

Nickel Catalysts on Carbon-Mineral Sapropel-Based Supports for Liquid-Phase Hydrogenation of Nitrobenzene

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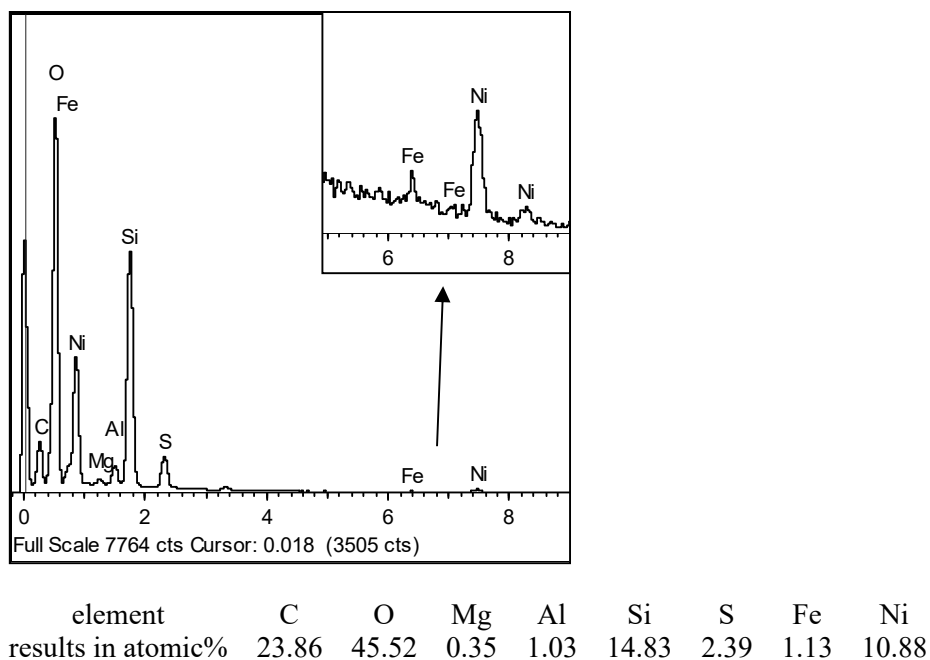


Figure S1. EDX spectra and atomic % of elements in sample Ni/CM-M, formate.

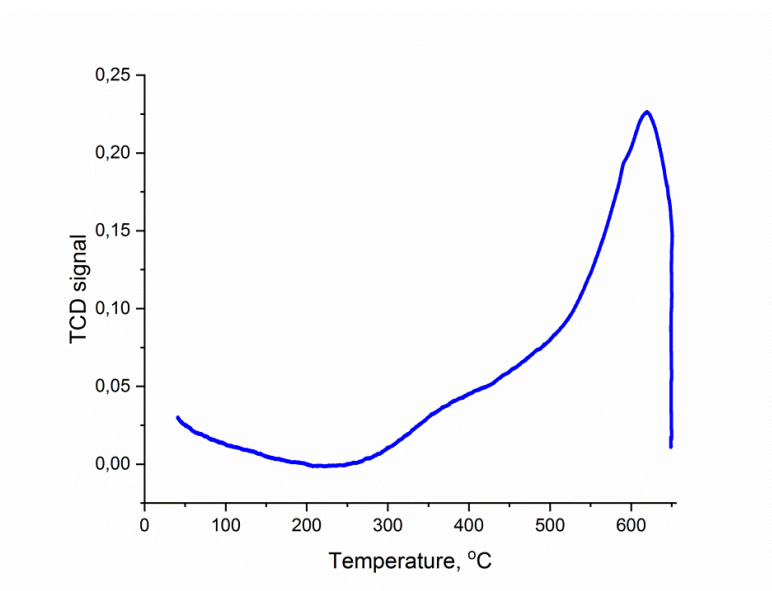


Figure S2. TPR profile of CMM support.

