

Supporting information

The Cooperative Effect of Co and CoO in Co/CoO Enabled Efficient Catalytic Hydrogenation and Demethoxylation of Guaiacol to Cyclohexanol

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Materials Characterization

The powder X-ray diffraction data of the synthesized materials were obtained on a RIGAKU Mini-Flex diffractometer with Cu α ($\lambda = 0.154$ nm, 40 kV, 15 mA) radiation source in a 2θ range of $5-80^\circ$. Various constituent elements, their chemical states, and oxidation states were determined by X-Ray photoelectron spectroscopy (XPS) on a Thermofisher Scientific (Model-ESCALAB Xi⁺) instrument.

The H₂ uptake capacity of materials were analyzed by using the H₂-TPD techniques employing Quantachrome, CHEMBETTM TPR instrument. The sample was preheated at 500 °C at a heating rate of 10 °/min under a continuous He gas flow for 30 min. Then, after cooling to 50 °C, 5% H₂ in N₂ gas was allowed to pass on the sample, then He was purged for 30 min and TPD analysis was performed at a temperature range of 50-700 °C with temperature ramped at 10 °C/min and finally cool to 50 °C.

The NH₃ adsorption ability of materials were analyzed by using the NH₃-TPD techniques employing Quantachrome, CHEMBETTM TPR instrument. The sample was preheated at 500 °C at a heating rate of 10 °/min under a continuous He gas flow for 30 min. Then, after cooling to 50 °C, 10% NH₃ in He gas was allowed to pass on the sample, then He was purged for 30 min and TPD analysis was performed at a temperature range of 50-700 °C with temperature ramped at 10 °C/min and finally cool to 50 °C.

Fourier transform infrared (FT-IR) analysis was conducted using the Bruker Tensor-II F- 27 instrument, with pyridine employed as the probe molecule for Pyridine-adsorbed FT-IR study.

The reduction behavior of the materials was investigated by temperature program reduction (H₂-TPR) analysis on a Quantachrome, CHEMBETTM TPR instrument. The sample was preheated at 500 °C at a heating rate of 10°/min under a continuous He gas flow for 30 min. Then, after cooling to 50 °C, 10% H₂ in Ar gas was allowed to pass on the sample at 50-700 °C and finally cool to 50 °C.

The specific surface area and porosity of the catalyst were determined by an N₂ adsorption-desorption isotherm measurement using a BELSORP MINI X instrument. The catalysts were degassed at 300 °C for 3 h before acquiring of adsorption isotherm. The specific surface area of catalysts was determined using the Brunauer - Emmett -Teller (BET) equation from adsorption data at P/P⁰ values between 0.05 to 0.3.

The size distribution of the metal nanoparticle and interplanar distance was calculated by high-resolution transmission electron microscopy (HRTEM). The analysis was conducted on FEI, Tecnai G2, F30 instruments. Before microscopy examination, the samples were ultrasonically dispersed in ethanol for 5–10 min and then dropped onto a holey carbon film supported by a copper TEM grid.

The morphologies and nanostructures of the synthesized materials were analyzed using Field Emission Scanning Electron Microscopy (FESEM), and the nanostructure of the material was analyzed using Transmission Electron Microscope (TEM) 200kV (JEOL JEM 2100).

Reaction procedure for the catalytic conversion of guaiacol and other substrates

In a typical procedure, guaiacol (0.5 mmol), catalyst (70 mg), and dodecane (10 mL) were taken in a 50 mL high-pressure reactor (Parr reactor). The reactor was sealed and flushed with H₂ gas and finally pressurized with 2.0 MPa H₂ gas. In a similar way, 0.5 mmol of other substrates was employed in a high-pressure reactor containing 70 mg catalyst, and 10 mL dodecane with 2.0 MPa H₂ gas. Then, the reaction was conducted for the desired time at a fixed temperature. After the reaction, the reactor was cooled. The catalyst was separated by centrifugation, and the reaction mixture was withdrawn from the reactor, centrifuged, and analyzed using gas chromatography by the internal standard method (hexadecane) (GC, Shimadzu GC-2010 Plus, SH-Rtx-5 column, column temperature 80-280 °C with 10 °C/min ramp, injector temperature 250 °C, FID 300 °C). The products of the reaction were confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra).

