adsorbed on Pt–Pt pair sites).^{32,43,44} The linear CO peak intensity decreases notably and the bridge-bound CO peak disappears simultaneously with the increasing Sn/Pt ratio. Such decrease could be due to the electronic effect caused by Sn species or the migration of Sn species onto Pt particle surfaces, suggesting the close interaction between Pt and Sn species exists in the prepared PtSn catalysts.^{32,45} This agrees well with the dispersion results detected by H₂–O₂ titration method (listed in Table 1).

Pyridine-FTIR spectra of the bimetallic $PtSnx/SiO_2$ -MTSG catalysts with different Sn/Pt ratio are shown in Fig. 4B. All the



Fig. 7 FTIR spectra of chemisorbed CO on reduced catalysts.

catalysts exhibit obvious Lewis acid sites evidenced by the bands at 1452 cm⁻¹ and 1609 cm⁻¹.³⁴ The catalysts with lower Sn/Pt ratio (below 1.6) show new bands at 1446 cm⁻¹ and 1596 cm⁻¹, which could be attributed to the adsorbed pyridine molecules bonded on the surface hydroxyl groups of silica.³⁵ However, both bands disappear with the increasing Sn/Pt ratio (above 3.3), on account of the coverage of surface hydroxyl groups by Sn species. It is clear that the intensity of the band at 1452 cm⁻¹ increases with the increasing Sn/Pt ratio, indicating the increasing surface acidity of PtSn catalysts. In order to correlate catalytic activity with the Lewis acid sites, the relative amount of Lewis acid sites in the PtSn catalysts are calculated.²⁴ As listed in Table S2,[†] the relative amount of Lewis acid sites increase from 5.1 µmol g⁻¹ to 56.4 µmol g⁻¹ with the Sn/Pt ratio, resulting from the increment of surface SnO_x species.

It was proposed that the reaction rate of acetic acid hydrogenation could be determined by the formation of acyl species or the reaction between H atoms and acyl species, depending on the ratio of the amount of Lewis acid sites *versus* the amount of exposed Pt active sites (denoted as L/Pt).⁷⁻⁹ However, none of these literatures distinguished the balance problem between Lewis acid sites and the exposed Pt active sites. Thus, in order to elucidate this balancing effect, the TOF based on exposed Pt atoms was correlated with the amount of Lewis acid sites. As



Fig. 8 Effect of L/Pt molar ratio on the catalytic activity. Reaction conditions: 270 °C, 2.6 MPa, H₂/AcOH (mol mol⁻¹) = 20.

shown in Fig. 8, the TOF_{Pt} increases with the increasing molar ratio of L/Pt in region I (from 0.18 to 0.54). Molar ratio of L/Pt is very low in this region, thus there is enough exposed Pt to provide dissociative hydrogen. So this increasing trend could originate from the increasing adsorption sites of AcOH. Hence, the determining step is the formation of acetyl. On the other hand, the catalytic activity barely changes with the further increment of L/Pt in region II (from 0.54 to 7.10). Such trend could be deduced that the Lewis acid sites in region II was so abundant that all the exposed Pt on catalyst surface could be involved in the reaction. Owing to the relative insufficient dissociated hydrogen, the hydrogenation is therefore controlled by the reaction between H and acyl species. Thus, conversion of AcOH decreases when the Sn/Pt ratio increases from 1.6 to 8.2. The decrease of ethanol selectivity could be attributed to either the decreasing of Pt dispersion or the increasing surface acidity of catalysts. Explanation for this speculation will be discussed in the next part.

3.3. Reaction model

As reported in literature, activated AcOH intermediate (activated by SnO_x species) can be hydrogenated to produce ethanol in the presence of surface-bonded H atoms activated by Pt active sites.⁹ However, the reaction path for the formation of AcOEt is still under ambiguous, which is essential to further understand the nature of the AcOH hydrogenation system. Based on the analysis on the influence of kinetics parameters, some preliminary results were achieved.

