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Transfer hydrogenation co-processing of phenolic compounds and cyclohexanol

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1. *Chemicals and materials*

The following materials were used in this study: nickel(II) nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$, 99.2 %, Lenreactiv), γ-Al_2O_3 (Angarsk Catalysts and Organic Synthesis Plant JSC), urea (99.8 %, Lenreaktiv), cyclohexanol (99 %, Sigma Aldrich), phenol (≥98 %, Vekton), dodecane (≥99 %, EKOS-1), pentadecane (≥98 %, EKOS-1), hydrogen (H_2, 99.99 %, Promgazservis), helium (He, 99.9999 %, Promgazservis), argon (Ar, 99.998 %, Promgazservis), vanillin (Ruskhim, 99.95 %), anisole (Alfa Aesar, 99 %), guaiacol (Acros Organics, 99 %), and 2,3-benzofuran (Sigma Aldrich, 99 %).

2. *Catalyst preparation and characterization*

The Ni/γ-Al_2O_3 catalysts were prepared using the deposition-precipitation method. Specifically, 12.53 g of $Ni(NO_3)_2$ $6H_2O$ and 6.39 g of urea were dissolved in 820 mL of distilled water. Subsequently, a predetermined amount of γ-Al_2O_3 (0.25-0.50 mm particle size fraction) was added to the solution to achieve catalysts with nominal nickel loadings of 10 wt% and 20 wt%. These catalysts were designated as Ni6/γ-Al_2O_3 and Ni18/γ-Al_2O_3, respectively. The resulting mixture was then heated to 90 °C and maintained at this temperature for 24 hours under constant stirring. After 24 hours, the mixture was allowed to cool to approximately 70 °C, after which it was filtered and the solid particles were thoroughly washed with 1 L of distilled water preheated to approximately 70 °C. The recovered solid particles were then air-dried, followed by drying in an oven at 60 °C for 12 hours. Finally, the dried materials were calcined in air at 300 °C for 3 hours. Prior to use in catalytic experiments, the catalyst samples were activated in a hydrogen flow at 650 °C.

The synthesized catalyst samples were subjected to a range of characterization techniques. The elemental composition of the catalysts was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES) with an Optima 4300 DV instrument (Perkin-Elmer, USA). Prior to ICP-AES analysis, the samples were activated in H_2 and subsequently passivated in air to prevent oxidation.

X-ray diffraction (XRD) studies were performed in transmission geometry using a STOE STADI MP diffractometer (STOE, Germany) equipped with a one-dimensional silicon strip MYTHEN2 1K detector. XRD patterns were collected using Mo Kα_1 radiation ($\lambda = 0.7093$ Å). Prior to XRD analysis, the catalyst samples were reduced according to the standard activation procedure and then passivated in air.

The textural properties of the catalysts were measured using an ASAP-2400 automated volumetric adsorption analyzer (Micromeritics Instrument Corp., USA). Before analysis, the activated samples were also passivated in air and then transferred to a specialized cell under an inert argon atmosphere. Following degassing at 150 °C and a residual pressure of 0.13 Pa for 7 hours, nitrogen adsorption-desorption isotherms were measured at liquid nitrogen temperature (−196 °C).

The Brunauer–Emmett–Teller (BET) method was used to determine the specific surface area (S_{BET}) from the obtained isotherms.

CO pulse chemisorption measurements were performed using a Chemosorb analyzer (Modern Laboratory Equipment, Russia). Approximately 14.3 mg of each oxygenated sample was placed in a U-shaped quartz tube and heated to 650 °C at a rate of 7 K min^{-1} under a hydrogen flow (50 mL min^{-1}). The temperature was maintained at 650 °C for 30 minutes, after which the hydrogen flow was replaced with helium, and the temperature was reduced to 30 °C. Subsequently, pulses of CO were introduced into the reactor until the outlet CO concentration, as monitored by a thermal conductivity detector, reached a steady state, indicating saturation of the catalyst surface. The tube was then purged with O_2 for 20 minutes, and the entire procedure was repeated. The amount of chemisorbed CO was estimated based on these two measurements.

