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Innovative cyclohexanone synthesis *via* transfer hydrogenation of phenol and cyclohexanol

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Materials and chemicals

The following reagents were used in this study: phenol (99.5%, Lenreactiv), cyclohexanol (99.0%, EKOS-1), 2-PrOH (99.8%, EKOS-1), pentadecane (98.0%, EKOS-1), dodecane (⩾99%, Sigma-Aldrich), Raney alloy (Al–Ni 50 : 50 mass%, Sigma–Aldrich), NaOH (99%, Leneactiv), [$Ni(OAc)_2 \cdot 4H_2O$, (99 % extra, Acros Organics], acetylacetone (⩾99%, Vecton) CO_2 (99.8%, Promgaz-servis, Russia), aluminum tri-sec-butoxide (97%, Acros Organic).

Catalyst preparation and characterization

Raney nickel was prepared according to a well-known leaching method using a Raney alloy.[S1] A quantity of 0.45 g of the alloy was added in portions to 5.63 ml of approximately 20% aqueous solution, which was prepared using 16.33 g of NaOH and 58 ml of distilled water, under stirring at 50 °C. Once the Raney alloy had been completely added (approximately 10–15 minutes), the mixture was stirred for a further 45–50 minutes at 50 °C until the evolution of H_2 stopped. The freshly prepared Raney nickel was washed with distilled water (200 ml) in portions until the pH was neutral, after which the catalyst was added to 25 ml of distilled water and stirred for 1.5 hours. After this time, water was decanted and changed with the solvent (pentadecane or cyclohexanol), and the mixture was kept in the fridge overnight. The following day, the solvent was changed with the reaction mixture and used in transfer hydrogenation.

In the initial stage of the preparation of Ni/Al_2O_3 the sol of Al_2O_3 was synthesized. This was achieved by adding 0.81 mL of acetylacetone to 38 ml of 2-PrOH, followed by the addition of 1 mL of aluminum tri-sec-butoxide to the resulting solution under stirring. Upon the formation of a white precipitate, 80 mL of methanol was added to the obtained suspension. After 15 minutes of stirring, the precipitate was dissolved, and 0.57 ml of distilled water was added to the resulting solution. The final mixture was left for 24 hours under stirring. On the second stage, the catalyst was prepared by the supercritical antisolvent coprecipitation method using the SAS-50 setup (Waters). A methanol solution containing 7.62 g of $Ni(OAc)_2 \cdot 4H_2O$ and Al_2O_3 sol was injected into a stream of supercritical CO_2. This resulted in a decrease in the solvent power of the carbon dioxide-methanol mixture, and precipitation occurred. After that, pure CO_2 was passed through the obtained powder for 20 min to remove a residual solvent. The catalyst was calcined at 300 °C for 3 h. Prior to use in transfer hydrogenation, 0.32 g of the oxidized catalyst was heated in H_2 stream (30 l h^{-1}) at 450 °C (heating speed 450 °C h^{-1}) for 45 minutes at the target temperature.

The nickel content, morphology, and texture of both synthesized catalysts were characterized (**Table S1**, **Figures 1 and S1**) using X-ray diffraction (XRD), X-ray fluorescence (XRF), N_2 physical adsorption, and high-resolution transmission electron microscopy (HRTEM). XRD studies were performed using a STOE STADI MP setup. The spectra were obtained using Mo Kα radiation (λ = 0.7093 Å) with a step size of 2θ = 0.015°. Prior to analysis, the catalyst samples were reduced according to the standard procedure and then passivated in air. The spent samples of both catalysts were used in reaction at 200 °C and then passivated in air. The textural characteristics of the catalysts were measured using an ASAP-2400 automated volumetric adsorption analyzer (Micromeritics Instrument. Corp.). Prior to analysis, the reduced samples were passivated in air, dried under vacuum at room temperature, and then placed in a special cell under an inert argon atmosphere. After degassing at 100 °C and a residual pressure of 0.13 Pa for 7 h, adsorption isotherms were measured at liquid nitrogen temperature (−196 °C). The surface area (S_{BET}) was determined by the Brunauer–Emmett–Teller method. The elemental composition of the carefully passivated Raney® nickel was determined using an X-ray fluorescence spectrometer ARL Advant'X 2247 (Thermo Fisher Scientific, USA) equipped with a Rh anode as an X-ray source.

