Supplementary Materials: Efficient Hydrogenolysis of Guaiacol over Highly Dispersed Ni/MCM-41 Catalyst Combined with HZSM-5

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Table S1. The reduction degrees of the Ni-based catalysts.

Catalyst	Ni Content (wt. %) [a]	Reduction Degree (%) [b]
Ni/M 0EG	14.61	89.6
Ni/M 1EG	14.54	53.7
Ni/H 1EG	14.13	99.4
Ni/M(H) 1EG	14.73	78.9

[a] The Ni content was analyzed by Atomic Absorption Spectroscopy (ICP-AES, PE OPTIMA 7000, PerkinElmer Inc., Santa Clara, CA, USA); [b] The reduction degree was determined by the TPR method.

The reduction degree of Ni metal was measured by the TPR method, and the details can be found in the previous literature [1]. According to the reduction procedure of various Ni-based catalysts before testing, pre-reduction was done at 450 °C for 4 h using a 5% H_2/N_2 gas flow.

Table S2. Hydrogenation activity of guaiacol on various catalysts with different Ni loading at 150 °C [a].

Catalyst	X_{GUA} %	$S_{Methoxycyclohexanol}$ %	$S_{Cyclohexanol}$ %	$S_{Methoxycyclohexane}$ %	$S_{Cyclohexane}$ % [b]
5 wt % Ni/M 1EG	14.5	92.4	3.4	0.1	0.4
10 wt %Ni/M 1EG	48.5	92.9	3.8	0.2	0.2
20 wt % Ni/M 1EG	97.4	93.9	5.3	0.5	0.2
30 wt % Ni/M 1EG	99.9	93.5	4.6	0.4	0.1
20 wt % Ni/M 1EG without reduction	0.2	100	0	0	0

[a] Reaction conditions: 1.0 g guaiacol, 9.0 g n-dodecane (solvent), 0.15 g Ni-based catalysts, 0.15 g commercial 5 wt % Pd/C and Ru/C catalyst, 120–200 °C, 5.0 MPa (ambient temperature), 1000 rmp/min, 120 min. For Ni/M 1EG +H, 0.15 g Ni/M 1EG catalyst with additional solid acid of 0.12 g HZSM-5; [b] There were some other products that mainly included 1,2-cyclohexanediol, 1,2-dimethoxycyclohexane, methylolcyclopentane, cyclopentane, etc.

Table S3. Hydrogenolysis activity of guaiacol over Ni/M(H) 1EG under different reaction times [a].

Reaction Time (min) [b]	0	30	30 [c]	60	90	120
X_{GUA} (%)	99.8	99.9	99.9	100	100	100
$S_{Methoxycyclohexanol}$	61.9	12.8	73.9	0.3	0.2	0
$S_{Cyclohexanol}$	2.5	0.9	12.1	0	0	0
$S_{Methoxycyclohexane}$	1.5	1.3	1.1	0	0	0
$S_{Methylolcyclopentane}$	7.4	8.1	2.4	0	0	0
$S_{Cyclohexane}$	24.6	67.3	5.6	87.9	87.6	84.1
$S_{Methylcyclopentane}$	1.1	3.5	0.1	5.8	5.9	4.8
$S_{Cyclopentane}$ [d]	0.5	5.1	1.0	4.9	5.1	10.3

[a] Reaction conditions: 1.0 g guaiacol, 9.0 g n-dodecane (solvent), 0.15 g Ni-based catalysts, 240 °C, 5.0 MPa (ambient temperature), 1000 rmp/min; [b] The reaction temperature was elevated to 240 °C in 34 min, and the reaction time was the length of time kept at 240 °C; [c] The reaction was comparatively performed on Ni/M 1EG; [d] There were some other products that mainly included *n*-hexane, *n*-pentane, methylcyclohexane, methylpentane, butane, etc.