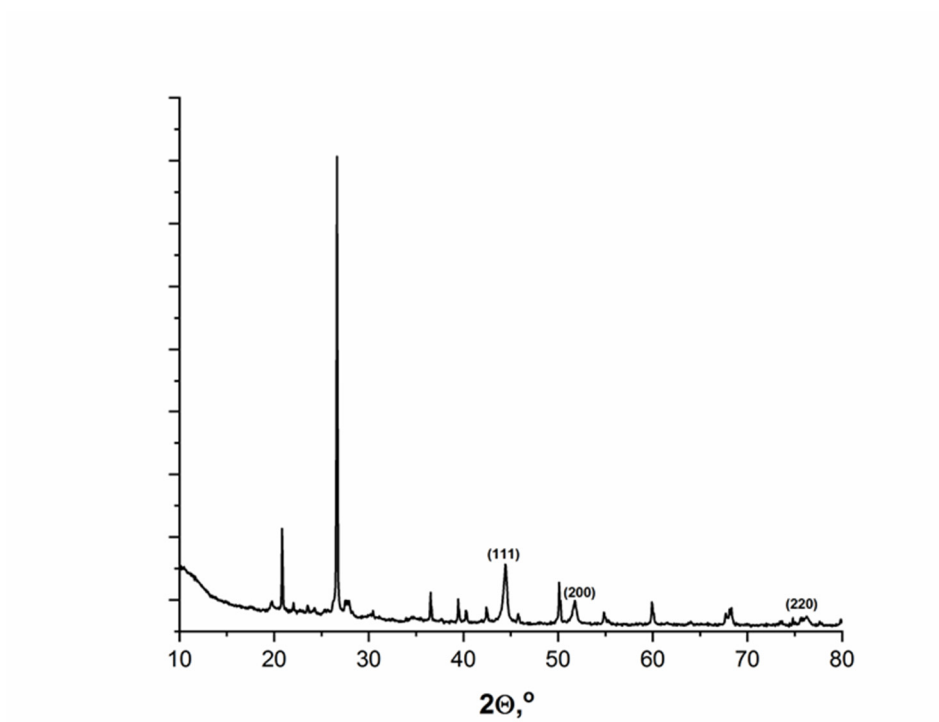


Figure S3. Diffraction patterns of Ni/CM-M sample reduced at 600 °C with $\text{Ni}(\text{NO}_3)_2$ as a precursor. Reflections associated with the nickel metal phase are noted.

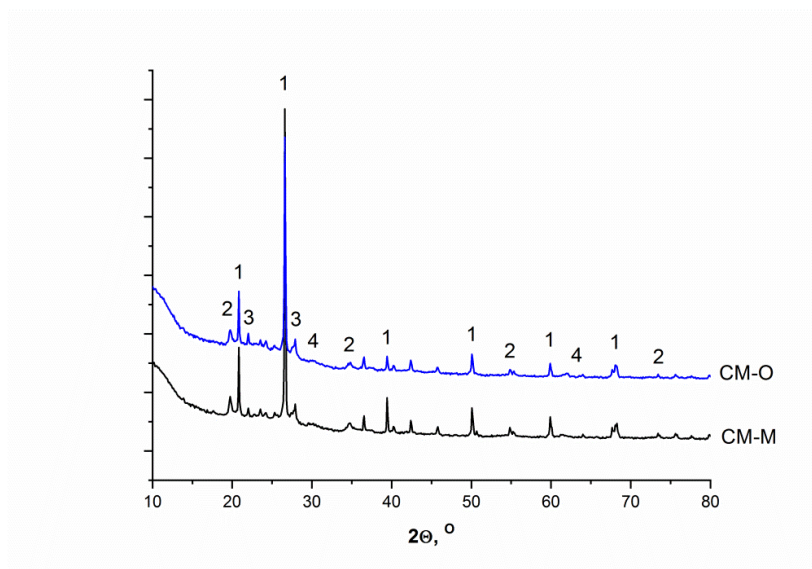


Figure S4. Diffraction patterns of CM-M and CM-O samples (1 – SiO₂, PDF # 01-070-3755, 2-muscovite KAl₂(Si₃Al)O₁₀(OH)₂, PDF #00-007-0025, 3 - albite (Na_{0.84}Ca_{0.16})Al_{1.16}Si_{2.84}O₈, PDF # 01-076-0927, 4 - microcline (K_{0.95}Na_{0.05})AlSi₃O₈, PDF # 01-084-1455).

