Direct catalytic conversion of furfural to 1, 5-pentanediol by hydrogenolysis of furan ring at mild conditions over Pt/Co_2AlO_4 catalyst

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Supplementary Information

1. Experimental section

Synthesis of Pt/Co_2AlO_4 and Li-modified Pt/Co_2AlO_4 catalysts by co-precipitation

Pt/Co-Al-CO_3^{2-} hydrotalcite-like (Co-Al-CO_3^{2-} HT) precursors were prepared by co-precipitation from an aqueous solution of cobalt and aluminium nitrate (solution A) and a basic solution (solution B). In solution A, a calculated amount of Pt nitrate was added for the co-precipitation.[6] The as-prepared precursor was calcined at 300 °C for 4 h with a ramp of 5 °C·min^{-1} in air to get the corresponded Pt/Co_2AlO_4 catalyst. The final Pt loading in the calcined catalyst determined by inductively coupled plasma (ICP-AES) was 1.8 wt.%.

Li-modified catalyst was also prepared by co-precipitation method. The procedure was the same as the synthesis of Pt/Co-Al-CO_3^{2-} hydrotalcite-like precursors, but with additional $LiCl·H_2O$ (Li/(Co+Al)=5wt.%) in Deionized water. The final Li loading in the calcined catalyst determined by EDX was 0.4 wt.%.

Characterization of the catalysts

X-ray diffraction pattern (XRD) was recorded with a Rigaku D/max-2550VB/PC diffractometer using Cu Ka radiation. Chemical analyses of the samples were performed by using inductively coupled plasma atomic emission spectrometry (ICP-AES). Transmission electron microscopy (TEM) were carried out with TECNAI 20S-TWIN. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP2020M sorption analyzer. Before the measurements, the samples were outgased at 280 °C for 6 h. GC–MS was carried out using an Agilent 7890A gas chromatograph connected to a 5975C mass spectrometer with Triple-Axis Detecter.

It can be seen from Fig S1, the catalyst is a typical spinel-like phase of composition Co_2AlO_4

with diffraction peaks at 18.98, 31.14, 36.76, 44.76, 55.64, 59.26 and 65.24°. There are no reflections corredsponding to platinum oxide, indicating that Platinum oxide is highly dispersed in the sample.

Hydrogenolysis of furful

The hydrogenolysis reaction was carried out in a stainless autoclave containing 0.4g furfural, 10ml EtOH, and 0.2 g catalyst at the reaction conditions of P_{H2} = 1.0-2.5 MPa and T = 110-140 °C under magnetic stirring. After reaction for 24 h, the reactor was cooled to room temperature. Then, the catalyst was separated by centrifugation, and the liquid was analyzed by a PerkinElmer Clarus 500 gas chromatography with a SE-54 column and a flame ionization detector (FID). The conversion and selectivity were determined based on the area normalization method. For confirmation, the content of 1,5-pentanediol was also tested by internal standard method (1-octanol as the internal standard). The results calculated by the two methods were consistent. The structural characteristics of products were further identified by GC-MS (Figure S3-S10).

2. Figures

XRD

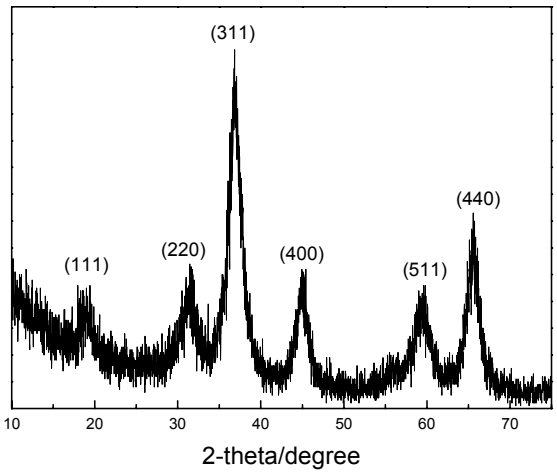

Figure S1 XRD pattern of the Pt/Co_2AlO_4 catalyst.