In addition, low-temperature Fourier Transform Infrared (FTIR) spectroscopy was employed to characterize the surface properties of the catalysts through CO adsorption. Prior to FTIR analysis, the catalyst samples were pressed into self-supporting pellets and reduced in a hydrogen atmosphere at 300 Torr and 650 °C for 1 hour. Following reduction, the samples were subjected to vacuum treatment at 10^{-4} Torr for 1 hour. FTIR spectra were recorded at -196 °C and room temperature using a Shimadzu IRTracer–100 spectrophotometer (Japan), with 200 scans in the range of 400-6000 cm^{-1} and a resolution of 4 cm^{-1}. CO was adsorbed at –196 °C and pressures ranging from 0.1 to 10 Torr. The resulting absorption spectra were normalized to the optical thickness of the tablets. The IR spectra were analyzed by deconvoluting the corresponding IR bands into individual Gaussian components. The concentrations of various surface sites were determined from the integral intensities of the observed characteristic absorption bands using integral absorption coefficients. The properties of the catalysts obtained from these analyses are summarized in **Tables S1-S3** and **Figures S1-S3**.

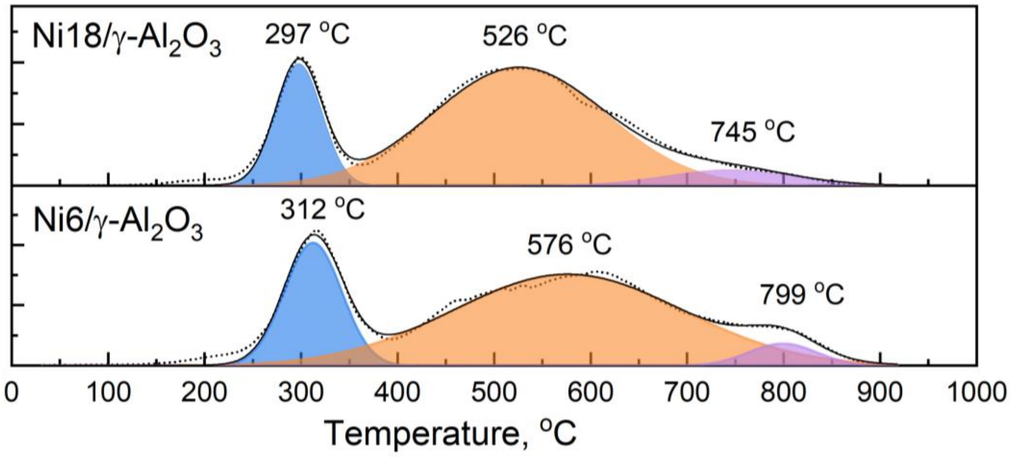


Figure S1. H_2-TPR data obtained for the nickel catalysts prepared by the deposition precipitation method.

Table S1. Nickel content and textural properties of the catalysts prepared by the deposition-precipitation method.

Sample	Ni content, wt.%	S_{BET}/m^2 g^{-1}	V_{pore}/cm^3 g^{-1}	D_{pore}/nm	d_{Ni}^{XRD}/nm
γ-Al_2O_3	-	228	0.53	11	-
Ni6/γ-Al_2O_3	6.1	198	0.50	9.6	<2
Ni18/γ-Al_2O_3	17.9	185	0.47	8.8	6.5

