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A Mechanism Study on Efficient Conversion of Cellulose to Acetol over Sn-Co Catalysts with Low Sn Content

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Efficient conversion of renewable cellulose to high value-added C3 chemicals is a great challenge in the field of biomass valorization. In this work, we found that the combination of Co and Sn could significantly improve the efficiency of cellulose conversion to acetol. 54.4% yield of acetol and 66.6% total yield of C3 products were obtained when using 2%Sn-10%Co/SiO₂ (2wt% Sn content) as a catalyst. However, using the same Sn content of 2%Sn-10%Ni/SiO₂, no acetol and only 7.1% yield of C3 products was produced. By studying the effect of different Sn and Co content on cellulose conversion, it was found that Sn species played an important role in catalyzing glucose conversion to C3 intermediates, while Co mainly played a role in hydrogenation, same as Ni. Study demonstrated that Sn-Co/SiO₂ can convert glucose to C3 intermediates more efficiently than Sn-Ni/SiO₂ catalyst at low Sn content. Moreover, Sn-Co/SiO₂ could effectively convert C3 intermediates to acetol at high temperature that is essential for the acetol production from cellulose, but under the same conditions, Sn-Ni/SiO₂ catalyst tended to catalyze polymerization of C3 intermediates. A series of characterization methods including AAS, TEM, HRTEM, EDS, XRD, ex-situ XPS, in-situ XPS, CO₂-TPD found that the combination of Sn and Co could significantly increase the noninteger valence SnO_x species in the catalyst. These species increased the basicity of the catalyst and were beneficial to catalyze the isomerization of glucose and the retro-aldol condensation of fructose.

Introduction

The development of renewable lignocellulosic resources to prepare high value-added chemicals and fuels is essential to reduce the dependence on traditional fossil resources.¹⁻³ Cellulose, as an important component of lignocellulose, has been reported to selectively produce glucose⁴, 5-hydroxymethylfurfural⁵, levulinic acid⁶ through hydrolysis, or ethylene glycol⁷, ethanol⁸⁻¹¹, and C5-C6 alkanes¹² through hydrogenolysis. However, in addition to lactic acid¹³, there are few reports on the production of other C3 chemicals from cellulose with high selectivity. The main reason is that compared with other products, the conversion of cellulose to C3 molecules usually requires more complex reaction processes such as hydrolysis, isomerization, retro-aldol condensation, dehydration, hydrogenation, etc¹⁴. Therefore, fine-tuning the properties of the catalyst to achieve efficient conversion of cellulose to high value-added C3 chemicals is of great significance for expanding the application of cellulose and developing a green and sustainable chemical industry.

The interaction between the metal and the support or the second metal can significantly change the physicochemical properties of the metal, including spatial distribution, chemical composition, electron transfer, acid-base properties, stability, etc.¹⁵⁻¹⁸ By designing and controlling these properties, the catalytic activity of the catalyst can be enhanced. In this work, we found that Sn and Co bimetals supported on silica (Sn-Co/SiO₂) exhibited good catalytic activity for cellulose conversion to acetol, which is an important intermediate for the preparation of medicines, acrolein, heterocyclic compounds and additives for food and cosmetics,19-²¹but acetol yield reported by other groups was unsatisfactory (<35%).²²⁻²⁴ 54.4% yield of acetol and 66.6% yield of C3 products were achieved in this work when the Sn content of the catalyst was only 2wt% (Sn/Co=0.2). However, in our previous research,²⁵ similar result required Sn content \geq 15wt% (Sn/Ni \geq 3) when Sn-Ni/SiO₂ was used as a catalyst. High Sn content means low atom utilization, so reducing the Sn content required by the catalyst is helpful for green and sustainable production. Therefore, a series of Sn-Co/SiO₂ catalysts with different Sn and Co contents were prepared to explore the role of Sn and Co in the catalytic reaction. A comparative study of Sn-Co/SiO2 and Sn-Ni/SiO2 with low Sn content was also conducted. Through the comparative study on the conversion of the intermediates glucose and glycerone and the catalytic characterization of these two types of catalysts, the main reason why Sn-Co/SiO₂ with low Sn content could effectively convert cellulose to acetol was proposed.