The following equation was used to calculate the conversion of reactant, product selectivity, and yield.

$$\text{Conversion} = \frac{C_0 - C_t}{C_0} \times 100\% \dots\dots (S1)$$

$$\text{Selectivity} = \frac{C_p}{C_0 - C_t} \times 100\% \dots\dots (S2)$$

C₀ is the initial reactant concentration, C_t is the reactant concentration after time t, and C_p is the product concentration at time t.

The response factor was calculated using the following expression:

$$\frac{\text{Area}_{\text{Analyte}}}{[\text{Analyte}]} = F \frac{\text{Area}_{\text{Internal standard}}}{[\text{Internal standard}]} \dots\dots (S3)$$

Where, F is the response factor, $\text{Area}_{\text{Analyte}}$, and $\text{Area}_{\text{Internal standard}}$ are areas under the peaks of Analyte and, Internal standard respectively. $[\text{Analyte}]$ and $[\text{Internal standard}]$ are concentrations of Analyte and Internal standard, respectively.

Synthesis of CoO

1.7 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added into 60 mL absolute ethanol under stirring, and 20 mL of oleic acid was added dropwise. The resulting solution was stirred for 1 h and transferred to 100 mL Teflon lined stainless steel autoclave and kept in the oven at 140 °C for 10 h. The solid material was centrifuged and washed with distilled water, followed by ethanol, and drying for 24 h at 60 °C. Finally, the solid was heated at 300 °C for 1 h under Ar atmosphere inside a tube furnace.

Table S1. Comparison of activation energy for guaiacol conversion over different catalysts.

Entry no.	catalyst	activation energy (E_a)/ kJ/mol	reference
1.	NiCo/SiO ₂ -ZrO ₂	55.9	1
2.	Co-Mo/ γ -Al ₂ O ₃	71.2	2
3.	Co-Ni/ γ -Al ₂ O ₃	58.7	2
4.	Ni-Cu/SiO ₂ -ZrO ₂ -La ₂ O ₃	89.1	3
5.	Mo ₂ C/AC	83	4
6.	Ni/SiO ₂ -Al ₂ O ₃	90.3	5
7.	Ni/RM (Red Mud)	97.5	5
8.	Ni@Pt	68.0	6
9.	Ni@Pd	95.0	6
10.	Pt/C	116.8	7
11.	Co/CoO-300-20	75.24	This study