The mass percentage of elements was estimated using QuantAS software. A high-resolution transmission electron microscope (ThemisZ, Thermo Fisher Scientific) operated at 200 kV was used for the investigation. For electron microscopy studies, the catalyst sample was deposited on perforated carbon substrates attached to aluminum grids using an ultrasonic disperser. Images were captured using a Ceta 16 CCD sensor (Thermo Fisher Scientific). Prior to analysis, the catalyst sample was carefully passivated by exposure to air.

Table S1. Ni content and textural properties of Raney nickel and Ni/Al_2O_3.

Sample	Metal content (mass%)	S_{BET}, m^2/g	$V_{pore}/cm^3\ g^{-1}$	D_{pore}/nm	D_{XRD}/nm
Raney nickel	87	79	0.055	2.5	3.0±0.5 (10.0±0.5[a])
Ni/Al_2O_3	87	81	0.12	6.3	9.0±0.5 (8.5±0.5[a])

[a] D_{XRD} of the spent samples treated at 200 °C for 3 h.

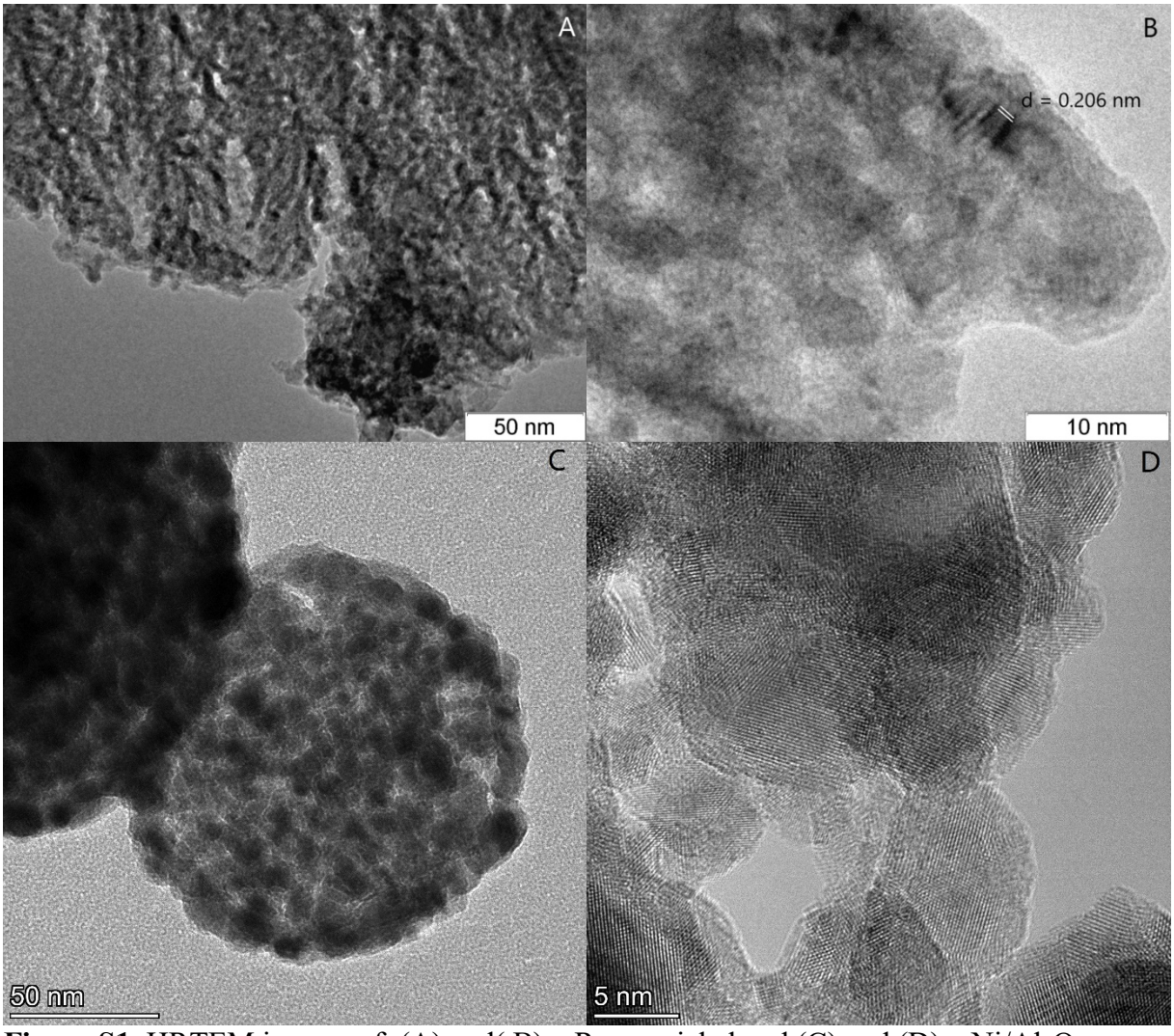

Figure S1. HRTEM images of: (A) and(B) – Raney nickel and (C) and (D) – Ni/Al_2O_3.

Catalytic tests

The catalytic experiments were conducted in two distinct configurations: a stainless steel 90 mL batch reactor for experiments conducted at temperatures 200–250 °C, and a 100 ml flask reactor for

experiments conducted at 150 °C and below temperatures. Both reactors were equipped with a stirrer and a sampler. The reaction mixture was prepared by dissolving phenol in pure cyclohexanol or a mixture of cyclohexanol with pentadecane. The amounts of each compound are provided in **Table S2**. Raney nickel or Ni/Al_2O_3 were added to the reaction mixture and the suspension formed was then placed in the reactor, and purged with argon. Then the reactor was heated to the target temperature