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adsorbed for 1 h. Then the physisorbed CO₂ was_{viele}maged here purging Ar for another 1 h. Subsequently, विदिम्लीम्टिकिफिट्लिय्ट्रिकि was performed from 40 °C to 900 °C at a heating rate of 10 °C/min.

Temperature-programmed reduction (TPR) was measured by a AutoChem II 2920 Chemisorption Analyzer. Before testing, the catalysts (100 mg) were pretreated at 500 °C for 1 h in an Ar flow. A 5% H₂/Ar mixture gas flow was used for the TPR test from 40 °C to 900 °C at a heating rate of 10 °C min⁻¹.

Catalyst test

In a typical catalytic experiment, 50 mg of substrate (cellulose, glucose or dihydroxyacetone), 34 mg of catalyst, and 10 mL of deionized water were added to a 25 mL autoclave (Anhui Kemi Machinery Technology Co., Ltd) equipped with a magnetic stirrer. After purging with H₂ for several times, 4 MPa of H₂ was charged into the reactor at ambient temperature. The reactor was quickly heated to the specified temperature and maintained for a certain period of time. After the reaction, the reaction solution was filtered, and the filtrate was analyzed by a high-performance liquid chromatography (HPLC, Waters 1525). The HPLC used Shodex RI-201H detector and Aminex HPX-87H column (Bio-Rad, 300 x 7.8 mm). 0.005M of H₂SO₄ aqueous solution was used as the mobile phase.

The calculation formulas are as follows:

Cellulose Conver	rion = 1	Masses of solid residue after reaction - Mass of catalyst
Centrose Conversion – 1		The initial masses of cellulose before reaction
The yield of product =		Masses of carbon in product
		Masses of carbon in substrate
Carbon loss -	Masses	of carbon in substrate - Masses of carbon in product
Callon 1088 = -		

Masses of carbon in substrate

Catalyst recycling

After the reaction, the catalyst was separated by centrifugation, and the recovered catalyst was directly added into the reactor for the next run.

Results and discussion

Catalytic Activity Test

The conversion of cellulose over Sn-Co/SiO₂ and Sn-Ni/SiO₂ with low Sn content was first compared, and the metal contents of the catalysts were shown in Table S1. When the catalysts did not contain Sn, whether it was 10%Co/SiO₂ or 10%Ni/SiO₂, only a small amount of C2-C4 products were produced, indicating that the absent of Sn cannot effectively catalyze the conversion of cellulose to C2-C4 products (Figure 1). Compared with 10%Ni/SiO₂, the 10%Co/SiO₂ catalyst obtained more acetol and less 1,2-propanediol (1,2-P). This demonstrated that the hydrogenation activity of Co was weaker than Ni, which was beneficial to the retention of acetol. Using 2%Sn-10%Ni/SiO₂ as the catalyst, there was still no acetol and only 7.1% yield of 1,2-propanediol was produced. In addition, 17.8% yield of sorbitol was detected, indicating that the catalyst was prone to catalyze the

Experiment section

Reagents

 α -cellulose (25 μ m), acetol and nanosilica (15 ± 5 nm) were purchased from Aladdin Chemistry Co., Ltd.; dihydroxyacetone and 1-hydroxy-2-butanone were purchased from Bidepharm Technology Co., Ltd.; lactic acid, glucose, Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, SnCl₄·5H₂O, NH₃·H₂O, acetone and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd.

