Co_3O_4 undergoes in-situ reduction to mediate lignin hydrodeoxygenation under mild conditions with high liquid yield and recyclability

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Materials. The reagents used in this experiment are all of analytical grade. Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and ammonia solution (NH_4OH, 25~28 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. $CoCO_3$ (99.0%) was purchased from Shanghai Haohong Biomedical Technology Co., Ltd. CoO (99.0%), $Co(OH)_2$ (99.9 %), Co_3O_4-Adamas (99.99%) and Co (99.99%) were purchased from Shanghai Adamas Reagent Co., Ltd. $CoCl_2{\cdot}6H_2O$ (99.0%) was purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd. Co_2O_3 was purchased from Shanghai Bide Pharmaceutical Technology Co., Ltd. Co_3O_4-Aladdin was purchased from Shanghai Jingchun Biochemical Technology Co., Ltd. Co_3O_4-J&K Scientific was purchased from Beijing Bailingwei Technology Co., Ltd. Co_3O_4-Energy Chemical was purchased from Anhui Zesheng Technology Co., Ltd. Co_3O_4-Macklin, diphenyl ether (98 %), 4-phenoxyphenol (99 %), 4,4'-oxydiphenol (99 %), 4,4'-oxybis(methylbenzene) (99 %), anisole (>99.8 %), benzyl ether (97 %), benzyl phenyl ether (98 %), 2-phenoxy-1-phenylethan-1-ol (98 %), 2-phenoxy-1-phenylacetone (98 %), guaiacol (99 %), methylcyclohexane (99 %), toluene (99 %), ethylbenzene (99 %), ethyl cyclohexane (99 %), isopropanol (>99.8 %), cyclohexane (>99.8 %), benzene (>99.8 %), cyclohexanol (>99.8 %), and phenol (>99.8 %), and Eugenol (98 %) were provided from

Shanghai Macklin Biochemical Co., Ltd. Enzymatic hydrolysis lignin from was purchased from Linyi Senhe Biomaterials Co., Ltd. H_2 was purchased from provided by a local company. All of the reagents could be used without further purification.