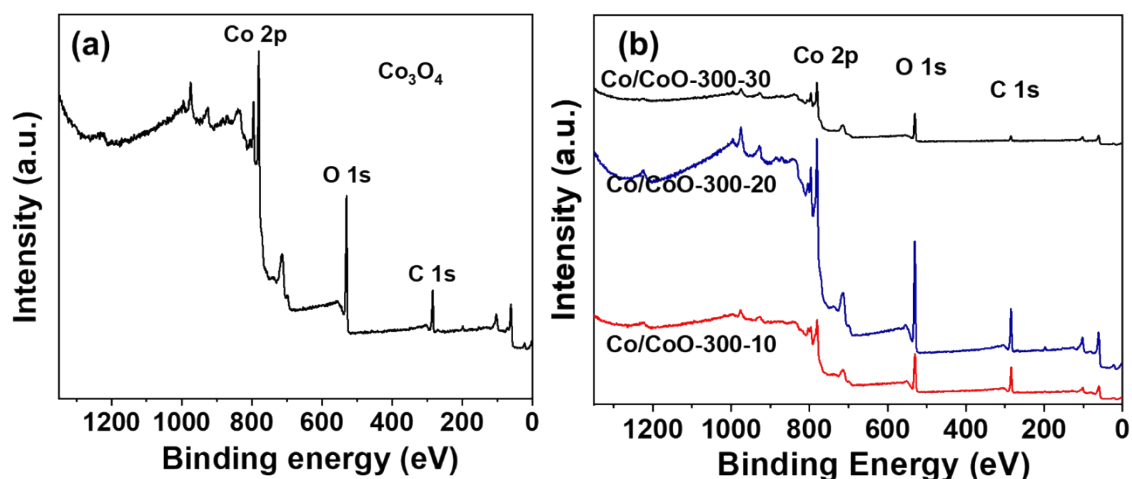


Fig. S1 XPS survey scans of (a) Co₃O₄ and (b) Co/CoO-300-t catalysts.

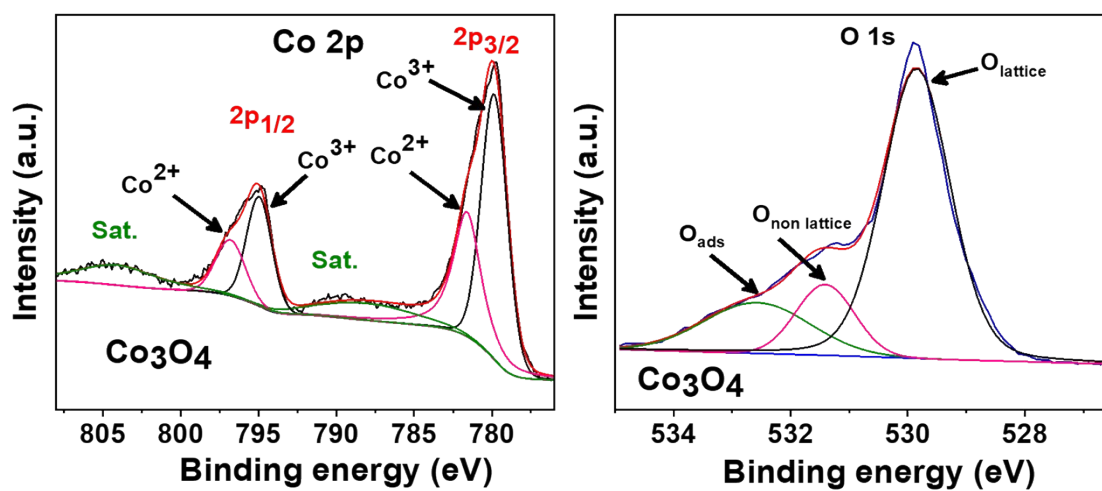


Fig. S2 High resolution deconvoluted XPS spectra of (a) Co 2p and (b) O 1s XPS spectra for Co₃O₄.

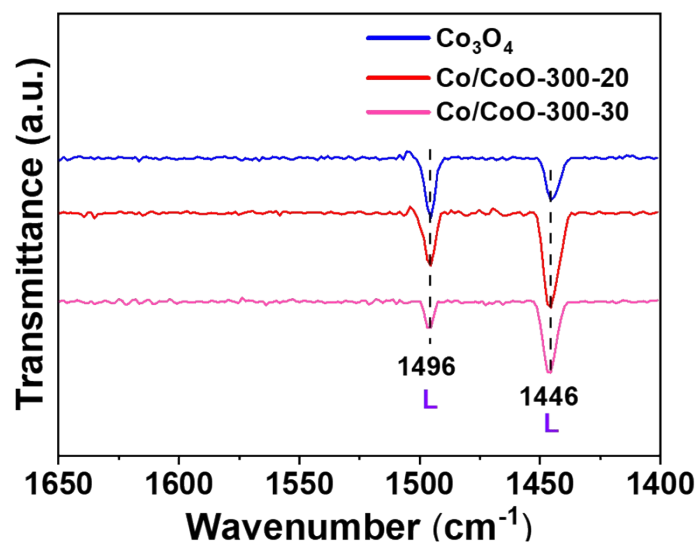


Fig. S3 FT-IR spectra of the pyridine adsorbed Co_3O_4 , Co/CoO-300-20 and Co/CoO-300-30 catalysts (L = Lewis acidic sites)