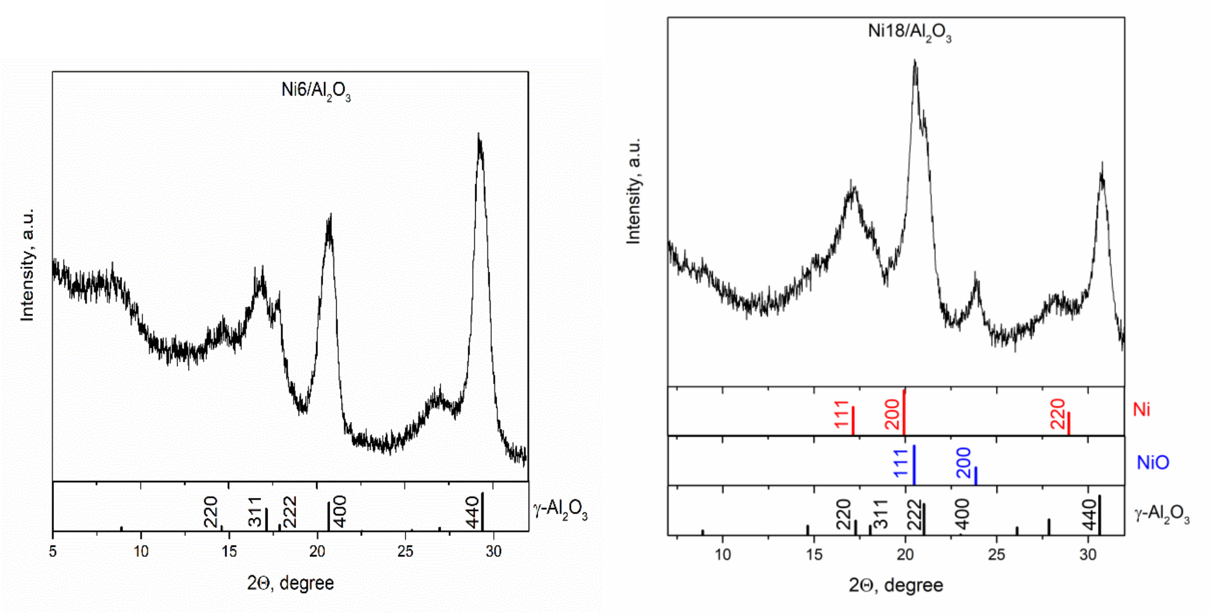


Figure S2. XRD data of the catalysts after activation in H_2 flow at 650 °C.