Catalysts preparation

The preparation process of Sn-M/SiO₂ is as follows: 2.0 g of nanosilica was added to a round bottom flask which contained 80 g of acetone. A certain amount of Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O was dissolved in 10 mL of deionized water, and then dropped into the above suspension at 45 °C. The solvent was removed using rotary evaporation after stirring for 24 hours. The sample was dried at 105 °C overnight, and calcined at 700 °C (1 °C/min) for 2 hours to obtain metal oxide supported silica (MOx/SiO2). 1.0 g of MOx/SiO2 was added to a round-bottom flask with 100 g of deionized water. A certain amount of SnCl₄ was dissolved in 10 mL of deionized water, then slowly dropped into the above suspension, and stirred at 45 °C for 24 hours. After that, the pH value of the solution was adjusted to 8.5 using NH₃·H₂O. The solid was separated by centrifugation after stirring for 6 hours, and dried at 105 °C overnight. After calcination at 700 °C (1 °C/min) in a muffle furnace for 2 hours, the solid powder was reduced in $\rm H_2$ flow at 400 °C (1 °C/min) for 2 hours. After cooling down to room temperature, the catalyst was purged with nitrogen for 2 hours, and then treated with 1% O₂/N₂ for another 0.5 hours to obtain a Sn-M/SiO₂ catalyst.

Catalysts characterization

Transmission electron microscopy (TEM) images were taken by a JEOL Model JEM-2010 LaB6 TEM system. High resolution transmission electron microscopy (HRTEM) and the energy dispersive X-ray spectroscopy (EDS) were performed by using a JEOL JEM-2100F field emission transmission electron microscope. The X-ray diffraction (XRD) measurements were collected by a TTR-III X-ray diffractometer using a Cu K α radiation beam, 2 θ range was 20–80°. The ex-situ X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer. The in-situ XPS was performed by another ESCALAB 250Xi X-ray photoelectron spectrometer, the data were recorded after in situ reduction of sample under hydrogen at 400 °C (1 °C/min) for 2 h.

Metal content was tested by an AA800 atomic absorption spectrophotometer (AAS). The sample treating process was as follows: a certain amount of sample was added to 6 M NaOH solution to dissolve the silica carrier. Then excess aqua regia was added to the above solution until the metal was completely dissolved. After that, the above solution was diluted to 100 mL for testing.

Temperature-programmed desorption of CO_2 (CO_2 -TPD) was carried out on a home-built reactor coupled to a gas chromatograph. 100 mg of catalyst were pre-treated in Ar flow at 500 °C for 1 h. After cooling down to 40 °C, CO_2 was introduced and

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hydrogenation of glucose instead of generating C3 products. However, when using 2%Sn-10%Co/SiO₂ as catalyst, an unexpected yield (54.4%) of acetol was obtained. In addition, 12.2% and 11.4% yields of lactic



Figure 1. Cellulose conversion over Sn-Ni/SiO₂ and Sn-Co/SiO₂ with low Sn content. Reaction conditions: 50 mg of cellulose, 34 mg of catalyst, 10 mL of deionized water, 4 MPa H₂, 250 °C, 1 h. EG, HB, 1,2-P and LA represent ethylene glycol, 1-hydroxy-2butanone, 1,2-propanediol and lactic acid, respectively.

acid and 1-hydroxy-2-butanone (HB) were detected, respectively. That is, after replacing the hydrogenation metal Ni by Co, the yield of C2-C4 products increased by 6 times from 13.4% to 78%, and the yield of C3 products increased by 9 times from 7.1% to 66.6%. Increasing the Sn content to 5%, the yield of C2-C4 small molecular products was increased to a certain extent for the Sn-Ni/SiO₂ catalyst, but still insufficient. This result is consistent with our previous research that Ni-Sn/SiO2 with Sn content <15% (Sn/Ni<3) could not convert cellulose to C3 products well.²⁵ However, for Sn-Co/SiO₂ catalyst, further increasing the Sn content had almost no effect on the activity of the catalyst, which indicated that the 2% Sn content was sufficient to effectively convert leen upose 43465 products.

