Electronic Supplementary Information

Towards efficient synthesis of sugar alcohols from mono- and poly-saccharides: Role of metals, supports & promoters

Anup P. Tathod[a] and Paresh L. Dhepe*[,a]

[a]*Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory,*
Dr. Homi Bhabha Road, Pune, 411 008, India.
E-mail: pl.dhepe@ncl.res.in;
Fax: +91 20-25902633; Tel: +91 20-25902024

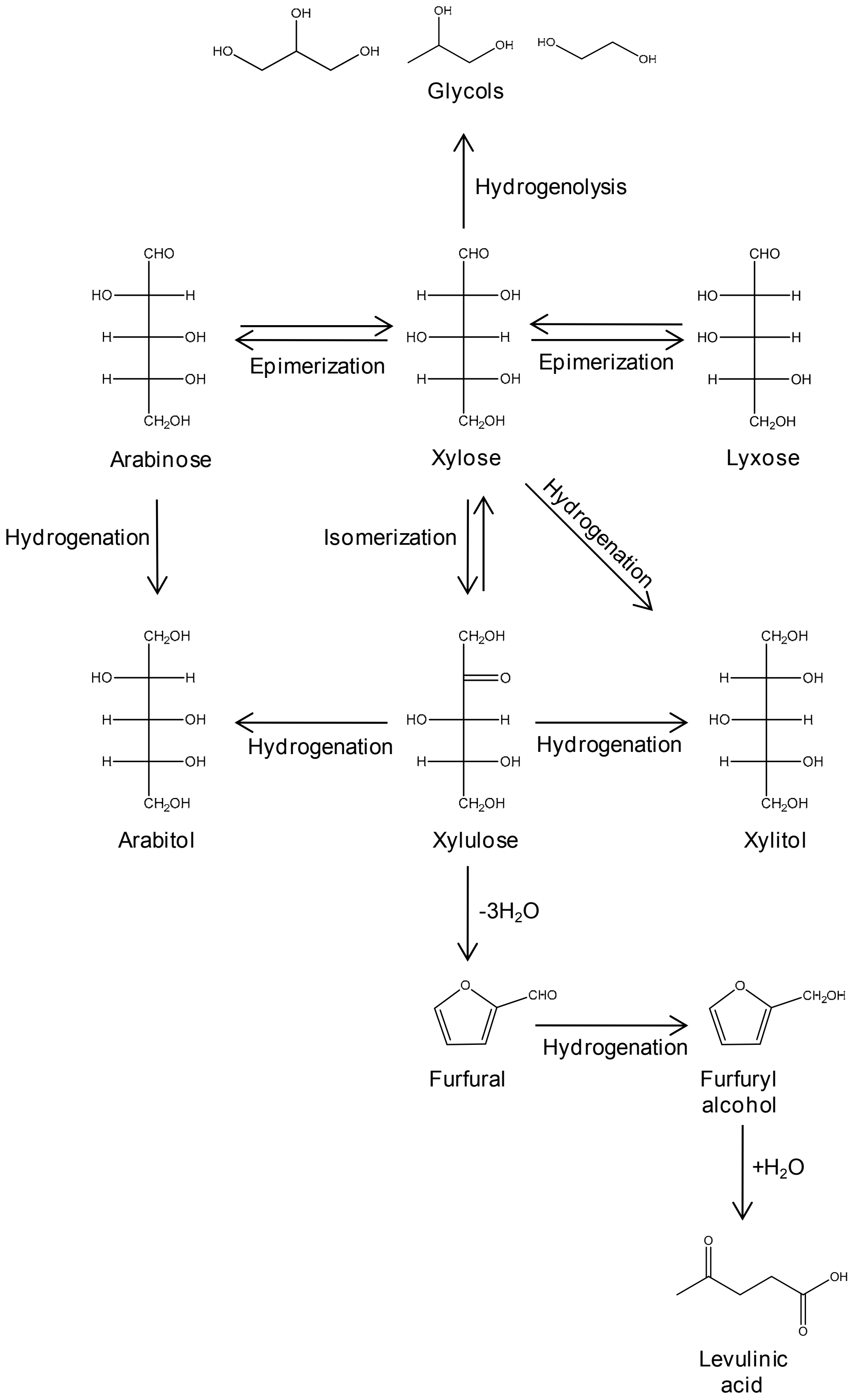

Fig. S1. Reaction network of xylose conversion in to various chemicals.