TEM

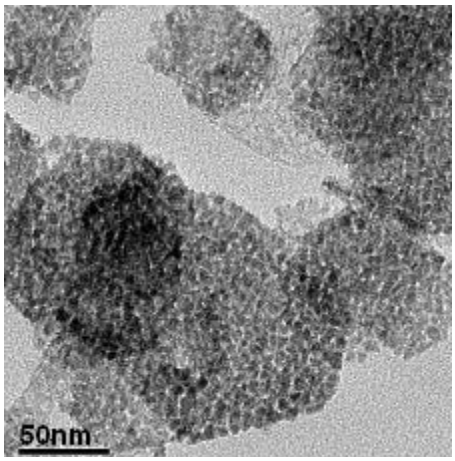

Figure S2 TEM images of Li-modified Pt/Co_2AlO_4.

N_2 sorption

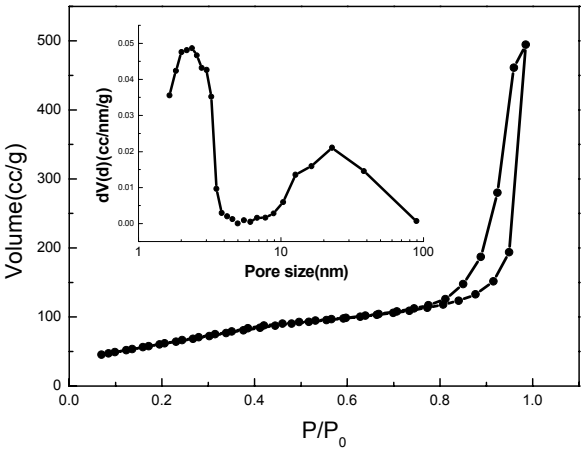

Figure S3 Nitrogen sorption isotherm and pore size distribution of the Pt/Co_2AlO_4 catalyst.

GC-MS

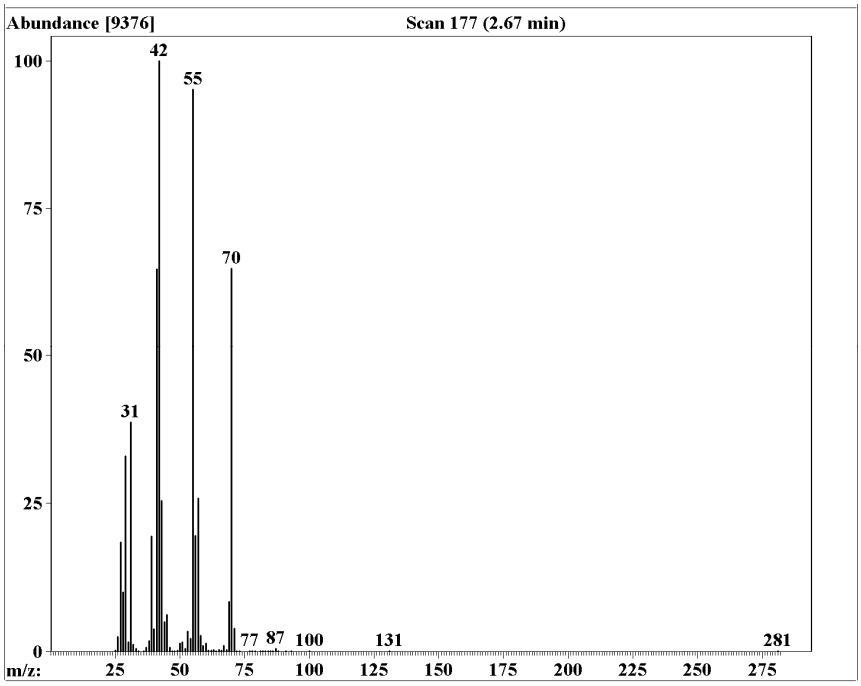

Figure S4. MS spectrum of 1-pentanol.