In order to explain why the combination of Sn and Co can significantly reduce the Sn content required by the catalyst, we investigated the effect of Sn and Co content on cellulose conversion. Table 1 showed the effect of Sn content on cellulose conversion at a Co content of 10 wt%. When 0.2 wt% Sn was incorporated into the catalyst, the yield of acetol increased from 5.3% to 12.6%. When the Sn content increased to 0.5%, 32.4% of acetol was obtained. This result was already better than the 5%Sn-10%Ni/SiO₂ catalyst (Figure 1), although the Sn content was only one tenth of it. The acetol yield increased to 54.4% when $2\%Sn-10\%Co/SiO_2$ was used as the catalyst. Further increasing Sn content, the yield of acetol did not change significantly, and the total C3 products yield was maintained at about 60%. When Sn content ≤0.5%, diols and sorbitol were detected, but these products disappeared when Sn content ≥1%. It demonstrated that a small amount of Sn could significantly inhibit the hydrogenation activity of the catalyst, and thereby inhibited the hydrogenation of glucose or other unsaturated intermediates, which is conductive to acetol production.

In order to investigate the role of Co in the reaction, we compared the effect of Co content on the conversion of cellulose over Sn-Co/SiO₂ catalysts at 2% and 5% Sn content, respectively. For both groups of catalysts, the influence of Co content on the catalytic activity was consistent. For 2%Snx%Co/SiO₂ catalysts, when the catalyst did not contain Co (Table 2, entry 1), only a small amount of C3 products were detected. However, with the incorporation of Co, the total yield of acetol and C3 products increased rapidly. When the Co content was ≥2%, the total yield of C3 products was maintained at about 60%, while the yield of acetol increased first and then decreased. At the same time, the yield of lactic acid gradually decreased, and when 2%Sn-15%Co/SiO₂ was used as the catalyst, 5.1% yield of 1,2-propanediol (1,2-P) was produced, which was generated by the hydrogenation of acetol. These results showed that Co provided active sites for the hydrogenation reaction. Catalyst with proper

Table 1. Cellulose conversion over a series of x%Sn-10%Co/SiO ₂ catalysts with different Sn contents. ^a									
		Yield %							
Entry	Catalyst	Acetol	HB	LA	1,2-P	EG	Sorbitol	C3	
1	10%Co/SiO ₂	5.3			5.7	7.3	10.1	11.0	
2	0.2%Sn-10%Co/SiO ₂	12.6	4.3		2.6	9.2	5.8	15.2	
3	0.5%Sn-10%Co/SiO ₂	32.4	9.2		1.4	6.5	2.1	33.8	
4	1%Sn-10%Co/SiO ₂	44.5	9.8	2.8				47.3	
5	2%Sn-10%Co/SiO ₂	54.4	11.4	12.2				66.6	
6	3%Sn-10%Co/SiO ₂	50.4	10.4	8.8				59.2	
7	5%Sn-10%Co/SiO ₂	51.2	11.5	5.8				57.0	
8	10%Sn-10%Co/SiO ₂	53.4	12.1	6.9				60.3	
9	15%Sn-10%Co/SiO ₂	49.7	11.3	13				62.7	
10	20%Sn-10%Co/SiO ₂	48.5	11.2	11.9				60.4	
11 ^b	10%Co/SiO ₂ +2%Sn/SiO ₂	31.2	15.4	2.2	0.7	4.6	1.1	34.1	

Reaction conditions: a 50 mg of cellulose, 34 mg of catalyst, 10 mL of H₂O, 250 °C, 4 MPa H₂, 1 h. HB, LA, 1,2-P and EG represent 1-hydroxy-2-butanone, lactic acid, 1,2-propanediol and ethylene glycol, respectively. ^b each catalyst was 34 mg.

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Table 2. Cellulose conversion over a series of Sn-Co/SiO2catalysts with different Co contents.^a