Preparation of ICP-AES samples

For the determination of metal contents in the catalysts by ICP-AES method, samples were prepared by dissolving known amount of catalyst in acidic solvent. M/AL (M=Pt, PtSn, PtGa, PtFe, Ru) catalysts were dissolved in freshly prepared aquaregia ($HCl:HNO_3 = 3:1$) while Pt/SA catalysts were first treated with HF and then HF was evaporated completely by heating at 60°C, the remaining solid part was mixed with aquaregia and allowed to dissolve. Catalyst in which carbon Black BP-2000 (C) was used as a support, was oxidized at 700°C for 6 h under the flow of oxygen (20 mL/min) and the remaining solid after oxidation was mixed with aquaregia. All ICP-AES samples were diluted with deionized water and filtered before analysis. Reaction mixtures were subjected to analysis after filtration (0.22 μm) without any treatment.

Temperature program desorption study of ammonia (NH_3-TPD)

Acid amounts of γ-Al_2O_3 (AL) and SiO_2-Al_2O_3 (SA) were determined by NH_3-TPD (carried out using Micrometrics Autochem-2910 instrument). In a typical experiment, sample (AL or SA) was activated in-situ at 550°C for 30 min, in a helium flow (30 mL/min). Then the temperature was allowed to decrease to 50°C. Next, 10% NH_3 in helium was passed over the sample at 50°C, for 1 h. Subsequently, temperature of the sample was increased and maintained for 30 min. at 100°C under the flow of helium gas (30 mL/min). This allowed to desorp any physisorped NH_3. Later, at the rate of 10°C/min temperature was increased from 100°C to 700°C in helium flow (30 mL/min). Figure S2 represents the NH_3-TPD profiles for AL and SA.