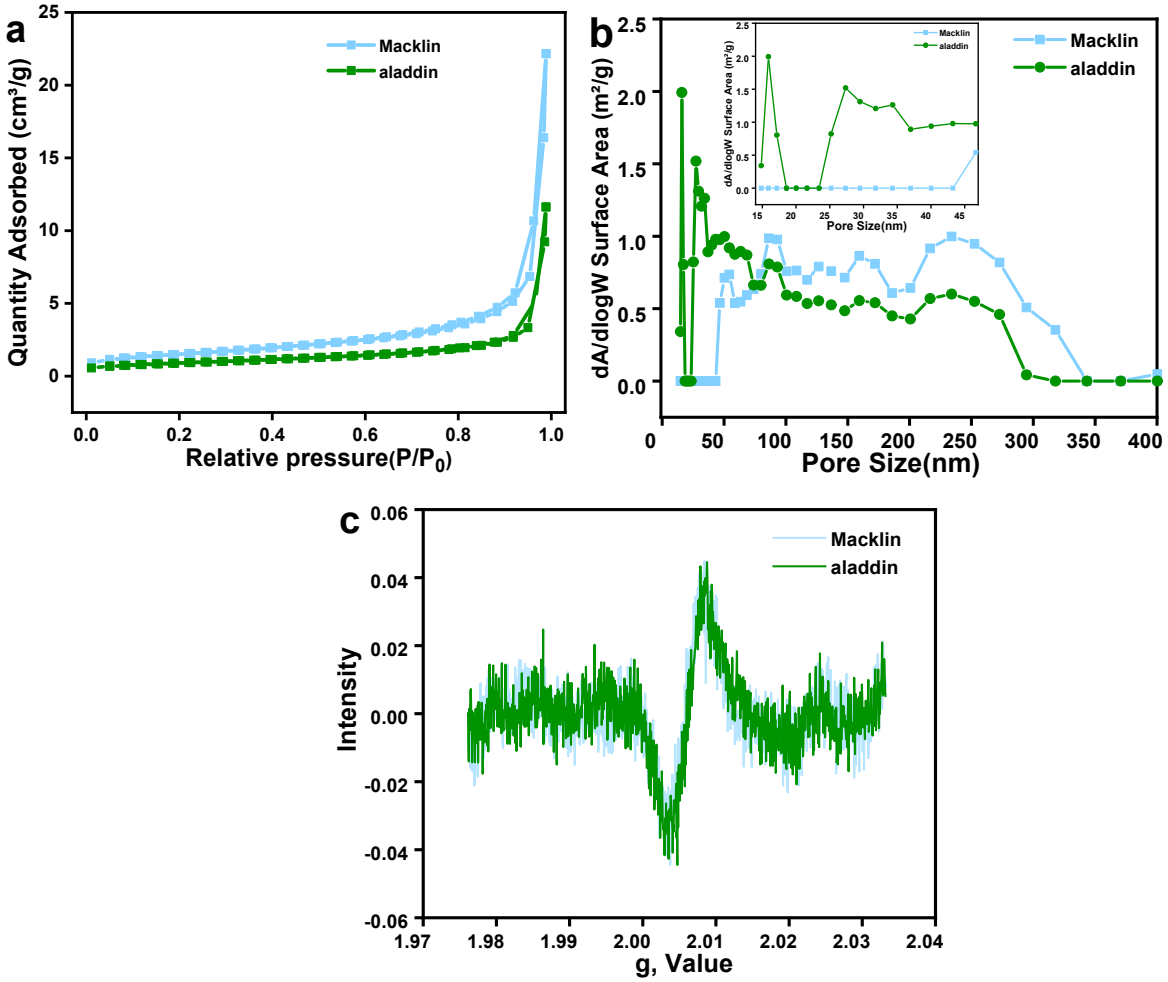

Figure S1. (a) N_2 adsorption–desorption isotherms, (b) the pore-size distribution curves, and (c) EPR spectra of Co_3O_4-Aladdin and Co_3O_4-Macklin.

Table S1. Summary of the Cobalt and oxygen functional groups content in Co_3O_4-Macklin and Co_3O_4-aladdin (determined by XPS).

Sample	area		ratio	area		ratio
	Co^{3+}	Co^{2+}	Co^{3+}/Co^{2+}	O_{surf}	O_{latt}	O_{surf}/O_{latt}
Co_3O_4-Macklin	23864	119482	0.20	60594	42734	1.42
Co_3O_4-aladdin	33190	142207	0.23	55243	37543	1.47

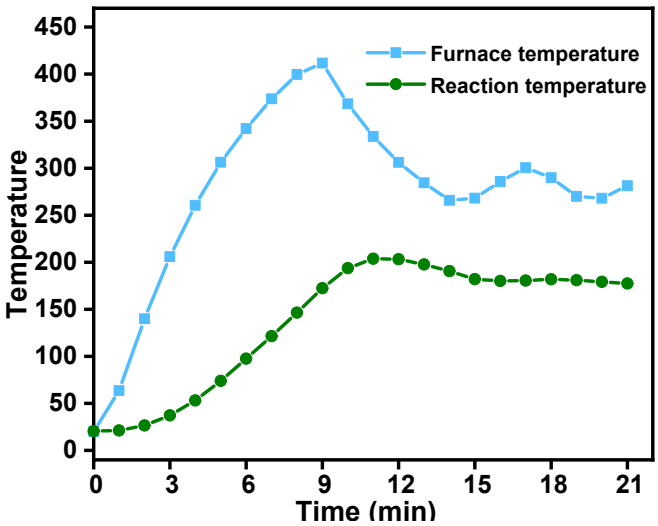

Figure S2. Time-dependent dynamic changes of furnace temperature and reaction temperature