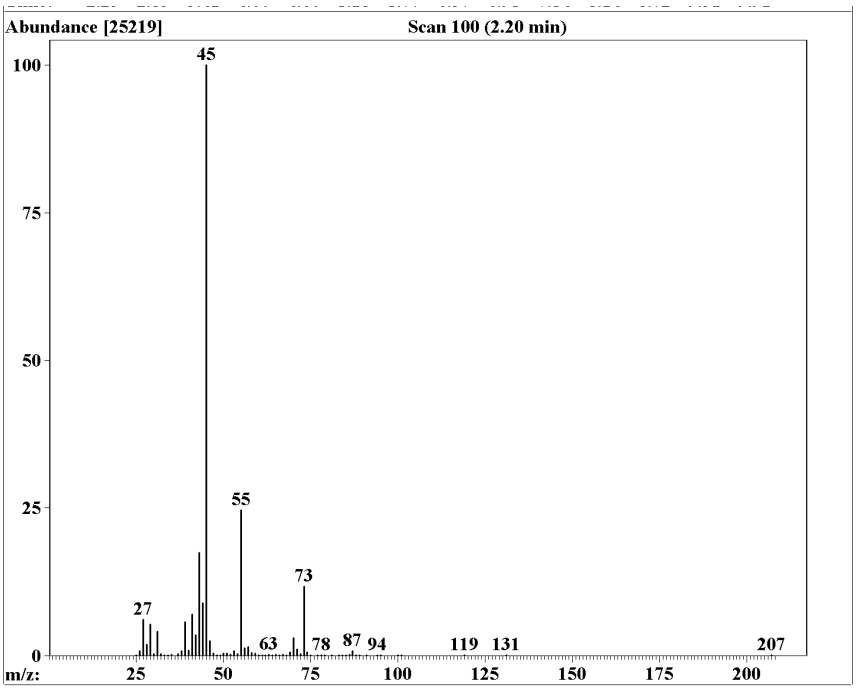

Figure S5. MS spectrum of 2-pentanol.

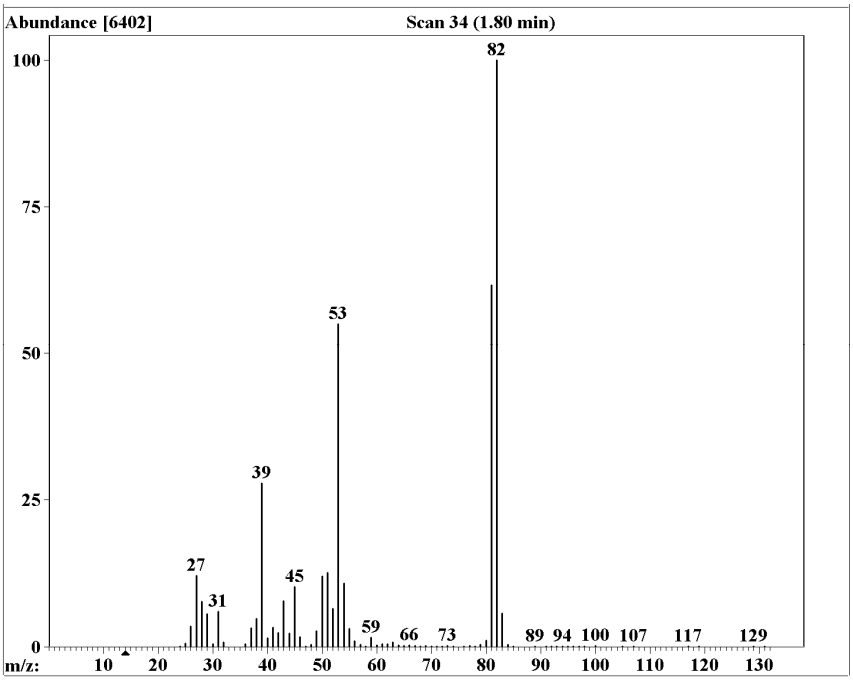

Figure S6. MS spectrum of 2-methylfuran.