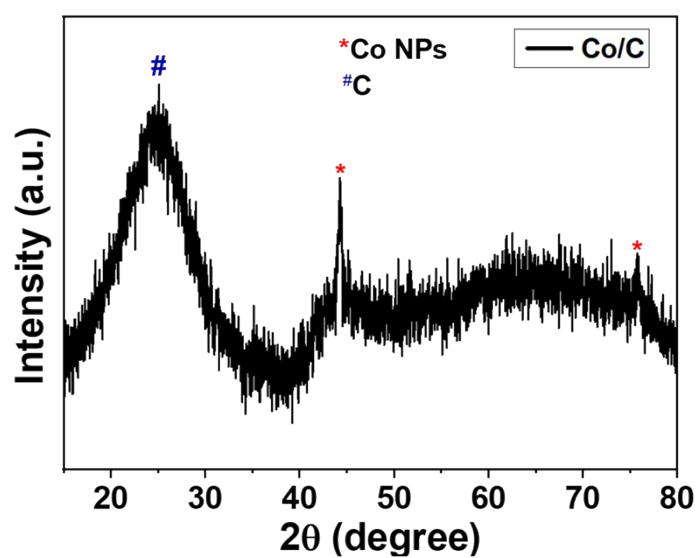


Fig. S4 XRD pattern of 10%Co/C (Co NPs JCPDS file no. 00-015-0806).