	_	Yield %				
Entry	Catalyst	Acetol	HB	LA	1,2-P	C3
1	2%Sn/SiO ₂	13.0	trace	4.1		17.1
2	2%Sn-1%Co/SiO ₂	28.6	6.4	15		43.6
3	2%Sn-2%Co/SiO ₂	44.7	10.7	16.3		61.0
4	2%Sn-5%Co/SiO ₂	51.8	11.1	11.4		63.2
5	2%Sn-10%Co/SiO ₂	54.4	11.4	12.2		66.6
6	2%Sn-15%Co/SiO ₂	45.0	8.2	4.6	5.1	54.7
7	5%Sn-2%Co/SiO ₂	32.5	6.1	27.1		59.6
8	5%Sn-5%Co/SiO ₂	46.1	9	15.3		61.4
9	5%Sn-10%Co/SiO ₂	51.2	11.5	6.4		57.6
10	5%Sn-15%Co/SiO ₂	57.2	11.8	7.4		64.6
11	5%Sn-20%Co/SiO ₂	55.5	11.3	8.1		63.6
12	15%Sn-2%Co/SiO ₂	30.6	6.5	30.6		61.2

Reaction conditions: ^a 50 mg of cellulose, 34 mg of catalyst, 10 mL of H_2O , 250 °C, 4 MPa H_2 , 1 h. HB, LA, 1,2-P and EG represent 1-hydroxy-2-butanone, lactic acid, 1,2-propanediol and ethylene glycol, respectively.

hydrogenation activity is conducive to the production of acetol. but excessive hydrogenation activity is disadvantageous, not only for the production of acetol but also the total C3 products. Similar results were also obtained in the 5%Sn-x%Co/SiO₂ experiments. When the Co content increased from 2% to 20%, the total yield of C3 products was maintained at about 60%, but more Co was beneficial to the production of acetol, and less Co was favorable to the production of lactic acid. When using 15%Sn-2%Co/SiO2 as catalyst, high yield (30.6%) of lactic acid was achieved. The above results indicated that Co in Sn-Co/SiO2 may mainly participate in the hydrogenation reaction, which was similar to the role of Ni in the Ni-Sn/SiO₂ catalyst as our previous research.²⁵

Intermediates study

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To explore the reason why the catalytic activity of Sn-Co/SiO₂ was significantly higher than that of Sn-Ni/SiO₂, we first used glucose (a reaction intermediate) as the substrate. As shown in Figure 2, when the reaction temperature was 250 °C (cellulose conversion temperature, Figure 1), for 5%Sn-10%Ni/SiO₂ catalyst, 22.3% yield of 1,2-propanediol and 4.5% of lactic acid were produced. Under the same reaction conditions, 43.2% yield of acetol and 9% of lactic acid were detected when 5%Sn-10%Co/SiO₂ was used as the catalyst. This was consistent with the results when cellulose was used as the substrate (Figure 1). However, if the reaction temperature decreased to 180 °C, C3 products yield improved significantly over 5%Sn-10%Ni/SiO₂ catalyst, in which 37.8% yield of acetol and 5.1% of lactic acid were generated, indicating the 5%Sn-10%Ni/SiO₂ can actually catalyze the glucose isomerization and fructose retro-aldol condensation to C3 intermediates. The low product yield at 250 °C may be due to the subsequent reaction of the C3 intermediates (glycerosone and glyceraldehyde). If the C3 intermediates cannot be quickly converted to a stable C3

product, they can easily polymerize and causerticathon loss.^{26,27} It could be seen from Figure 29 that when the reaction temperature increased from 180 °C to 250 °C, the carbon loss increased from 50% to 65%, indicating that 5%Sn-10%Ni/SiO₂ catalyst was more likely to catalyze the



Figure 2. a) Glucose and b) glycerosone conversion over 5%Sn-10%Ni/SiO₂ and 5%Sn-10%Co/SiO₂ at different reaction temperatures. GL represents glycerol. Reaction conditions: 50 mg of substrate, 34 mg of catalyst, 10 mL of H₂O, 4 MPa H₂. The reaction was carried out at 250 °C, 1 h for Figure 2a left, and 180 °C, 30 min for Figure 2a right and Figure 2b left, and 200 °C, 5 min for Figure 2b right. The reaction time of each substrate is based on the full conversion of each substrate.

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polymerization of C3 intermediates at high temperature. However, for 5%Sn-10%Co/SiO₂ catalyst the change in reaction temperature had no significant effect on the reaction results. Similar products distribution and carbon loss were achieved, indicating that the C3 intermediates could be efficiently converted to acetol no matter at high or low temperature.

