A mechanism study on efficient conversion of cellulose to acetol over Sn-Co catalysts with low Sn content

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Table S1. Metal contents of Sn-M/SiO_2 catalysts.

	Content(wt%)[a]			Atom%(Sn/M)	
Catalyst	Sn	Co	Ni	Bulk[a]	Surface[b]
2%Sn-10%Co/SiO_2	2.1	9.5		0.110	0.097
2%Sn-10%Ni/SiO_2	2.2		9.3	0.117	0.095
5%Sn-10%Co/SiO_2	5.2	9.4		0.275	0.093
5%Sn-10%Ni/SiO_2	5.4		9.5	0.281	0.084

[a] measured by AAS; [b] measured by XPS.

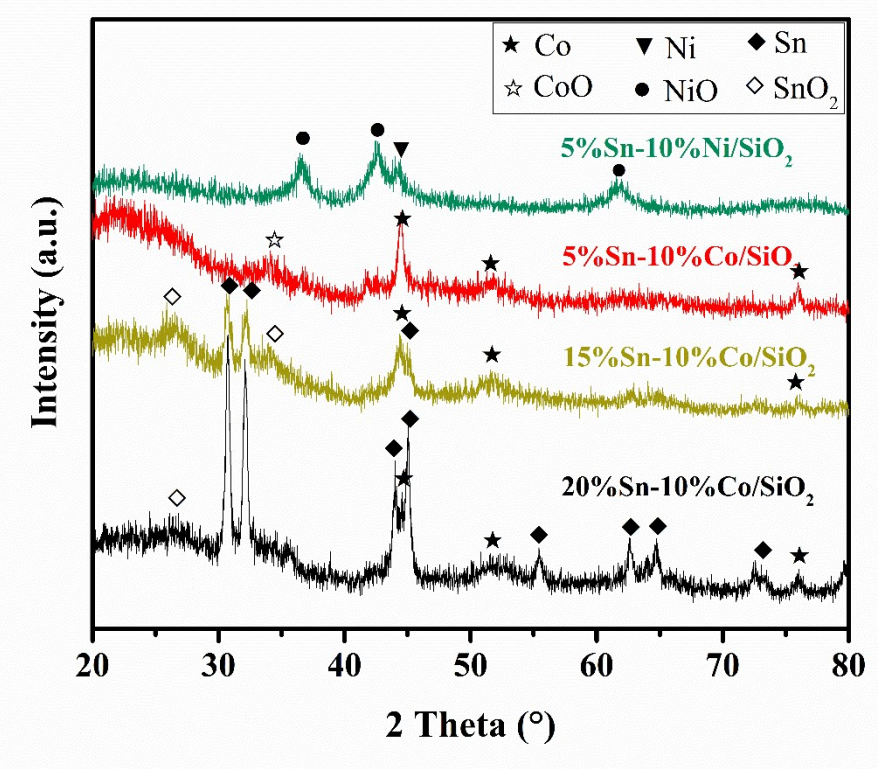

Figure S1. XRD patterns of Sn-M/SiO_2 catalysts

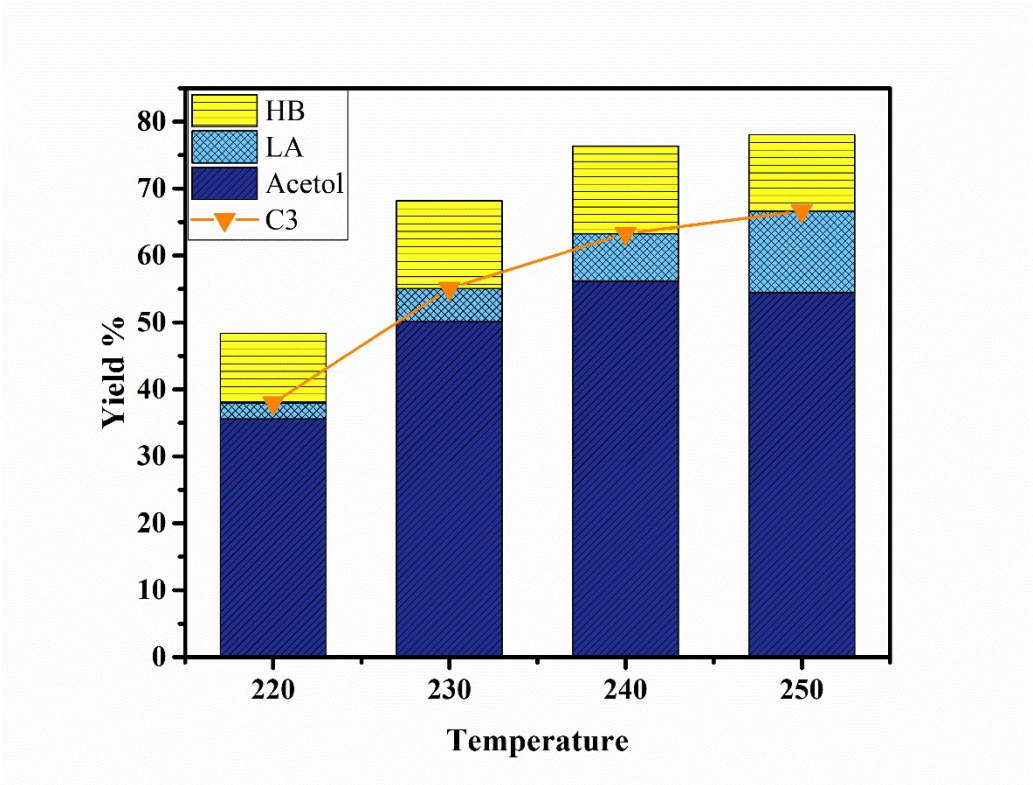

Figure S2. Effect of reaction temperature on cellulose conversion. Reaction conditions: 50 mg of cellulose, 34 mg of catalyst, 10 mL of H_2O, 4 MPa H_2, 1 h..

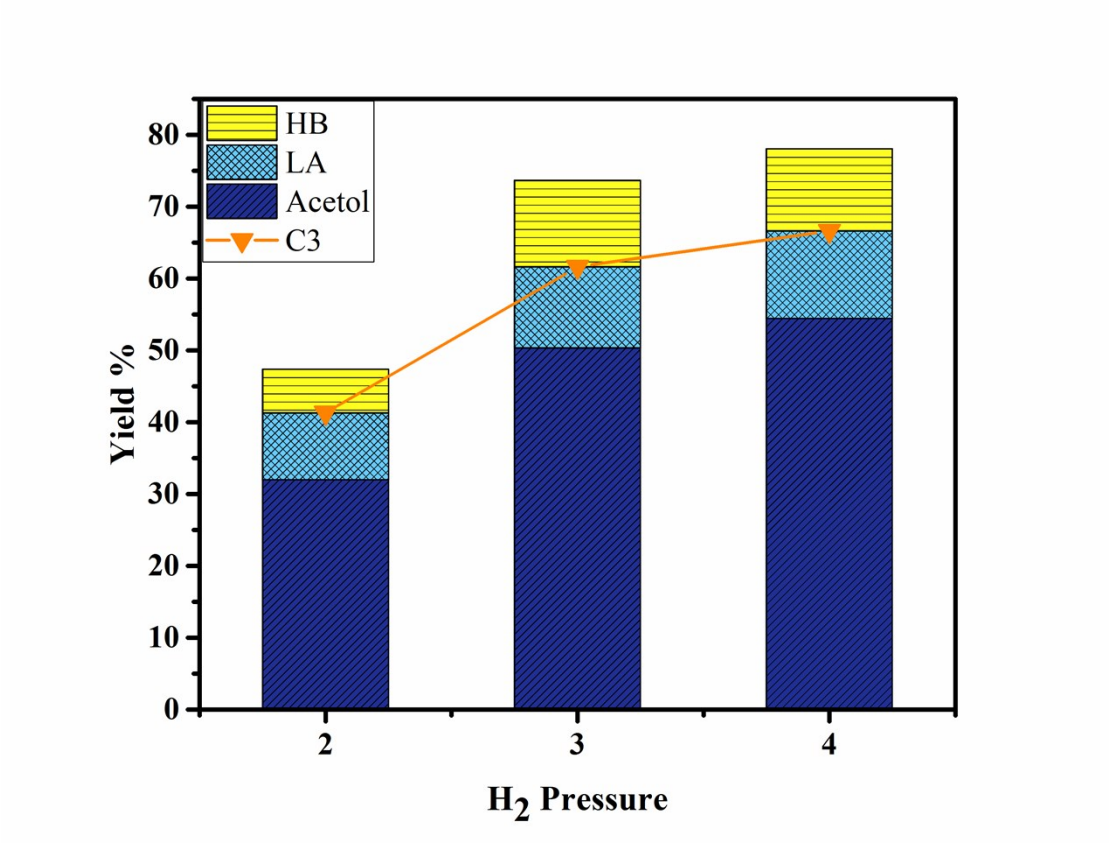

Figure S3. Effect of H_2 pressure on cellulose conversion. Reaction conditions: 50 mg of cellulose, 34 mg of catalyst, 10 mL of H_2O, 250 °C, 1 h.