The influence of residence time on the conversion of AcOH as well as the selectivity of ethanol and AcOEt was evaluated by varying the space velocity of AcOH. As shown in Fig. 9, AcOH conversion increases with the increase of residence time and achieve *ca.* 100% after the residence time exceeds 130 s. When the residence time is not long enough, the selectivity of ethanol remains constant. However, when the residence time is further increased, for example above 130 s, the selectivity of ethanol shows an increasing trend, indicating that partial of AcOEt could be conversed to ethanol through deep-hydrogenation. Similar results were obtained by the study on other kinetic



Fig. 9 Hydrogenation performance of AcOH over PtSn1.6/SiO₂-MTSG catalyst as a function of residence time. Reaction conditions: 270 °C, 2.6 MPa, H₂/AcOH (mol mol⁻¹) = 20.



Scheme 1 Schematic model of AcOH hydrogenation to ethanol and AcOEt over the PtSn1.6/SiO₂-MTSG catalyst.

parameters such as temperature, pressure and H_2 /AcOH molar ratio (listed in Table S3†). According to the variation of the catalytic performance, parallel reactions may exist in AcOH hydrogenation system.

Hence, a schematic model regarding the hydrogenation of AcOH over PtSn1.6/SiO₂-MTSG catalyst is proposed (Scheme 1), in which the formation of ethanol and AcOEt are proposed to be parallel reactions. According to literatures, AcOH is firstly dissociated into adsorbed acetyl on Lewis acid sites. Then the acetyl intermediates could combine with H atoms activated by metallic Pt to form adsorbed acetaldehyde. The adsorbed acetaldehyde species then can undergo hydrogenation to form ethoxy groups.9 In the parallel reactions model, ethoxy groups can not only react with activated H atoms but also those adsorbed acetyl, which produced ethanol and AcOEt respectively. Affluent activated H atoms could favor the formation of ethanol, while the limited amount of activated H atoms may lead to the formation of AcOEt. Therefore, the competitive effect of two reactions could lead to the changes of products selectivity. Moreover, the hydrogenation of AcOEt to ethanol could occur by deep-hydrogenation when more H atoms were provided. Herein, one can infer that the synergy effect among Pt and SnO_x species is responsible for the hydrogenation of AcOH into ethanol. The parallel reaction mechanism for AcOH hydrogenation proposed by this study may provide valuable help in catalyst design and process development.

The long-term catalytic behavior results are also shown in Fig. 9. It is demonstrated that the well fabricated PtSn1.6/SiO₂-MTSG catalyst remains its excellent activity and ethanol selectivity in the hydrogenation of AcOH into ethanol. It shows a prospective future in the massive synthesis of ethanol by AcOH hydrogenation from an industrial application viewpoint.

4. Conclusions

In summary, a well fabricated $PtSn/SiO_2$ catalyst with high dispersion of Pt particles and large amount of Lewis acid sites was prepared by MTSG method. The synergy between Pt and Sn species was remarkably enhanced compared with those prepared by IM method, consequently resulting in excellent activity and ethanol selectivity. According to the investigations on the influence of Sn/Pt ratio, the amount of Lewis acid sites increased accompanied with a decline of Pt dispersion with the increasing Sn/Pt ratio. Excess high Sn/Pt ratio could inevitably lead to severe coverage of Pt particle surface by SnO_x species. The TOF_{Pt} increased with the increasing molar ratio of L/Pt and then remained nearly unchanged. Therefore, a balancing effect between exposed Pt and Lewis acid sites should be responsible for the superior catalytic performance of PtSn/SiO₂-MTSG catalyst. Meanwhile, a parallel reaction paths model was proposed for the hydrogenation of AcOH based on the kinetic parameter analysis, in which ethanol and AcOEt were formed competitively through the adsorbed ethoxy, derived from the dissociated adsorption of AcOH.

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