In order to further prove the above points, we used C3 intermediate glycerone as a substrate for comparative study. For 5%Sn-10%Ni/SiO₂ catalyst, when the reaction was carried out at 180 °C, the total yield of acetol, 1,2-P and LA reached 50.9%. However, when the reaction temperature increased only 20 °C to 200 °C, the total yield of C3 products dropped to 42.1%, and the carbon loss increased from 27% to 33%. Glycerol was produced in similar yields and that was not detected when cellulose or glucose was used as the substrate. It demonstrated that in the initial heating stage (ambient temperature to 180 °C), glycerone could be hydrogenated to glycerol over 5%Sn-10%Ni/SiO2. In contrast, for 5%Sn-10%Co/SiO₂, the increase in temperature did not affect the yield of the products, and the carbon loss was almost unchanged. These results were consistent with the results when cellulose and glucose were used as substrates, further proving that Sn-Co/SiO₂ could effectively convert C3 intermediates to acetol at high temperature, but Sn-Ni/SiO₂ catalyst tended to catalyze polymerization of C3 intermediates.

Since the hydrolysis of cellulose usually needs to be carried out at a high temperature (> 200 °C), ²⁸ there is a contradiction for 5%Sn-10%Ni/SiO₂ catalyst, that is, the generated C3 intermediates were easy to polymerize. The mismatch of reaction temperature led to low target product yield and high carbon loss. However, for the 5%Sn-10%Co/SiO₂ catalyst, the C3 intermediates can still be effectively converted to acetol under high temperature conditions, which ultimately resulted in high acetol yield and low carbon loss.

According to previous researches,^{25,29} both the isomerization of glucose and the retro-aldol condensation of fructose are catalyzed by Sn species. The combination of Sn and different metals may change the physico-chemical properties and thus the catalytic activity of Sn species. Although there was no significant difference between Sn-Ni and Sn-Co in catalyzing these reactions at 5% Sn level (Figure 2), this may be because the Sn sites were sufficient. To better reflect the difference M^{K} the activity of Sn species, the catalytic activities of Sn-Ni and Sn-Co catalysts with lower Sn content (2%) were compared. As



Figure 3. Glucose (left) and glycerosone (right) conversion over 2%Sn-10%Ni/SiO₂ and 2%Sn-10%Co/SiO₂ catalysts. Reaction conditions: 50 mg of substrate, 34 mg of catalyst, 10 mL of H₂O, 4 MPa H₂, 180 °C. The reaction time was 30 min for the left and 5 min for the right. The reaction time of each substrate is based on the full conversion of each substrate.

shown in Figure 3, using glucose as substrate, the yield of small molecule products over 2%Sn-10%Ni/SiO₂ was much lower and the carbon loss was much higher than those over 2%Sn-10%Co/SiO₂. This was obviously different from the comparison results of 5% Sn content (180 °C, Figure 2a right). In order to rule out it was caused by the subsequent reaction of the C3 intermediates, we compared the catalytic effects of the two catalysts on glycerone conversion. As shown in Figure 3 (right), both 2%Sn-10%Ni/SiO₂ and 2%Sn-10%Co/SiO₂ could efficiently catalyze the conversion of glycerone, and the carbon loss of 2%Sn-10%Ni/SiO₂ was even slightly less than that of



Scheme 1. Reaction scheme of cellulose conversion to acetol over Sn-Co/SiO₂ and Sn-Ni/SiO₂ with low Sn content.

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 25 nm
 25 nm
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 Figure 4. TEM images of a) 2%Sn-10%Co/SiO₂ b) 5%Sn-10%Co/SiO₂, c) HRTEM image of 5%Sn-10%Co/SiO₂, d) EDS mapping of 5%Sn-10%Co/SiO₂, tem images of e) 2%Sn-10%Ni/SiO₂ f) 5%Sn-10%Ni/SiO₂, g) HRETM image of 5%Sn-10%Ni/SiO₂, h) EDS mapping of 5%Sn-10%Ni/SiO₂ and the corresponding particle size distribution histograms.