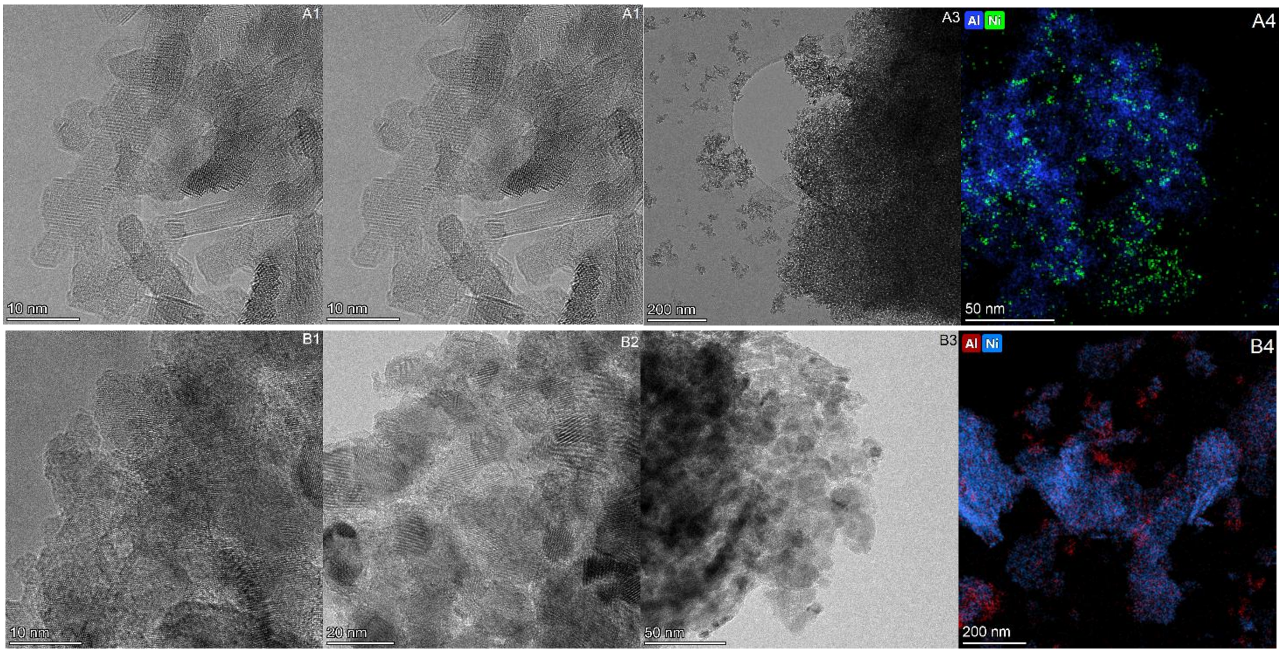


Figure S3. TEM micrographs and EDX maps of Ni6/γ-Al_2O_3 (A) and Ni18/γ-Al_2O_3 (B) after activation in H_2 flow.

Table S2. Data of CO pulse adsorption of the catalysts prepared by the deposition-precipitation method.

Sample	Amount of CO, μmol g^{-1}	Ni^0 surface area available, m^2 g^{-1}
Ni6/γ-Al_2O_3	120	4.7
Ni18/γ-Al_2O_3	148	5.8

Table S3. Concentration of Lewis acid sites obtained from FTIR spectra of adsorbed CO.

Sample	Concentration of Lewis acid sites, μmole/g			
	νCO 2176–2200 cm^{-1} (weak)	νCO 2205–2215 cm^{-1} (medium)	νCO 2235 cm^{-1} (strong)	Total amount
γ-Al_2O_3	380	23	2	405
Ni6/γ-Al_2O_3	612	31	14	657
Ni18/γ-Al_2O_3	326	13	–	339

3. *Catalytic experiments*

Initially, 0.20 g of the catalyst sample was activated in a quartz tube at 650 °C (heating rate of 450 K h^{-1}) for 45 minutes under a hydrogen flow (30 L h^{-1}). Following activation, the catalyst sample was cooled to room temperature and then introduced into a reaction mixture consisting of 5.7 mmol of the phenolic compound, 1.5 mmol of dodecane (internal standard), 50 g of cyclohexanol, and 40 g of pentadecane (used as an inert solvent). The resulting suspension was transferred to a 285-mL batch reactor equipped with a magnetic stirrer and a sampling port. Subsequently, the reactor was purged with argon and heated to the target temperature of either 200 or 250 °C, with heating times of 15 and 25 minutes, respectively. The qualitative and quantitative composition of the collected samples was determined using a Shimadzu GCMS-QP2010 SE equipped with a 30 m quartz DM-35 column. The products were identified using a peak retention time and mass spectra, which were compared with the data from the NIST and Wiley7 electronic mass spectral libraries. The conversion of the initial substrates was quantified using the internal standard method, employing dodecane as the internal standard.

The conversion of the initial phenolic substrate and product yields were calculated according to equations (1) and (2), respectively:

$$Conversion\ (\%) = \frac{X^0_{Subtrate} - X_{Subtrate}}{X^0_{Subtrate}} * 100\%\ (1)$$

$$Yield\ (\%) = \frac{X_{product}}{X^0_{Subtrate}} * 100\%\ (2)$$

where $X_{product}$ is the mole fraction of the product, $X^0_{Substrate}$ and $X_{Substrate}$ are the initial and final mole fractions of the phenolic compound.