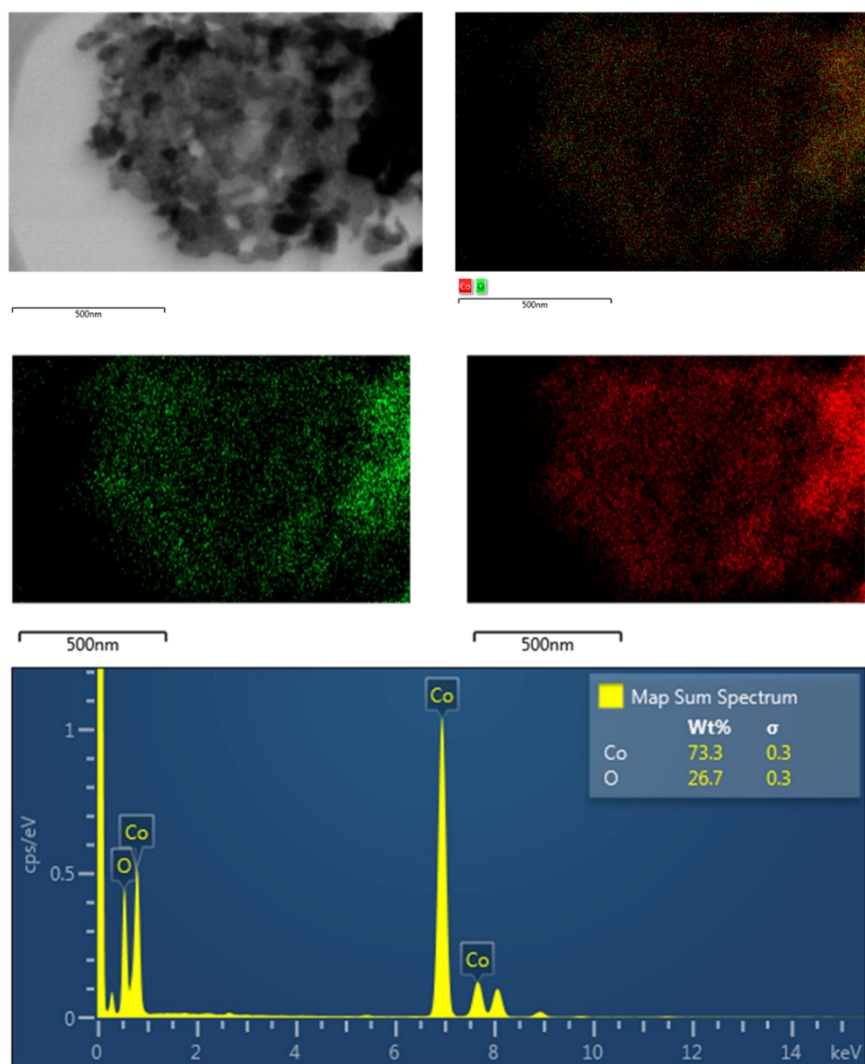


Fig. S5 Atomic distribution of Co and O obtained from TEM for Co/CoO-300-20.

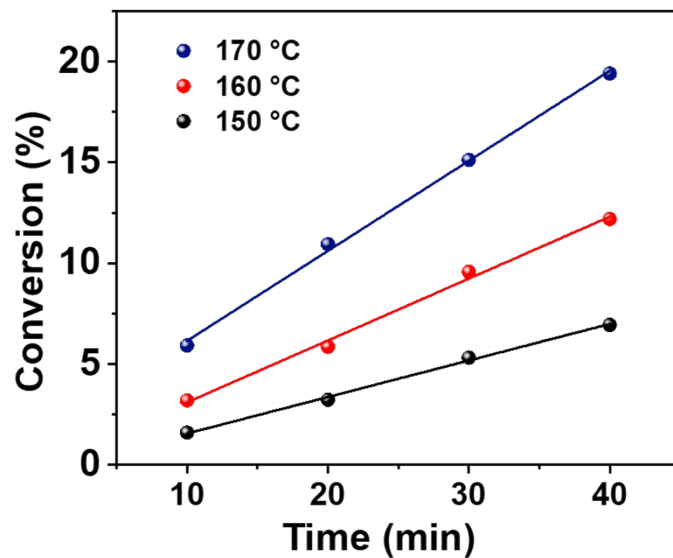


Fig. S6 Percent conversion of guaiacol versus time plot for Co/CoO-300-20 catalysts: guaiacol (0.5 mmol), catalyst 70 mg, dodecane (10 mL), temperature (170 °C), H₂ (20 bar).

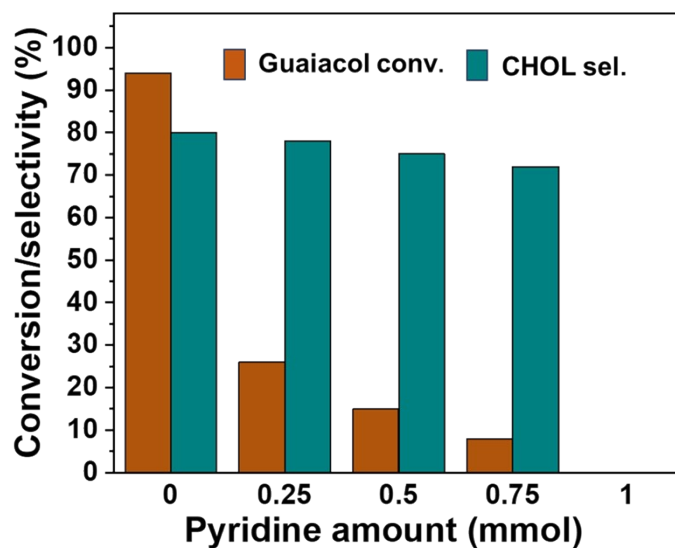


Fig. S7 Poisoning experiment on Co/CoO-300-20 using pyridine: guaiacol (0.5 mmol), catalyst 70 mg, dodecane (10 mL), temperature (170 °C), H₂ (20 bar), time (2h).