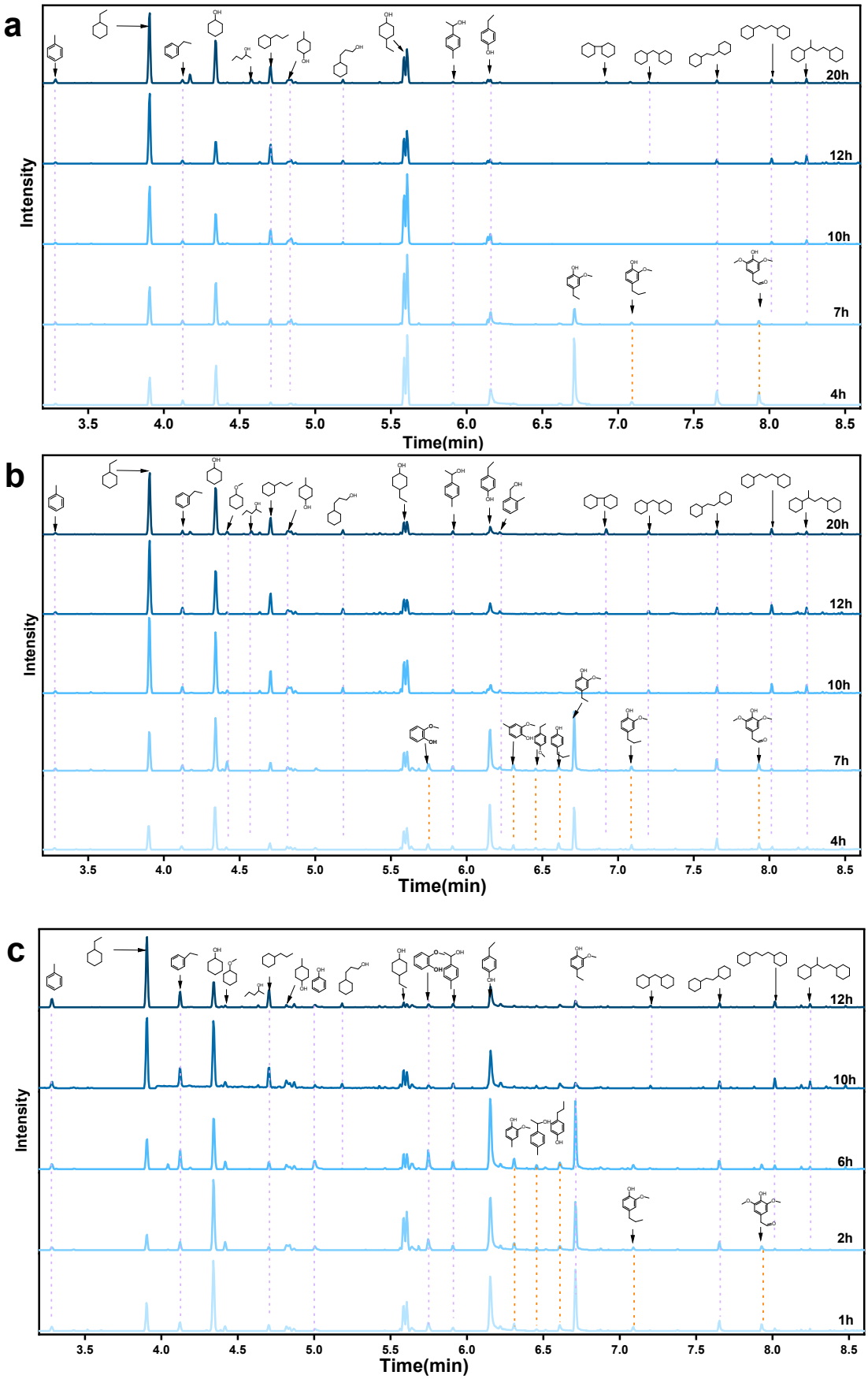

Figure S3. Total ion chromatograms of the products from the HDO of enzymatic lignin over Co_3O_4 under different temperatures, (a) 220 °C, (b) 240 °C, (c) 260 °C (Reaction condition: 100.0 mg

catalyst, 700 rpm, 1~20 h, and 2MPa H_2 at RT).