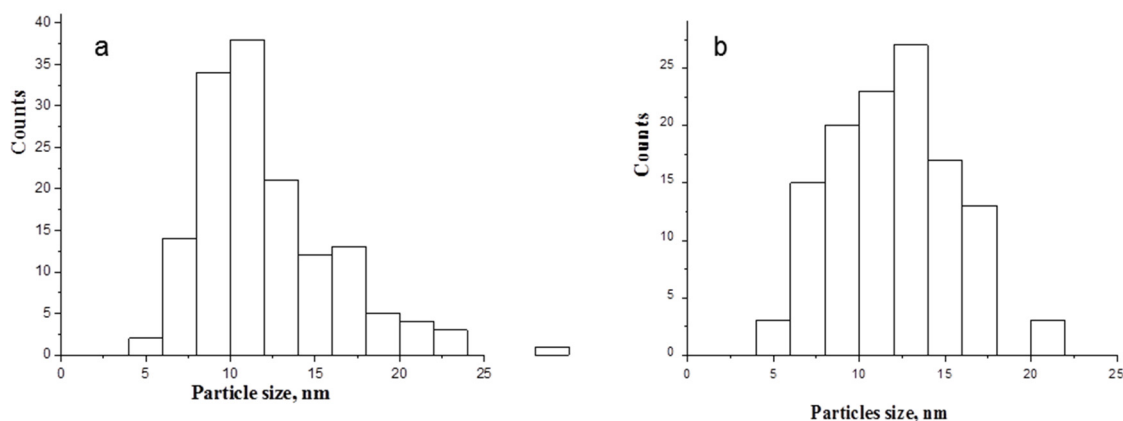


Figure S5. Size distribution of nickel particles from TEM data: a – Ni/CM-M, nitrate; b – Ni/CM-M, formate.

On figure S5 histograms are presented for samples prepared using the same support CM-M but different nickel precursors, nitrate and formate. It follows from these data that a fairly uniform distribution is formed, and the average particle size for these catalysts is close (11.8–12.1 nm). The closeness of the sizes of supported nickel for these samples is consistent with the XRD data.

It should be noted that it is not always possible to obtain correct data on the particle size distribution, since the carbon-mineral support from sapropel contains high-density mineral components and it is difficult to identify particles of the introduced metal. In samples obtained from nickel sulfate, a new phase is formed, which also does not allow one to determine the size of nickel particles correctly from TEM data.

Table S1. The comparison of the studied catalysts activity with other catalysts in the reaction of liquid-phase nitrobenzene hydrogenation

No	Catalyst	Reaction conditions	Conversion, %	Selectivity for aniline, %	Reference
1	Pd/carbon foam	P(H ₂)=2 MPa, T=10-50°C, 5-240 min, methanol	99.1	99.8	<i>Int. J. Mol. Sci.</i> 2022 , 23(12), 6423; https://doi.org/10.3390/ijms23126423
2	Pd/MnFe ₂ O ₄	P(H ₂)= 2 MPa, 40-180 min, 10-50 °C, methanol	96	96	<i>Int. J. Mol. Sci.</i> 2022 , 23(12), 6535; https://doi.org/10.3390/ijms23126535
3	Palladium-containing anion exchangers	P(H ₂) = 0.1 MPa, 20°C, ethanol	≥99	≥99	<i>Petrol Chem.</i> 2016 , 56 (2), 146-150 DOI: 10.1134/S096554411602002X
4	Ru/MN270 (hypercroslinked polystyrene)	P(H ₂)=0.2 MPa, 180 °C, 30 min, i-propanol	97	98	<i>Bulletin of Science and Practice</i> 2018 , 4(12) http://doi.org/10.5281/zenodo.2254348
5	Ru/fulleride nanospheres C60	P(H ₂)=3 MPa, 80 °C, 240 min, ethanol	≥99	90	<i>ACS Catal.</i> 2016 , 6, 6018–6024 DOI: 10.1021/acscatal.6b01429
6	Pd/carbon nanoglobules	P(H ₂)=0.5 MPa, 50 °C, 60 min, ethanol	≥99	≥99	<i>Catalysis Letters</i> 2020 , 150 (3), 888-900 DOI: 10.1007/s10562-019-02974-6
7	Ni/TiO ₂	P(H ₂)= 1.96 MPa, 140 °C, 60 min,	60	≥99	<i>Chinese J Catal</i> 2012 , 33 (8), DOI: 10.1016/S1872-