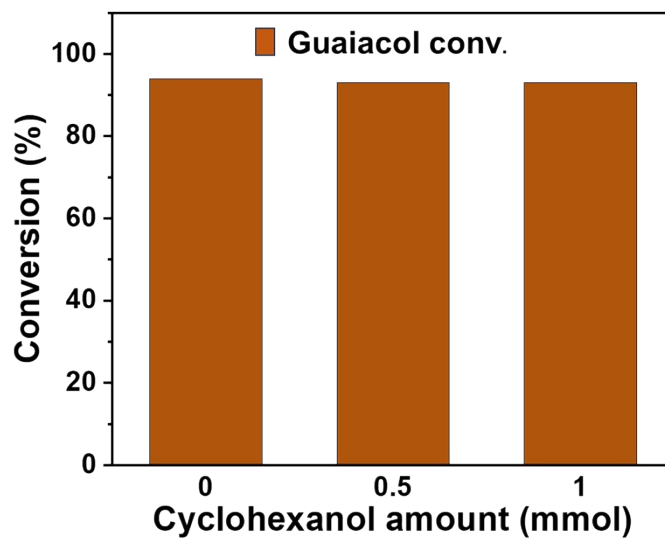


Fig. S8 Poisoning experiment using cyclohexanol over Co/CoO-300-20: guaiacol (0.5 mmol), catalyst 70 mg, dodecane (10 mL), temperature (170 °C), H₂ (20 bar), time (2h).

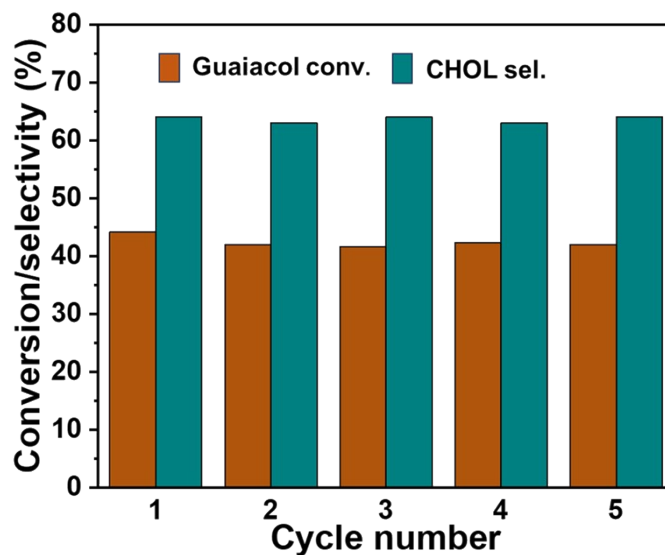


Fig. S9 Co/CoO-300-20 recyclability test up to 5 cycles: guaiacol (1 mmol), catalyst 140 mg, dodecane (10 mL), temperature (170 °C), H₂ (20 bar).

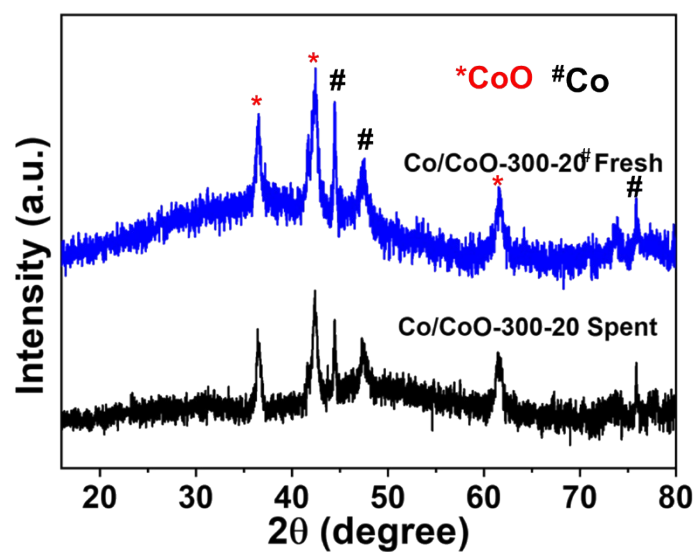


Fig. S10 XRD patterns of fresh and spent Co/CoO-300-20.