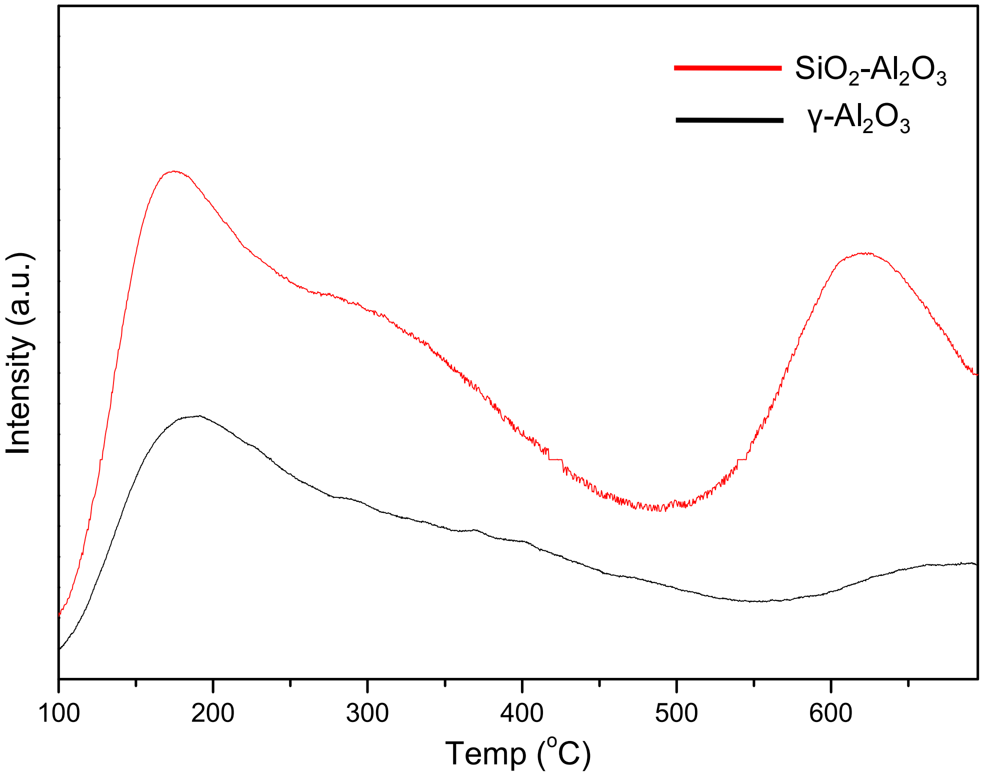

Fig. S2. NH_3-TPD profiles of γ-Al_2O_3 and SiO_2-Al_2O_3

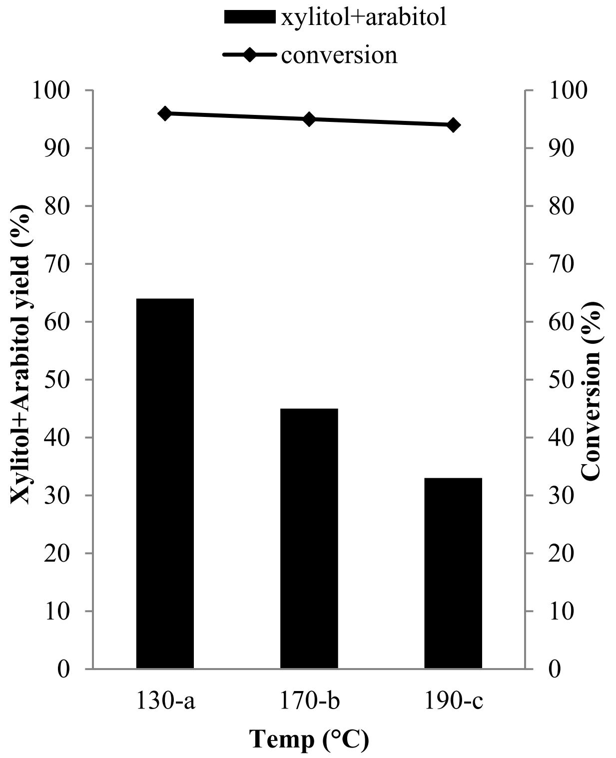

Fig. S3. Effect of temperature in the conversion of xylose.

Reaction condition: xylose 0.15 g, catalyst (Pt(3.5)/AL) 0.075 g, water 35 mL, 16 bar H_2 at R.T., a:6 h, b:1 h, c:15 min.