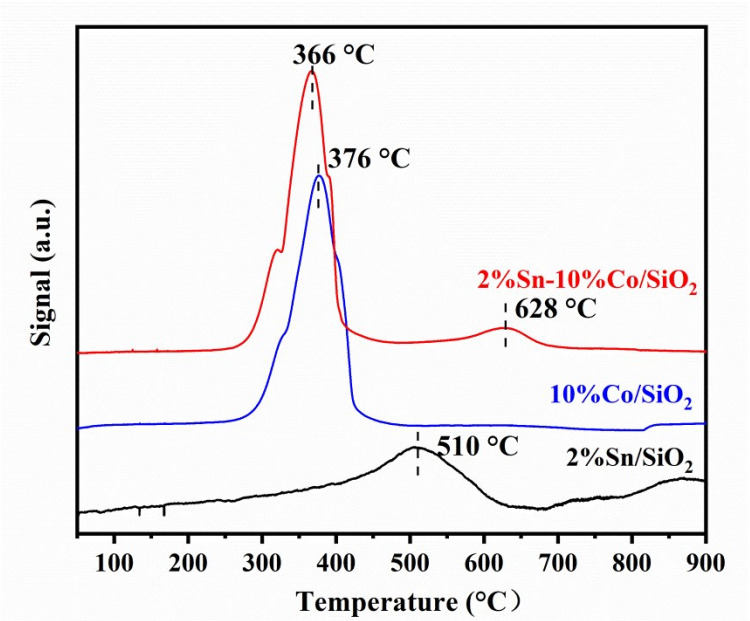

Figure S4. H_2-TPR profiles for 2%Sn/SiO_2, 10%Co/SiO_2 and 2%Sn-10%Co/SiO_2. The signal of 2%Sn/SiO_2 is increased by 6 times.

In order to detect the oxidation state of Sn and Co, H_2-TPR was carried out. For 2%Sn/SiO_2, the reduction peak at 510 ℃ is attributed to the reduction of SnO_2, and

the reduction peak at >800℃ should be attributed to the reduction of tin oxides interacted with silica, which is more difficult to be reduced. For Co/SiO_2, an overlapping peak at 376 °C was observed, indicating that cobalt oxides are easily reduced. When Sn and Co were co-loaded on SiO_2, the reduction peak of tin oxides significantly shifted to low temperature. The reduction peak at high temperature (>800°C in 2% Sn/SiO_2) moved to 618°C, and the peak at low temperature (510 °C in 2% Sn/SiO_2) disappeared, which should overlap with the reduction peak of cobalt oxides. The presence of Co significantly promoted the reduction of tin oxides. This could be because Co promoted the dissociation of H_2 to active H, and the active H migrated onto tin oxides to promote its reduction. According to the results of H_2-TPR, the reduction temperature of 400 °C in this work can reduce most of the cobalt oxides, but only part of the tin oxides, which is consistent with the results of XPS, XRD and HRTEM.

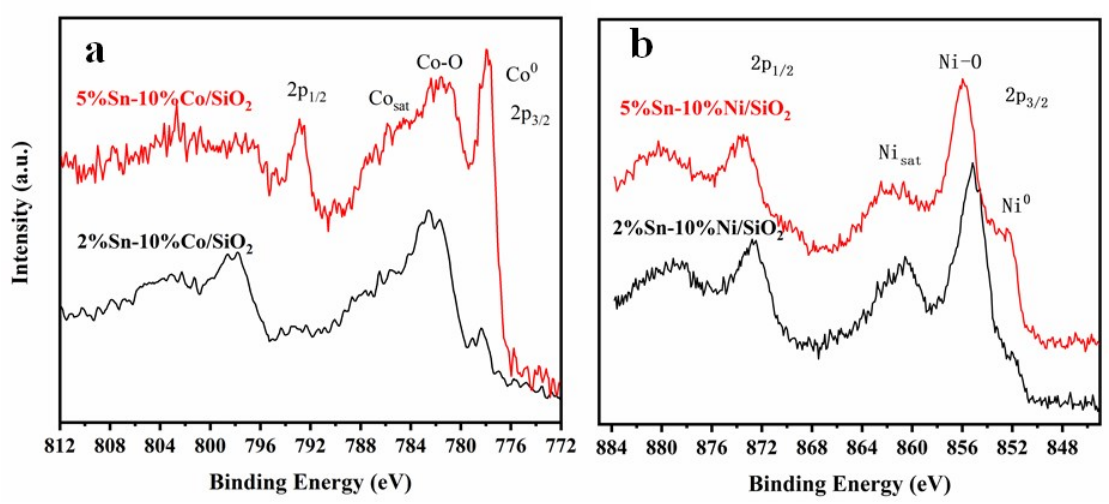

Figure S5. Ex-situ XPS spectra of a) Co and b) Ni of Sn-M/SiO_2 (M=Ni or Co).