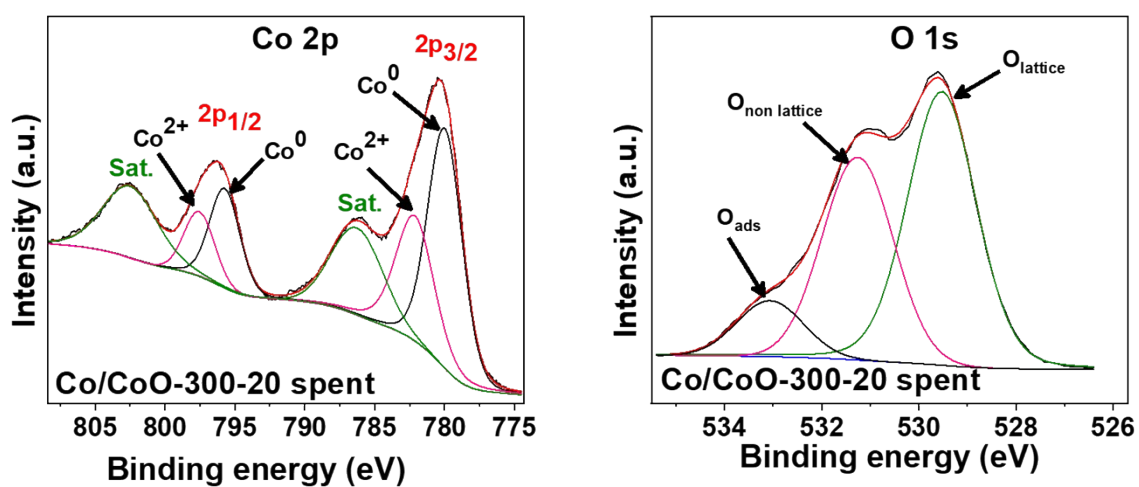


Fig. S11 Deconvoluted high resolution XPS spectra of Co 2p and O 1s for Co/CoO-300-20 spent catalyst.

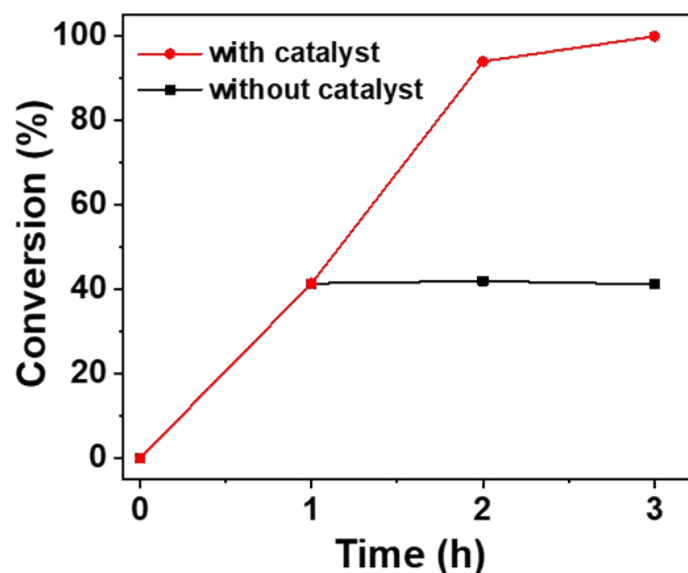


Fig. S12 Hot filtration test (Reaction conditions: guaiacol (0.5 mmol), catalyst 70 mg, dodecane (10 mL), temperature (170 °C), H₂ (20 bar)).

References

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