over a period of 15–20 minutes. The duration of the experiments was 3 hours after the target temperature was reached. The qualitative and quantitative composition of the collected samples was analyzed using a Shimadzu GCMS-QP2010 SE equipped with a 30 m quartz DM-35 column (bonded and cross-linked 35% diphenyl/65% dimethyl polysiloxane, ID 0.25 mm, df 0.25 μm). The products were identified by peak retention time and mass spectrum, which were compared with the corresponding data for pure compounds or with the NIST and Wiley electronic mass spectral libraries. The yield of cyclohexanone was calculated using chromatographic data, taking into account sensitivity coefficients to the internal standard. The conversion of phenol (equation 1) was evaluated using the internal standard method with dodecane as an internal standard.

$$Conversion\ (mol\%) = \left(1 - \frac{n(phenol)_{in}}{n(phenol)_{fin}}\right) \times 100\%, \qquad (1)$$

where $n(\text{phenol})_{in}$ and $n(\text{phenol})_{fin}$ - amounts of phenol in initial and final reaction mixtures.

Table S2 Reaction conditions in transfer hydrogenation experiments.

Entry	Catalyst	*T*, °C	m(Phenol)/ mmol	m(Cyclohexanol)/ mmol	m(Pentadecane)/ mmol
1	Raney nickel	82	38	380[a]	0
2		100	38	380	0
3		150	38	380	0
4		150	6.3	380	0
5		150	3.2	380	0
6		137	6.3	64	115
7		200	38	77	115
8		200	38	190	72
9		200	38	380	0
10		200	0	380	0
11		200	0	77	115
12	Ni/Al_2O_3	150	38	380	0
13		200	38	77	115
14		200	38	190	72
15		200	38	380	0
16		250	38	380	0

[a] Cyclohexanol was replaced with 2-PrOH

References

S1 J. Freel, W. J. M. Pieters and R. B. Anderson, *J. Catal.*, 1969, **14**, 247; https://doi.org/10.1016/0021-9517(69)90432-1.