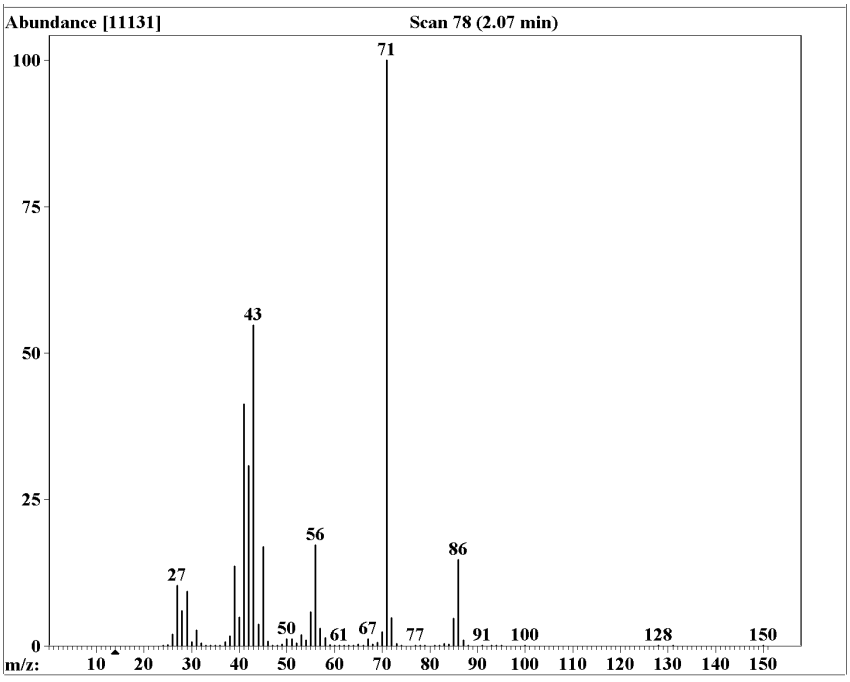

Figure S7. MS spectrum of 2-methyl-tetrahydrofuran.

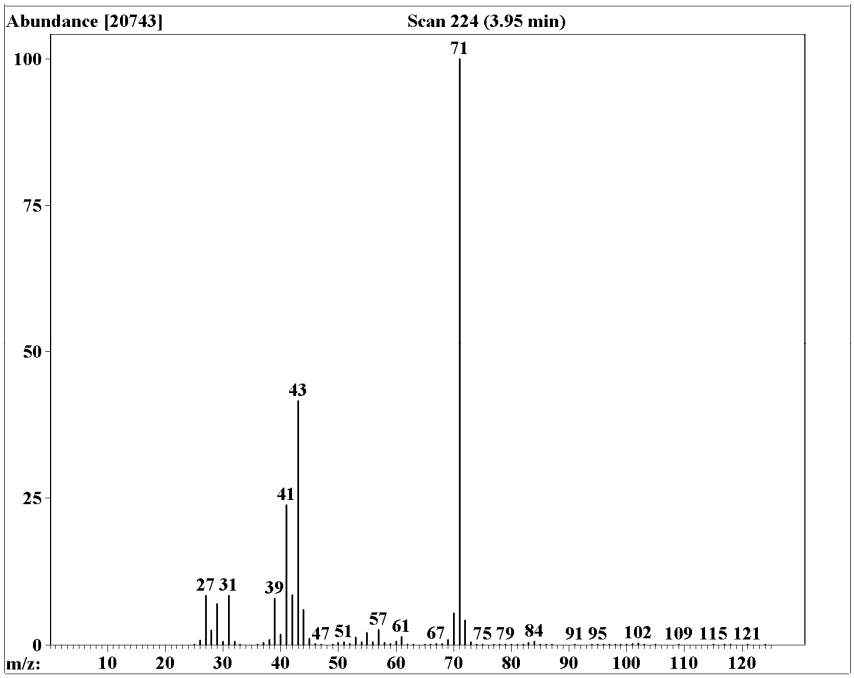

Figure S8. MS spectrum of tetrahydrofurfuryl alcohol.