		ethanol			2067(11)60398-7
8	Ni/Fullerene C60	P(H ₂)=1 MPa, 80 °C 20 min, ethanol	99.5	≥99.9	Chemical Engineering Journal , 2020 , <i>382</i> (15),122911. https://doi.org/10.1016/j.cej.2019.122911
9	Ni/γ-Al ₂ O ₃	P(H ₂)=4 – 8 MPa, 50 or 80 °C, 50 min Ethanol or scCO ₂	13-73	62-99	Journal of Catalysis 2009 , 264 (1), 1-10. https://doi.org/10.1016/j.jcat.2009.03.008
10	Ni/CM-M	P(H ₂)=2 MPa, T=90 °C, 60 min, ethanol	65	≥99	This work

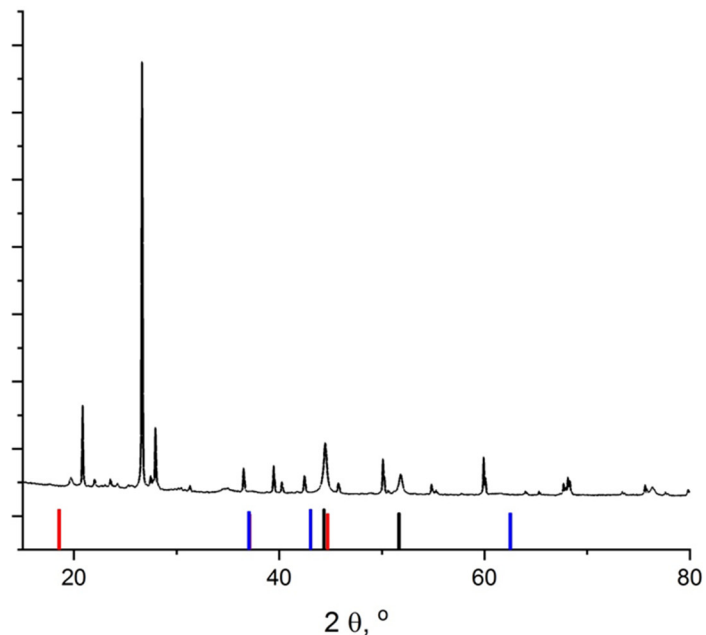


Figure S6. Diffraction patterns of Ni/CM-M sample reduced at 350 °C (red line - basic reflections of NiO₂, PDF # 01-085-1977; black line – basic reflections of Ni, PDF # 03-065-380, blue line – basic reflections of NiO, PDF # 01-071-4750).

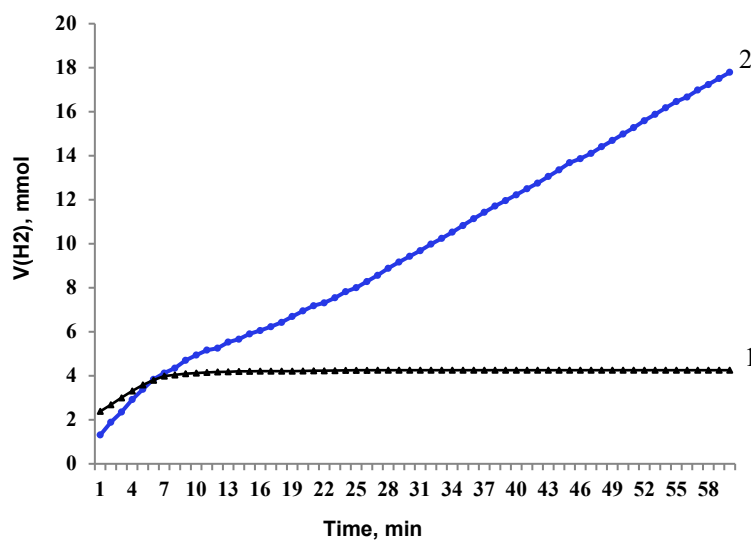


Figure S7. Hydrogen absorption curves for hydrogenation of nitrobenzene on Ni/CM-M with nickel nitrate as a precursor, reduced at: 1 - 350 °C, 2 – 650 °C (the reaction conditions: hydrogen pressure 2 MPa, temperature 90 °C, and time 60 min).