4. *Kinetic data of transformations of phenolic compounds*

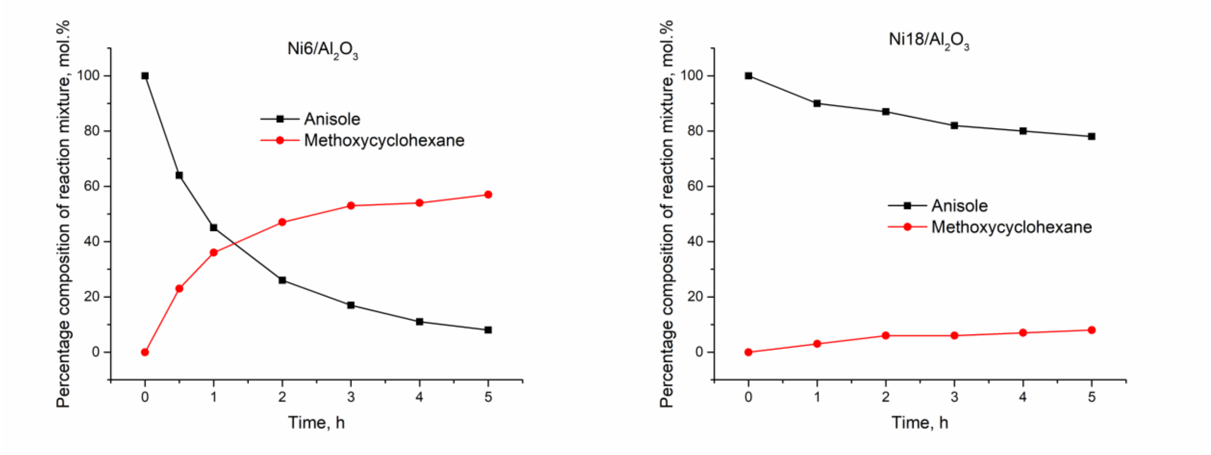


Figure S4. Percentage composition of the reaction mixtures as a functions of time. Anisole, 250 °C.

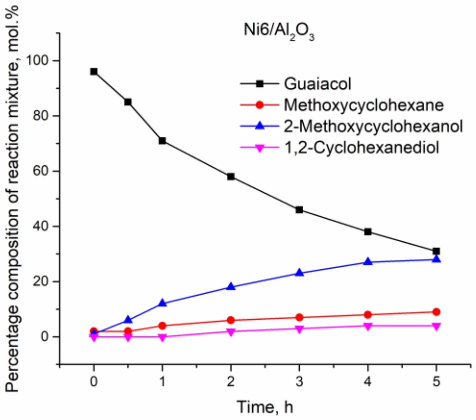


Figure S5. Percentage composition of the reaction mixtures as a functions of time. Guaiacol, 200 °C.

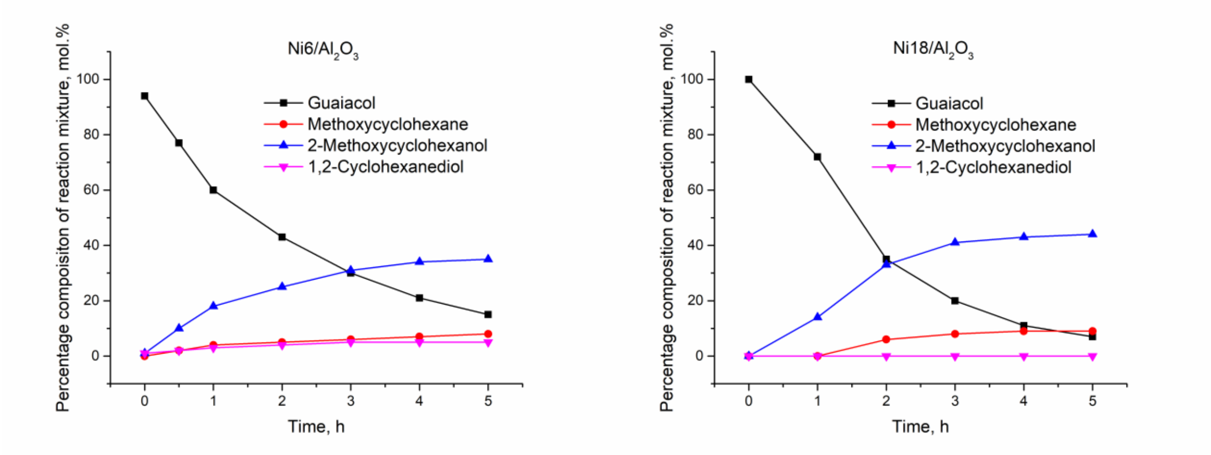


Figure S6. Percentage composition of the reaction mixtures as a functions of time. Guaiacol, 250 °C.