2%Sn-10%Co/SiO₂, indicating that the significant difference in glucose conversion was not caused by the subsequent conversion of C3 intermediates, but by the conversion of glucose to the C3 intermediates, and significant carbon loss for 2%Sn-10%Ni/SiO₂ could be caused by the convertion of glucose to form humins. That is, Sn combined with Co can significantly improve the activity of Sn species in catalyzing glucose isomerization and fructose retro-aldol condensation to C3 intermediates, and inhibit the formation of humins.

Summarizing the above results, it could be seen that low Sn content of Sn-Co/SiO₂ had a better catalytic activity than Sn-Ni/SiO₂ for two main reasons (Scheme 1): (1) Sn-Co/SiO₂ catalyst could more effectively catalyze the isomerization of glucose and the retro-aldol condensation of fructose to generate C3 intermediates and inhibit the formation of humins and sorbitol. (2) Sn-Co/SiO₂ could efficiently catalyze the conversion of C3 intermediates to acetol at high temperature, while Sn-Ni/SiO₂ tended to catalyze the polymerization of C3 intermediates. Since the hydrolysis of cellulose to glucose

needs to be carried out at a high temperature, the good match of cascade reaction conditions makes $Sn-Co/SiO_2$ can effectively catalyze the conversion of cellulose to acetol.

Structure-activity relationship study

A series of characterizations were carried out to explore what affect the activity of the Sn species in the two types of catalysts. The morphology and element distribution of the catalysts were shown in Figure 4. The metal particles of all catalysts are well dispersed on the silica support. For the 2%Sn-10%Co/SiO₂ catalyst, the average size of metal particles was only 1.9 nm. When the Sn content increased to 5%, the average size increased to 3.3 nm. Metal particles with average size of 1.9 nm and 2.8 nm were observed over 2%Sn-10%Ni/SiO₂ and 5%Sn-10%Ni/SiO₂, respectively. The EDS mapping results indicated that all elements were well distributed on both types of catalysts. Through the above results, it can be seen that Sn-Co/SiO₂ and

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 $Sn-Ni/SiO_2$ are not significantly different in morphology, particle size and elements distribution. These factors are not the reasons that affect the activity of the catalysts.

Due to the low Sn content and well dispersion of the catalysts, it was difficult to observe the diffraction peaks of Sn species from the XRD patterns for both two types of catalysts even if the Sn content was 5%. Only the diffraction peaks of metallic Co or Ni and their oxides were observed (Figure S1). However, from HRTEM images of 5%Sn-10%Co/SiO₂ (Figure 4c), lattice fringes with lattice spacing of 0.290 nm and 0.334 nm could be seen, which correspond to Sn(200) and SnO₂(111), respectively. It indicated that the reduction temperature of 400 °C could reduce part of Sn species to the metallic Sn, but some of them were still not reduced or just partially reduced. This was confirmed by the XRD pattern of the Sn-Co/SiO₂ catalyst with high Sn content, in which the



Figure 6. In-situ XPS spectra of Sn 3d of 2%Sn-10%M/SiO₂ (M=Ni or Co).

diffraction peaks of metal Sn and oxidized Sn species were detected (Figure S1). H₂-TPR was also Carried 3000 and 3000 same conclusion was obtained (Figure S4). For 5%Sn-10%Ni/SiO₂, the lattice fringes of Sn (200) were also observed.