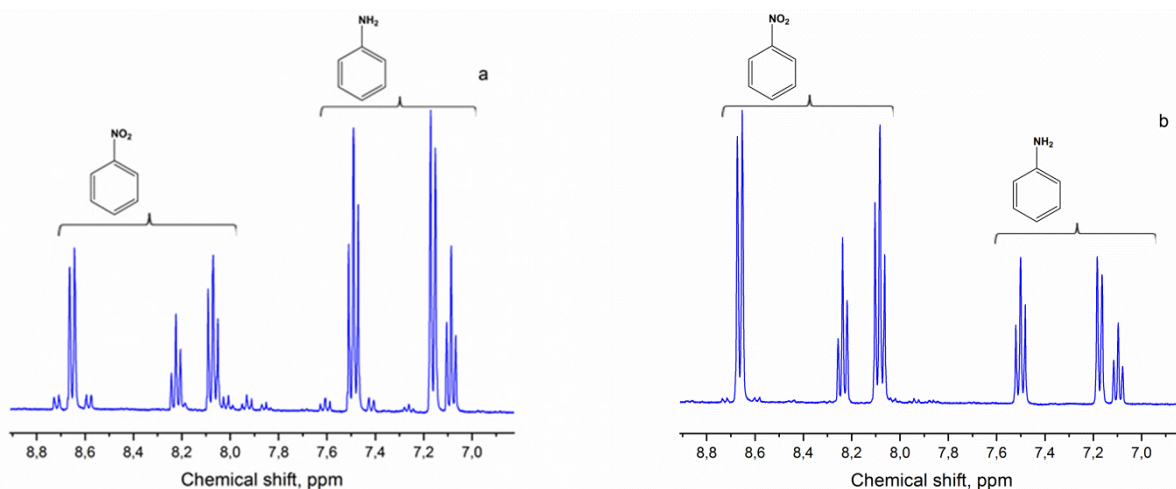


Figure S8. NMR (¹H) spectra of nitrobenzene hydrogenation reaction products using nickel catalysts based on sapropels of various nature with Ni(NO₃)₂ as a precursor (a – Ni/CM-M, b – Ni/CM-O).

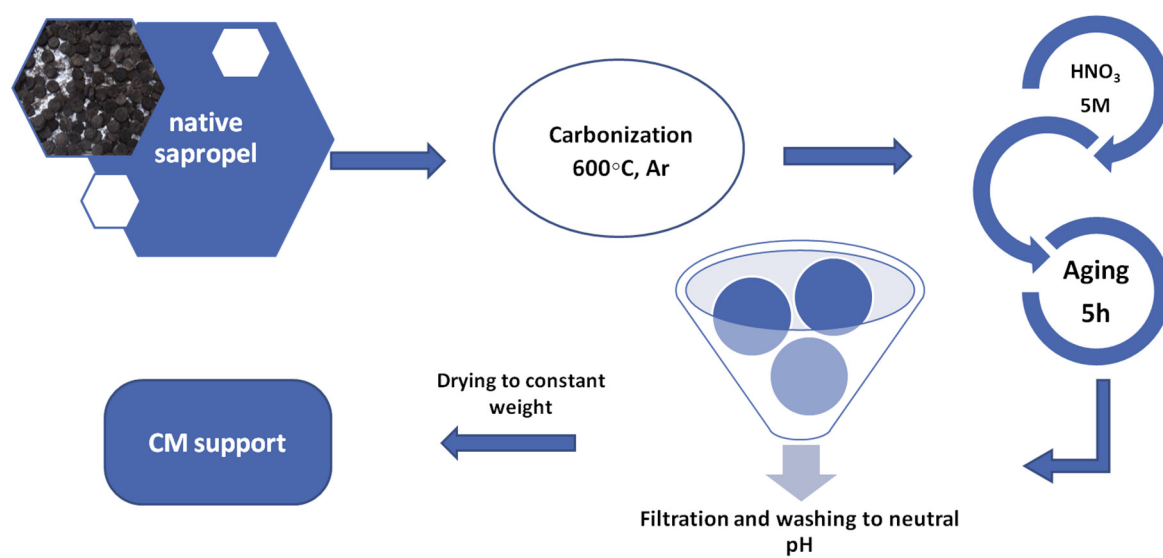


Figure S9. Scheme for the synthesis of CM support from sapropel.