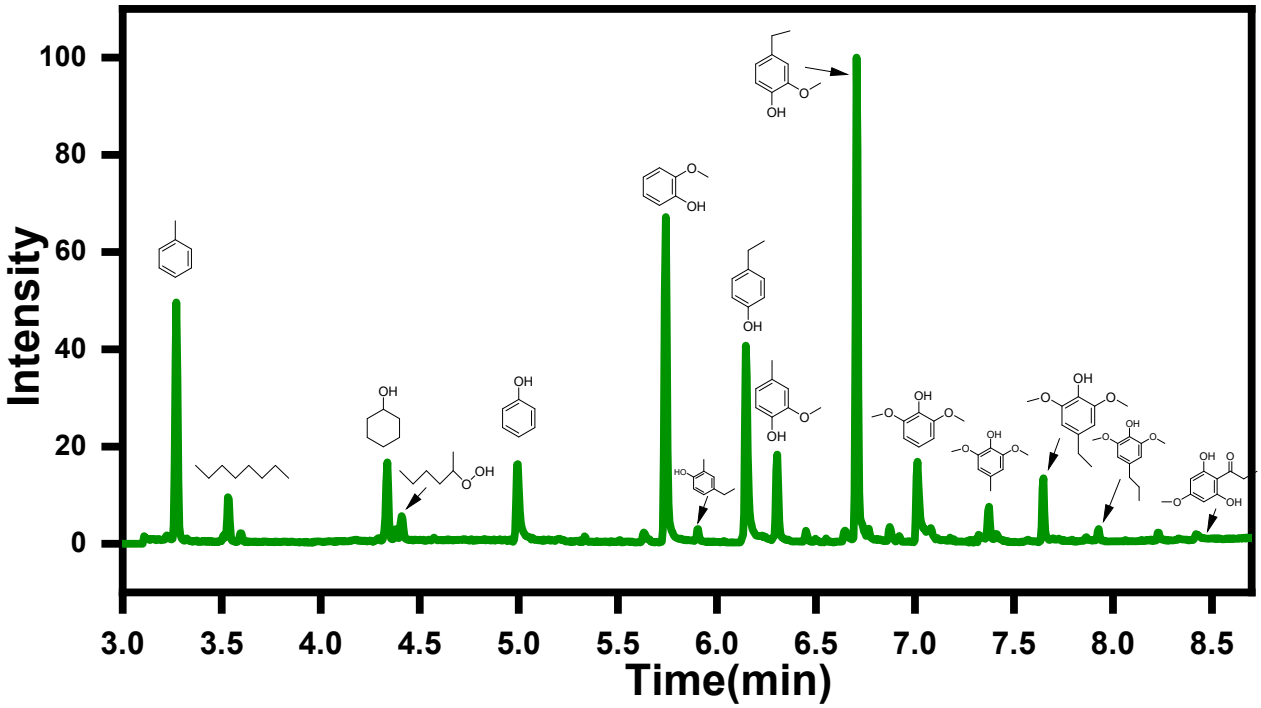

Figure S4. Total ion chromatograms of the products from the HDO of enzymatic lignin without Co_3O_4 Reaction condition: 240 °C, 700 rpm, 10 h, and 2MPa H_2 at RT).

