Electronic Supplementary Information (ESI)

Hydrotreatment of lignin dimers over NiMoS-USY: effect of silica/alumina ratio[†]

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Product analysis of Kraft lignin hydrotreatment (2D GC × GC-MS-FID analysis)

The liquid phase obtained after hydrotreatment of KL was analyzed by GC × GC-MS-FID (Agilent 7890B–5977A, Agilent). The separation of the products was achieved first with a GC column equipped with a mid-polar phase (VF-1701MS, 30 m × 250 μ m × 0.25 μ m), followed by a non-polar phase column (DB-5MS UI, 1.2 m × 150 μ m × 0.15 μ m). The GC injector and flame ionization detector were maintained at 280 °C and 250 °C, respectively. The initial temperature of the oven was 40 °C for 1 min and then heated up to 280 °C at a rate of 2 °C /min. Thermal modulation was maintained at 8 s. The chromatographic image (MS/FID) was analyzed using GCImage software for multidimensional chromatography. Pyridine was used as an internal standard during the analysis. The product selectivities were estimated by the ratios of individual component blob volumes to the total blob volume of the identified products in the liquid phase.



Fig. S1 N2 physisorption isotherms and BJH pore size distribution of USY zeolites (Y12, Y30, and Y80) and NiMo impregnated catalysts.







 Fig.
 53
 Ethylamine-TPD

 measurements
 over
 (a)
 NiMoY12,

 NiMoY30, and NiMoY80 catalysts, (b)
 Parent
 Y-zeolites, and (c)
 the

 relationship
 between
 the
 Brønsted
 acid site density and SAR.



Fig. S4a XPS results showing the deconvolution of Ni2p core level spectra of the sulfided catalysts.



Fig. S4b XPS results showing the deconvolution of S2p core level spectra of the sulfided catalysts.





Fig. S5a TEM



Fig. S5b High Angle Angular Dark field (HAADF)-TEM micrograph showing a characteristic area of the as-synthesized NiMoY12 and NiMoY30 and their corresponding energy dispersive X-ray (EDX) a



Fig. S6 The yield of products from the reaction of PPE over Y30 at 345 °C, 50 bar, and 1000 rpm after 6 h in an autoclave reactor.

$$Initial \ rate \ of \ reaction \ = \ \frac{mmol \ of \ ethylbenzene \ and \ phenol \ formed \ at \ 35 \ min}{Time \ (h). \ mass \ of \ catalyst}$$

$$Initial \ rate \ of \ transalkylation \ = \ \frac{mmol \ of \ total \ phenolic \ dimers \ formed \ at \ 35 \ min}{Time \ (h). \ mass \ of \ catalyst}$$

$$Turn \ over \ frequency \ (TOF) \ = \ \frac{Initial \ rate \ of \ reaction \ at \ 35 \ min}{Total \ acidity \ of \ the \ catalyst}$$

Table S1 Initial rate of reaction, TOF, and transalkylation rate measured at 35 minutes for 2-phenethyl phenyl ether (PPE)

Catalyst	Initial rate of (Cβ-O-4) cleavage in PPE, mmol g ⁻¹ h ⁻¹	TOF35 (h ⁻¹)	Initial rate of trans-alkylation, mmol g ⁻¹ h ⁻¹
Y30	8.4	20	15
NiMoY12	78	114	24
NiMoY30	61	106	26
NiMoY80	50	104	14



Fig. S7 Observed phenol and cresols after 35 min of hydrotreatment of DHDPM at 345 °C, 50 bar, and 1000 rpm over NiMoY30.



Fig. S8. XRD patterns of Y zeolite with a SAR of 5.1 before and after calcination in air at 550 °C and 6 h.



Fig. S9 XRD patterns of the recovered catalysts after sulfidation and reaction with PPE at 345 °C, 50 bar, and 1000 rpm for 6 h.



Fig. S10 2D GCxGC chromatogram showing the spectrum of products formed during hydrotreatment of Kraft lignin over NiMoY30 at 400 °C, 35 bar H₂, and 1000 rpm.