The XPS spectra of Co and Ni are shown in the figures S5. Whether it is Co or Ni, both zero valence and the oxidation state coexist on the catalyst surface. According to H_2-TPR, a reduction temperature of 400 °C should be able to reduce most of the cobalt oxides, but the ex-situ XPS showed only a small part of Co^0, and most of which was in the oxidation state. This was because the Co^0 on the surface of the catalyst was oxidized after treatment with 1% O_2/N_2 mixed gas. It can be proved by the in-situ XPS (Figure S6), that is, a large amount of Co^0 exists on the catalyst surface. A similar phenomenon was also found in Sn-Ni/SiO_2 catalysts. Sn/M (M=Co or Ni) on the catalyst surface was also analyzed. As shown in the table below, for the 2%Sn-10%M/SiO_2 catalyst, the surface Sn/M ratio was similar. Increasing the Sn content to 5%, the surface Sn/M ratio did not change significantly, even slightly decreased. This may be due to the interaction between Sn and metal M to allow Sn to enter the inside of the particles, resulting in a low surface Sn/M ratio. In addition, the change of metal particle size may also affect the surface Sn/M ratio. Compared with the reaction results, the surface Sn/M value has no positive correlation with the catalytic activity, so the surface Sn/M should not be the main factor affecting the catalytic activity.

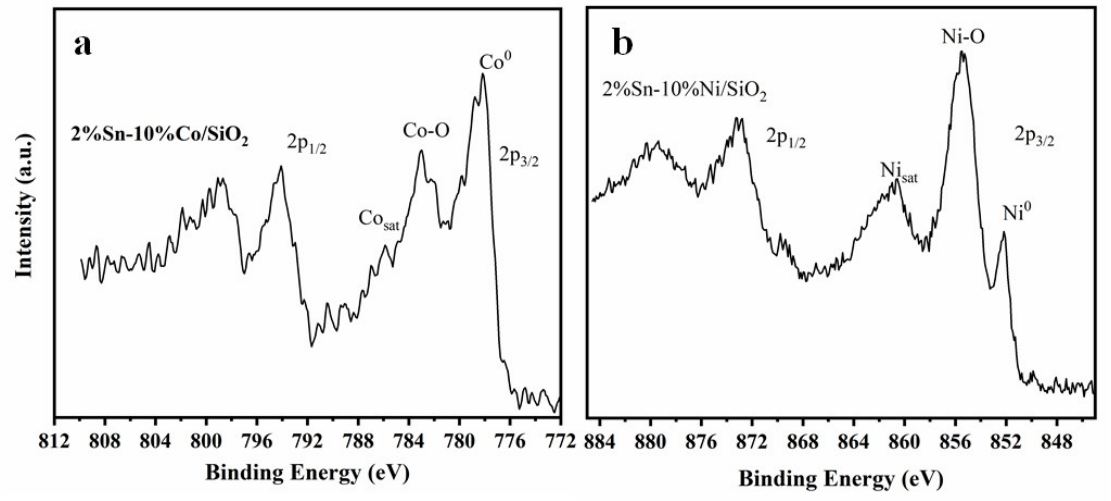

Figure S6. In-situ XPS spectra of a) Co and b) Ni of 2%Sn-10%M/SiO_2 (M=Ni or Co).

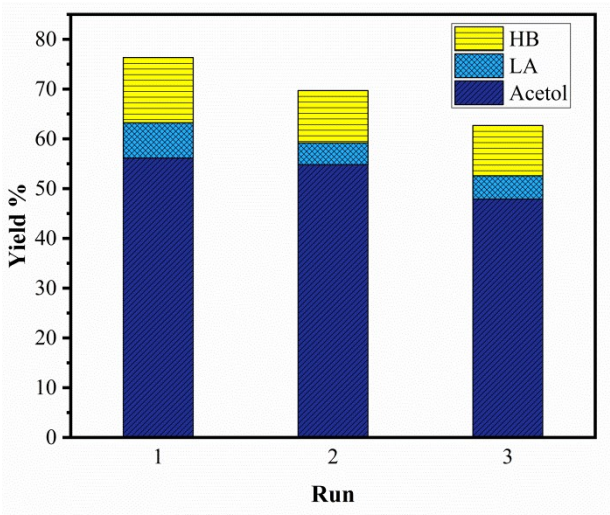

Figure S7. Recycle of 2%Sn-10%Co/SiO_2 catalyst. Reaction conditions: 50 mg of cellulose, 34 mg of catalyst, 10 mL of H_2O, 240 °C, 4 MPa H_2, 1 h.