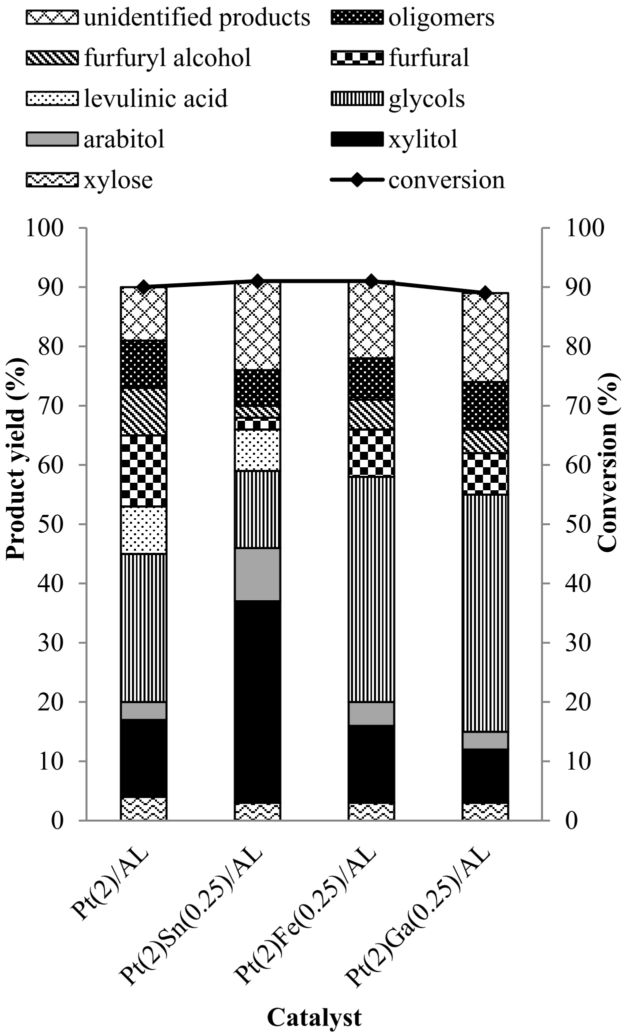

Fig. S4. Effect of bimetallic catalysts on the conversion of hemicellulose.

Reaction condition: hemicellulose (xylan, oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190^{o}C, 16 bar H_2 at R.T., 16 h.

Effect of residual Cl^- on the catalytic activity

Determination of presence of Cl^- on catalyst:

In the preparation of PtSn/AL bimetallic catalyst, Sn precursor $SnCl_2{\cdot}2H_2O$ was dissolved in 3M HCl (Experimental section), hence contribution from any residual HCl present on the catalyst in these reactions cannot be ignored. To ascertain these facts we first checked whether there is any presence of Cl^- on the catalyst by subjecting the catalyst to silver chloride test. 0.075 g of Pt(3.5)Sn(3.5)/AL catalyst was suspended in the distilled water (35 mL) and the resulting solution was stirred for 30 minutes over magnetic stirrer at R.T (30-35°C). Next, by filtration, solid catalyst was separated from the water. The filtrate (water) was then titrated with 0.01M aq. solution of $AgNO_3$. Formation of white precipitate (AgCl) was observed to confirm the presence of Cl^- in the solution. Similar experiments were also performed with Pt(3.5)Sn(0.22)/AL, Pt(3.5)Sn(0.43)/AL, Pt(3.5)Sn(0.87)/AL and Pt(3.5)Sn(1.75)/AL catalysts to confirm the presence of Cl^- in all these catalysts. Next, to check the effect of Cl^- on reaction, some experiments were carried out by using xylose and hemicellulose (xylan) as substrates. The catalytic results are represented in Table S1. Results show that even if we add higher quantity of HCl during the synthesis of catalyst, most of it is lost during calcination and reduction steps. Above results and discussion help us in arguing the point that there is almost no contribution from Cl^- in the reaction and that decrease in the activity at higher Sn content may be the effect of Pt and Sn and not of Cl^-.

Table S1. Effect of residual Cl^- in the conversion of xylose and hemicellulose.

Sr. No	Catalyst	Conv. (%)	xylitol	arabitol	Glycols^	levulinic acid	furfural	furfuryl alcohol	pH
1*	Pt(3.5)/AL	94	25	8	27.1	7	9	6.2	5.61
2*	Pt(3.5)/AL$	90	17	10	24	6	11	7	5.28
3*	Pt(3.5)Sn(0.43)/AL$	99	66	13	11.8	2.6	0	1	5.32
4*	Pt(3.5)Sn(0.43)/AL#	98	69	8	9	3	1.1	1	5.08
5@	Pt(3.5)/AL	94	16	2	23.1	10	10.4	7	5.66
6@	Pt(3.5)/AL$	96	14	6	21	8.1	12.2	6	5.25
7@	Pt(3.5)Sn(0.43)/AL$	94	35	15	16.3	6.5	0	2	5.34
8@	Pt(3.5)Sn(0.43)/AL#	95	37	16	15	7.5	1	3	5.06

^ Glycols = glycerol+ethylene glycol+1,2-propanediol

* Reaction condition: xylose 0.15 g, catalyst 0.075 g, water 35 mL, 190°C,16 bar H_2 at R.T., 15 min.

@ Reaction condition: hemicellulose (xylan, oat spelt) 0.15 g, catalyst 0.075 g, water 35 mL, 190°C,16 bar H_2 at R.T., 16 h.