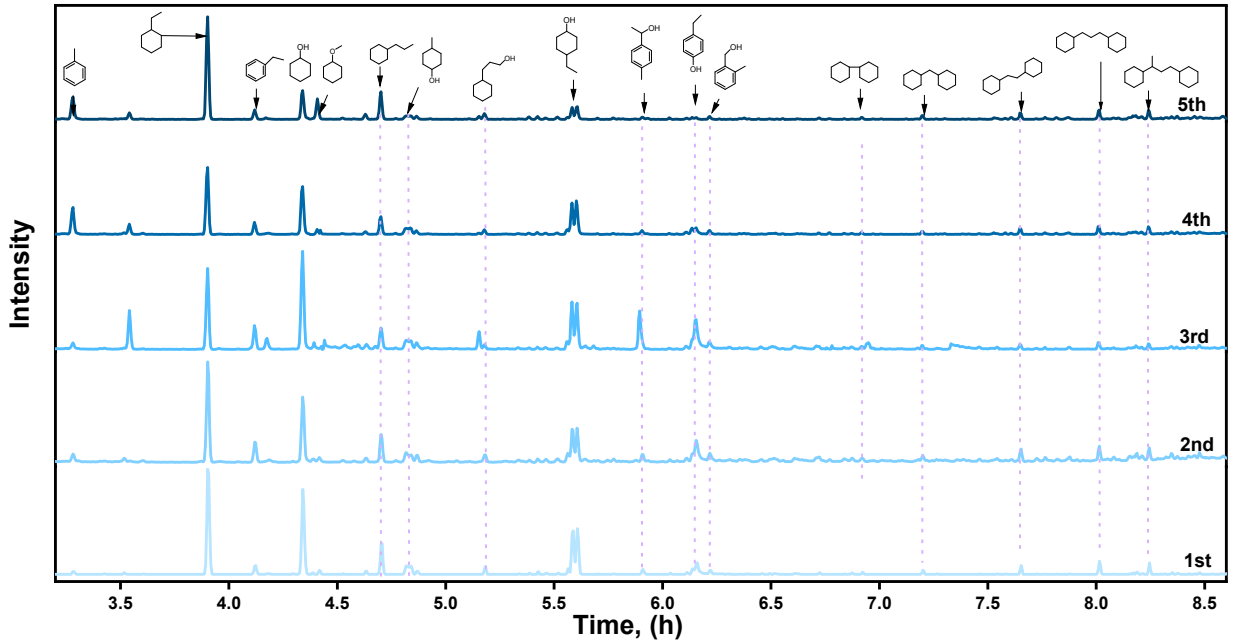

Figure S5. Total ion chromatograms of the products from the HDO of enzymatic lignin catalyzed by reused Co_3O_4. Reaction conditions: 240 °C, 100.0 mg catalyst, 700 rpm, 10 h, and 2MPa H_2 at RT.

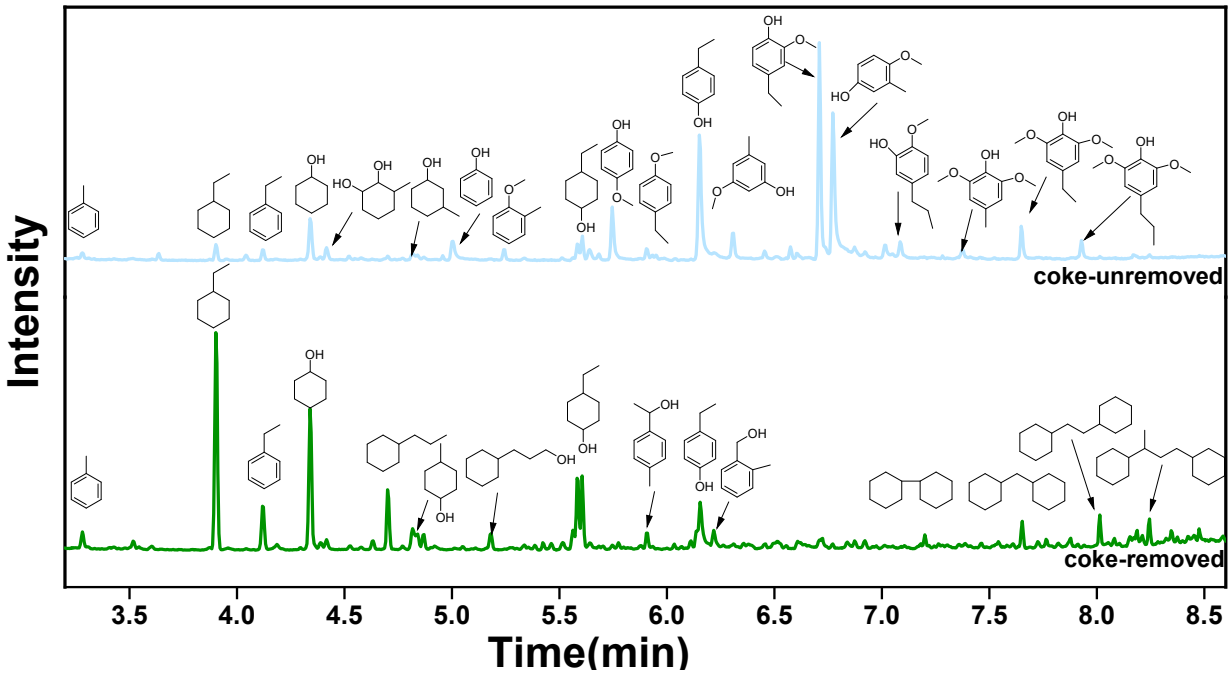

Figure S6. Total ion chromatograms of the products from the HDO of enzymatic lignin catalyzed by Co_3O_4 (after coke removal and without coke removal) in its second use. Reaction conditions: 240 °C, 100.0 mg catalyst, 700 rpm, 10 h, and 2 MPa H_2 (initial pressure at RT).