The electronic state of Sn species has a significant effect on the cellulose conversion. According to our previous research, unsupported Sn⁰ and SnO₂ cannot catalyze the isomerization of glucose and retro-aldol condensation of fructose. However, the supported Sn (Sn/SiO2) or Ni3Sn4 alloy can form a slightly positive valence of metal Sn (Sn^{δ +}) and noninteger valence of SnO_x species. These species provide basic sites to catalyze the conversion of glucose to C3 molecules. Therefore, ex-situ XPS analyses of the two types of catalysts were carried out to explore the differences in the electronic states of Sn species. It is difficult to distinguish Sn²⁺ and Sn⁴⁺ by peak fitting because they have similar binding energies. As shown in Figure 5, for the unsupported Sn powder, the binding energy at 483.3 eV was attributed to Sn⁰, and the binding energy at 486.7 eV was attributed to Sn²⁺ and Sn⁴⁺. Due to the interaction between Sn and the support, the binding energy of Sn species in both types of catalysts increased. However, comparing the peak positions of Sn oxides in the two types of catalysts, the overall binding energy of the oxidation state Sn species was 2%Sn-10%Ni/SiO₂ (487.2 eV)> 2%Sn-10%Co/SiO₂ (487.1 eV)> 5%Sn-10%Ni/SiO₂ (486.9 eV)= 5%Sn-10%Co/SiO₂ (486.9 eV). The smaller binding energy means there are more noninteger valence (or lowvalence state) SnO_x species.²⁵ Coincidentally, the three catalysts with low binding energy have good activity in catalyzing the isomerization of glucose and retro-aldol condensation of fructose as shown in Figure 2, which further proved that the SnOx species is important active sites for catalyzing glucose conversion to C3 molecules.

For 2%Sn-M/SiO₂(M=Ni or Co) catalysts, ex-situ XPS results showed that the difference in binding energy of Sn $3d_{5/2}$ was only 0.1 eV (487.2 vs 487.1 eV). However, the activity of the two catalysts was different dramatically (Figure 3). Considering that ex-situ condition may cause the active SnO_x species on the catalyst surface to be oxidized when the catalyst was exposed to the air, resulting in non-obvious differences in the ex-situ data, in-situ XPS analysis was performed. As shown in Figure 6, the binding energy of Sn oxides in 2%Sn-10%Ni/SiO₂ catalyst



Figure 7. CO_2 -TPD profiles of 2%Sn-10%M/SiO₂(M=Ni or Co). was 487.2 eV. However, the binding energy in 2%Sn-

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10%Co/SiO₂ catalyst was significantly reduced to 486.9 eV. It indicated that replacing Ni with Co significantly increased the SnO_x species in the catalyst. The SnO_x species can provide basic sites for the catalyst. As the characterization results of CO₂-TPD (Figure 7), 2%Sn-10%Co/SiO₂ with more SnO_x species has more basicity, which was the main reason why 2%Sn-10%Co/SiO₂ can catalyze glucose to C3 molecules more efficiently.

Conclusion

ARTICLE

The efficiency of catalyzing cellulose to acetol over Sn-Co/SiO₂ was much higher than that of Sn-Ni/SiO₂ at low Sn content (\leq 5 wt%). Using 2%Sn-10%Co/SiO₂ as a catalyst, 54.4% yield of acetol and 66.6% total yield of C3 products were obtained. However, no acetol and only 7.1% yield of C3 product was produced when 2%Sn-10%Ni/SiO₂ was used as the catalyst. The study found that there were two main reasons for the better performance of Sn-Co/SiO₂. On the one hand, at low Sn content, Sn-Co/SiO₂ could convert glucose to C3 intermediates more efficiently than Sn-Ni/SiO₂ catalyst. On the other hand, Sn-Co/SiO₂ catalyst could effectively convert C3 intermediates to acetol under high temperature reaction conditions, but Sn-Ni/SiO₂ tend to catalyze the polymerization of C3 intermediates to form humins. Since the hydrolysis of cellulose needs to be carried out at high temperature, the good match of the cascade reaction conditions caused the Sn-Co/SiO₂ could effectively convert cellulose to acetol. A series of catalyst characterizations indicated that the combination of Sn and Co could significantly increase the noninteger valence SnO_x species in the catalyst, which increased the basicity of the catalyst and facilitated the reactions of glucose isomerization and fructose retro-aldol condensation.

Conflicts of interest

There are no conflicts to declare.

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Table of contents



 $Sn-Co/SiO_2$ with low Sn content can effectively catalyze cellulose conversion to acetol, but $Sn-Ni/SiO_2$ cannot. The catalytic mechanism was studied systematically.