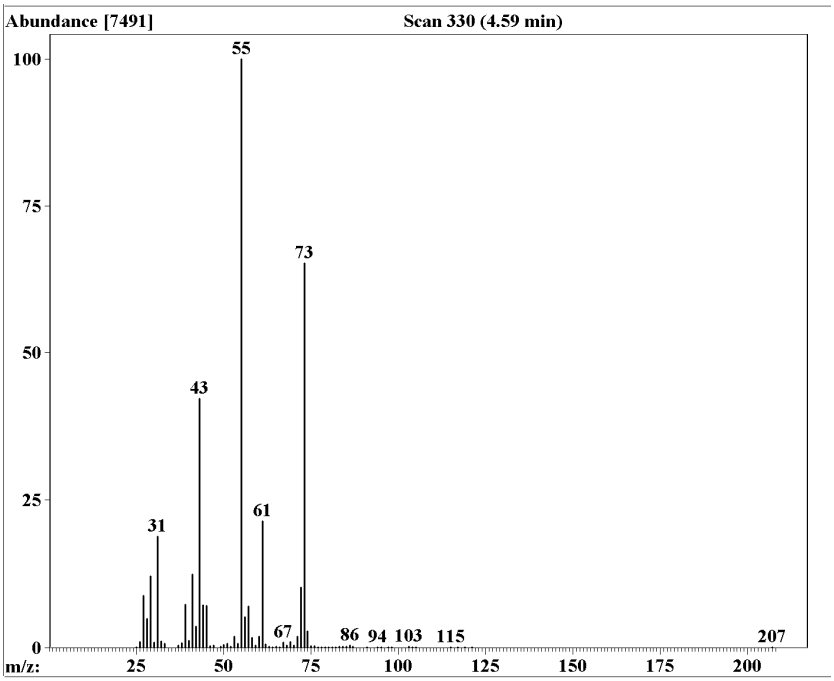

Figure S9. MS spectrum of 1,2- pentanediol.

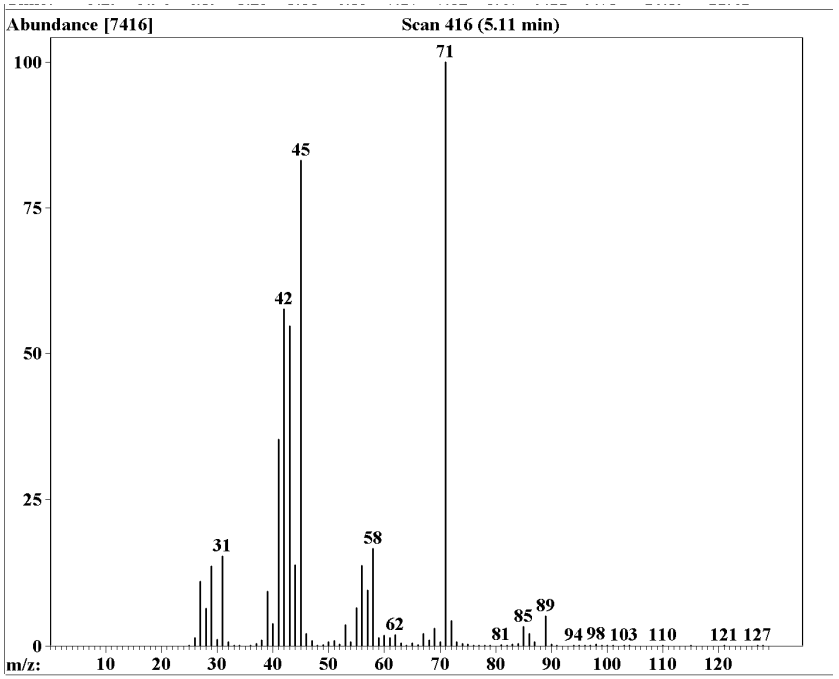

Figure S10. MS spectrum of 1,4- pentanediol.

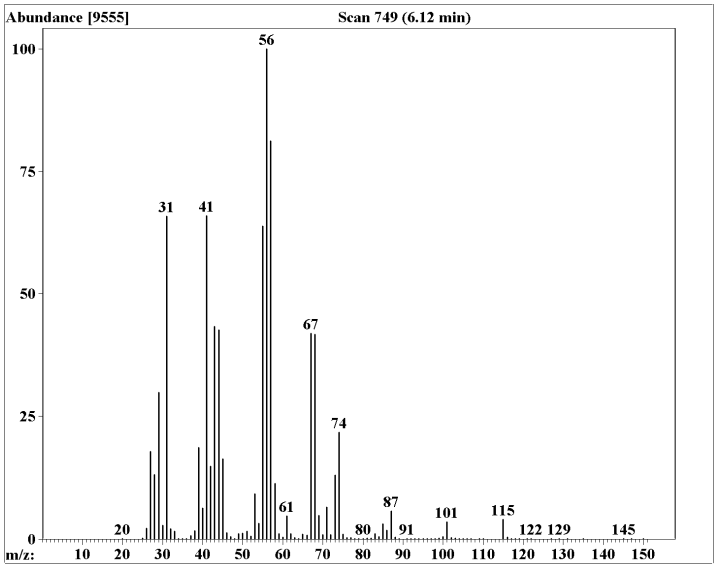

Figure S11. MS spectrum of 1,5- pentanediol.