$ During synthesis of 0.075 g of Pt(3.5)Sn(0.43)/AL catalyst, 0.062 mL of HCl was used.

During the synthesis of 0.075 g of Pt(3.5)Sn(0.43)/AL catalyst, 0.5 mL of HCl was used instead of 0.062 mL of HCl.

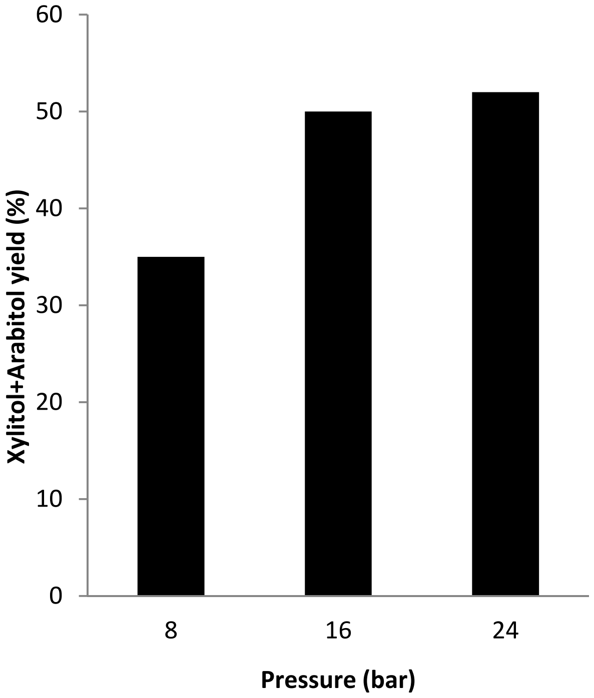

Fig. S5. Effect of pressure in the conversion of hemicellulose.

Reaction condition: hemicellulose (xylan, oat spelt) 0.15 g, catalyst (Pt(3.5)Sn(0.43)/AL) 0.075 g, water 35 mL, 190°C, 16 h.

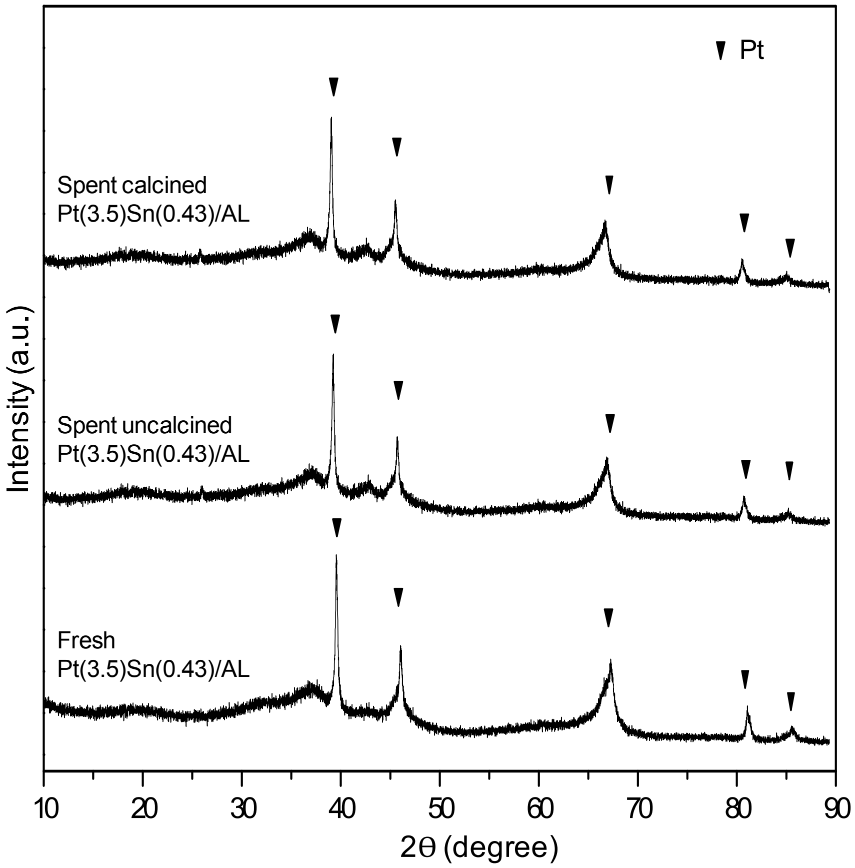

Fig. S6. XRD patterns for spent catalyst, Pt(3.5)Sn(0.43)/AL used in the conversion of hemicellulose (xylan, oat spelt).