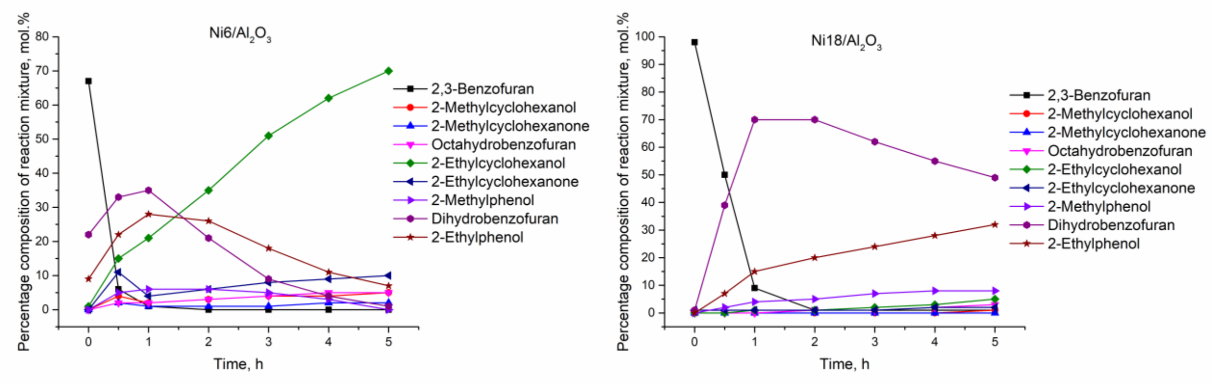


Figure S7. Percentage composition of the reaction mixtures as a functions of time. 2,3-Benzofuran, 200 °C.

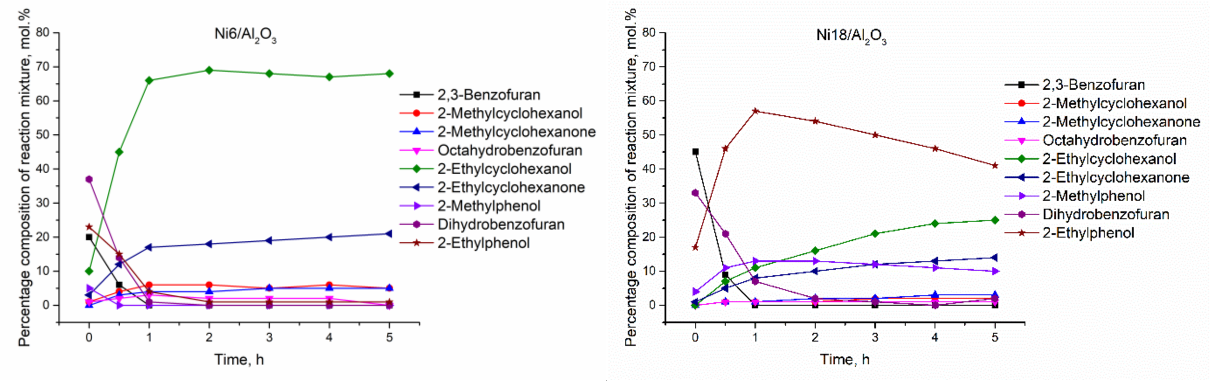


Figure S8. Percentage composition of the reaction mixtures as a functions of time. 2,3-Benzofuran, 250 °C.