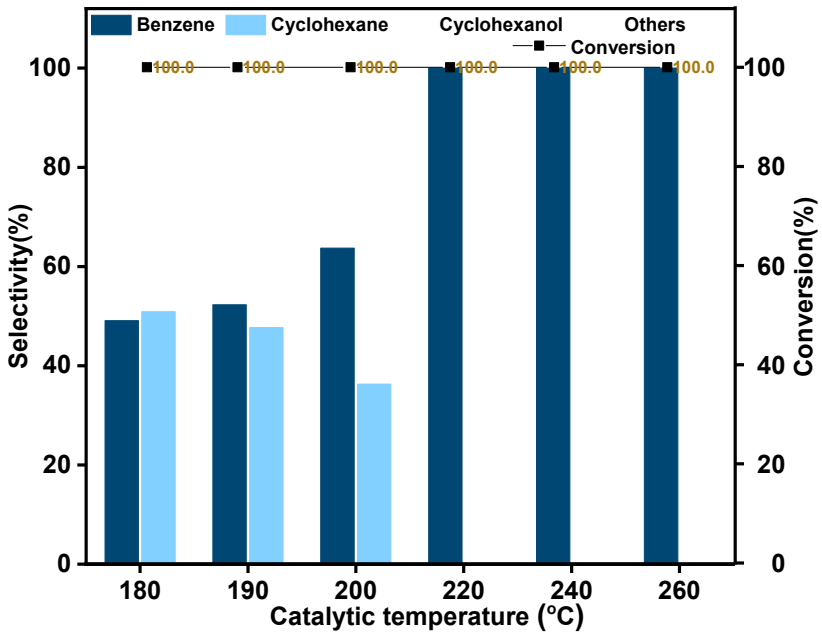

Figure S7. The catalytic performance of Co_3O_4-Aladdin under different temperatures. The reaction conditions are as follows: 2 MPa H_2, 6h, 5 mL n-heptane.

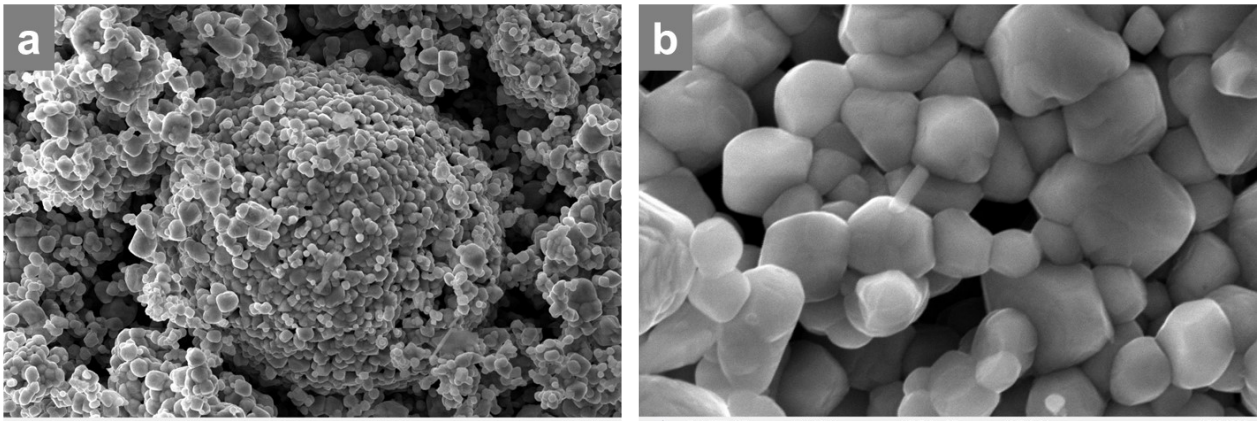

Figure S8. SEM images of reused Co_3O_4: (a) low magnification, (b) high magnification.