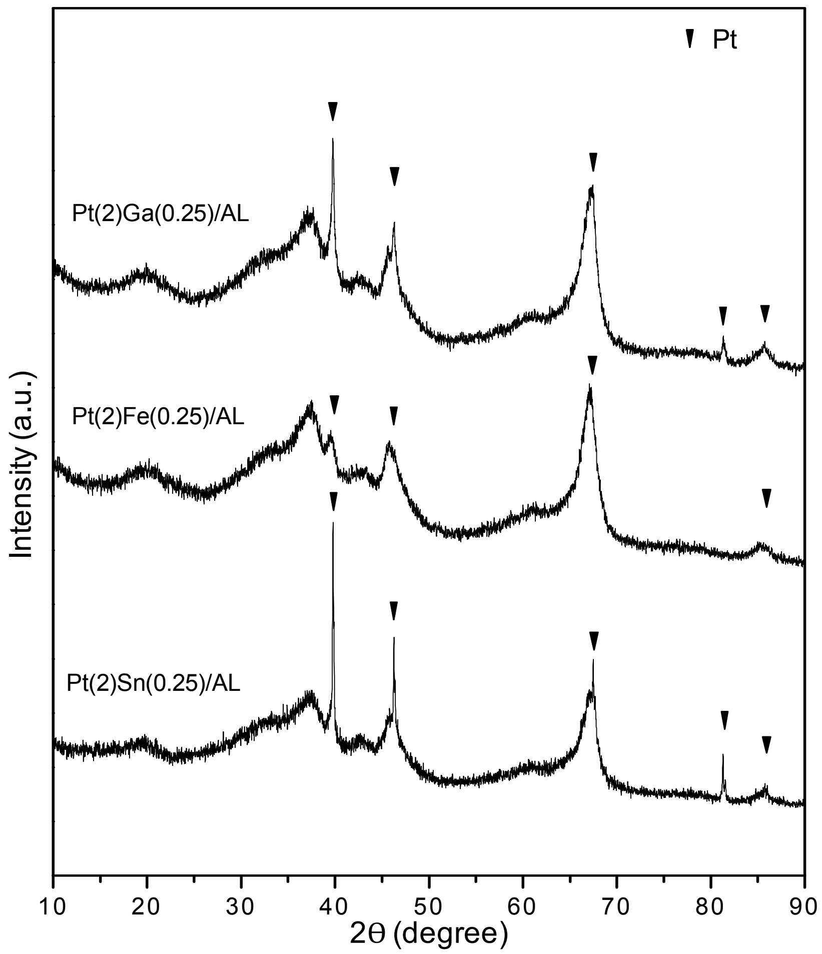

Fig. S7. Comparison of XRD patterns for PtSn/AL, PtFe/AL and PtGa/AL catalysts.