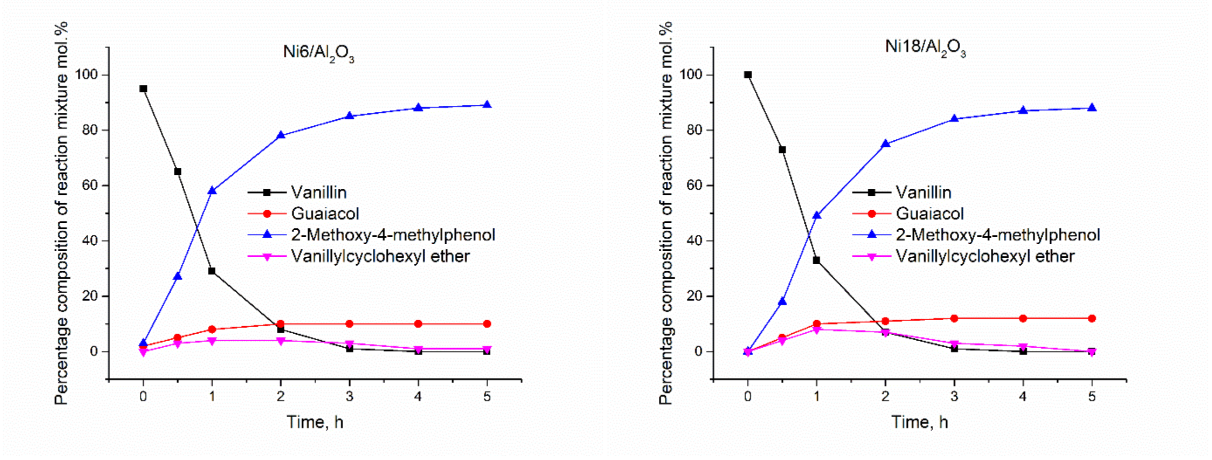


Figure S9. Percentage composition of the reaction mixtures as a functions of time. Vanillin, 250 °C.

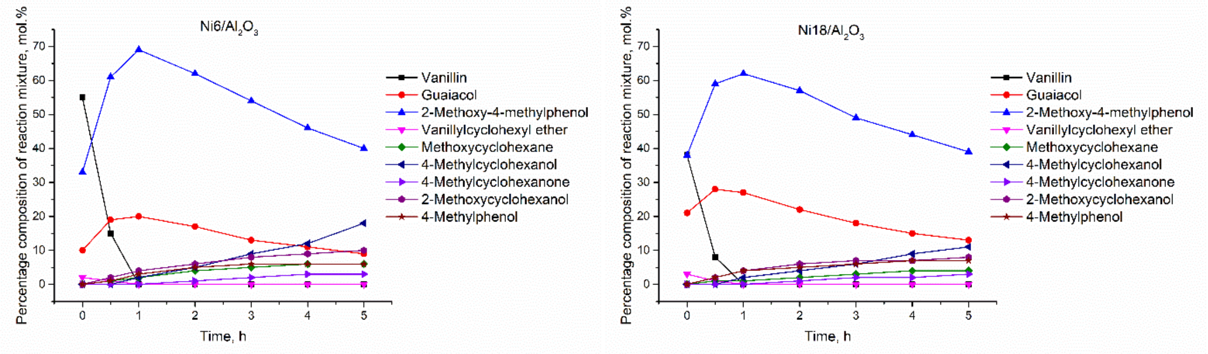
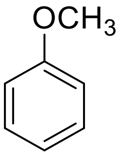
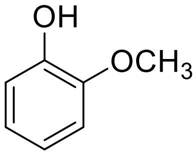
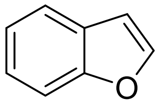
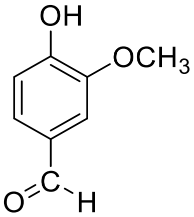


Figure S10. Percentage composition of the reaction mixtures as a functions of time. Vanillin, 250 °C.

5. *Cyclohexanol conversion*

Table S4. Content of cyclohexanol and cyclohexanone in the final reaction mixtures obtained under different reaction conditions.

Phenolic compound	Catalyst	*T*/°C	Content*, mol.%	
			Cyclohexanol	Cyclohexanone
 anisole **1**	$Ni6/\gamma\text{-}Al_2O_3$	200	92	7
		250	75	12
	$Ni18/\gamma\text{-}Al_2O_3$	200	93	7
		250	78	18
 guaiacol **5**	$Ni6/\gamma\text{-}Al_2O_3$	200	92	6
		250	81	12
	$Ni18/\gamma\text{-}Al_2O_3$	200	93	7
		250	78	14
 2,3-benzofuran **7**	$Ni6/\gamma\text{-}Al_2O_3$	200	91	7
		250	75	14
	$Ni18/\gamma\text{-}Al_2O_3$	200	92	8
		250	73	22
 vanillin **12**	$Ni6/\gamma\text{-}Al_2O_3$	200	94	6
		250	77	14
	$Ni18/\gamma\text{-}Al_2O_3$	200	93	7
		250	74	16

* After 5 hours