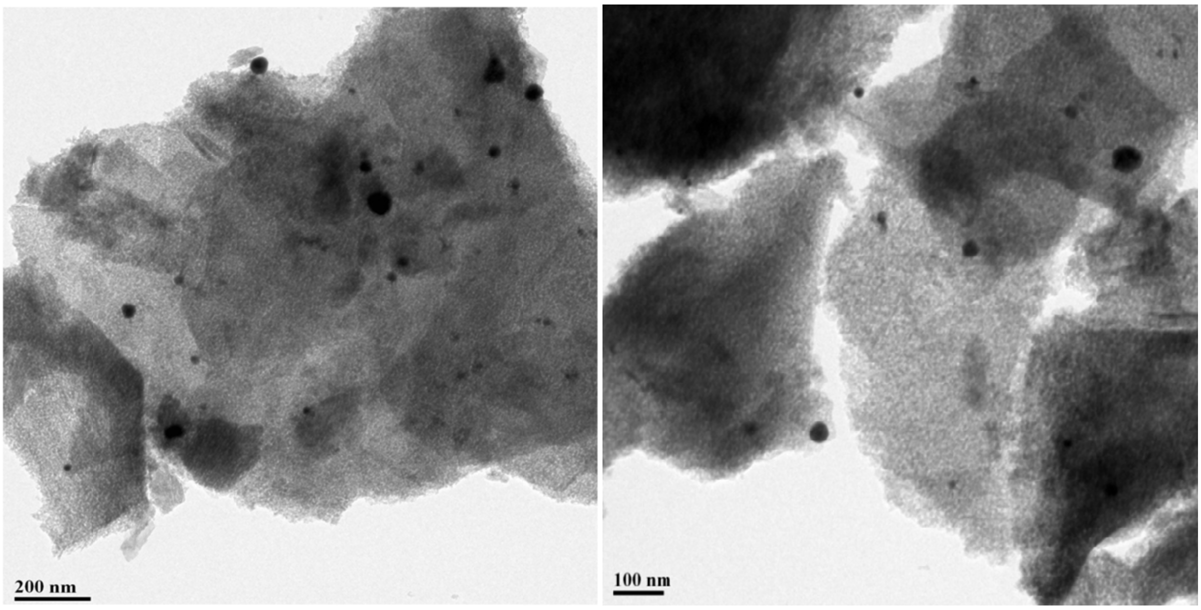

Fig. S8. TEM images of spent and calcined Pt(3.5)Sn(0.43)/AL catalyst used in the conversion of hemicellulose (xylan, oat spelt).

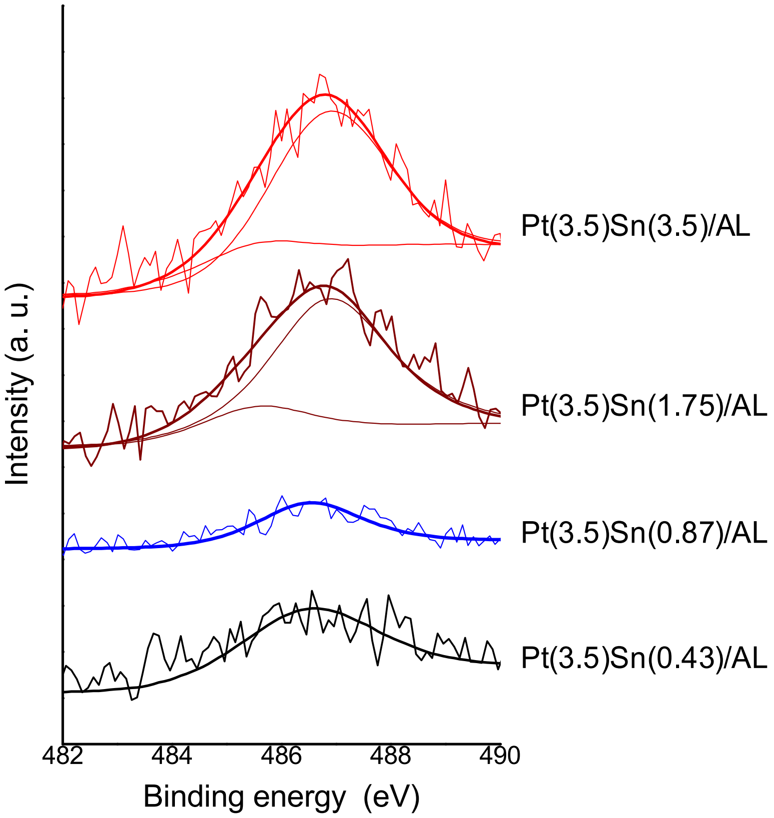

Fig. S9. XPS spectra of PtSn/AL bimetallic catalysts.