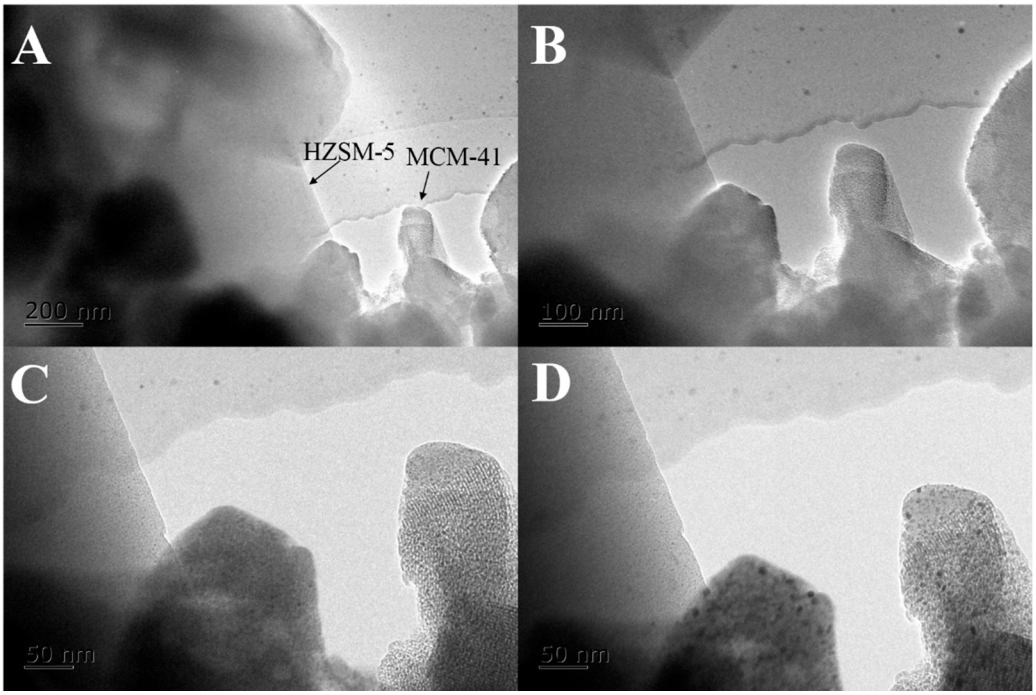

Figure S1. TEM pictures of synthesized Ni/M(H) 1EG sample with different electron beam irradiation times (the time is increasing from **A** to **D** photos corresponding to 1min, 3min, 4min and 5min).

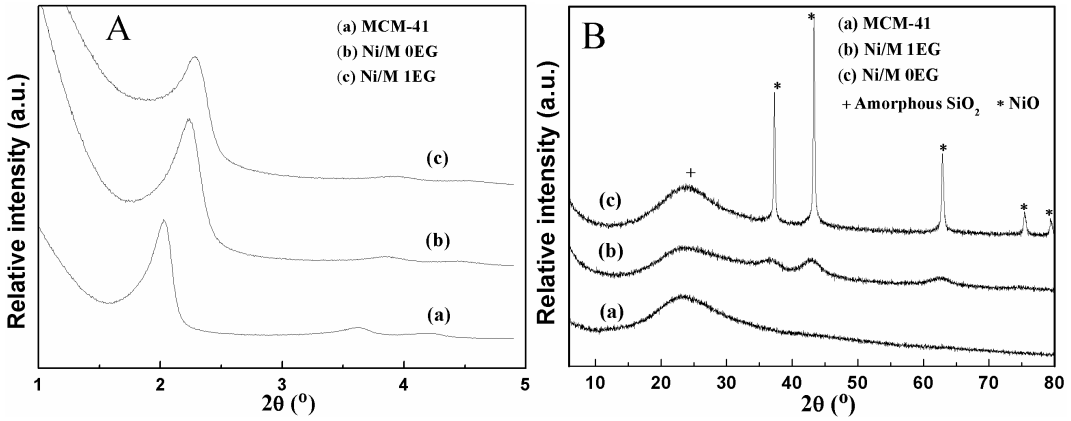

Figure S2. The XRD patterns of MCM-41 and MCM-41-supported catalysts: (**A**) low-angle XRD patterns; (**B**) high-angle XRD patterns.

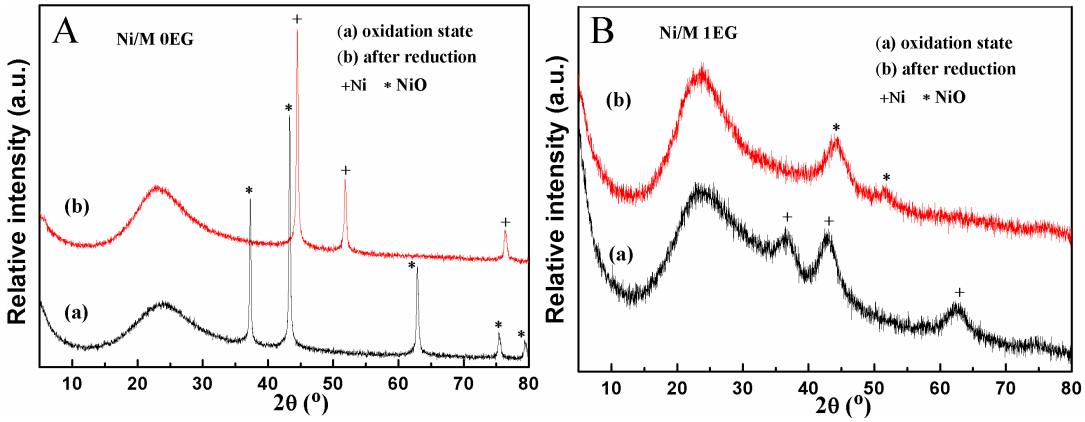

Figure S3. The XRD patterns of various catalysts before and after reduction (**A**) Ni/M 0EG and (**B**) Ni/M 1EG. Reduction conditions: reduction at 450 °C for 4 h under atmospheric pressure of 100% H_2.

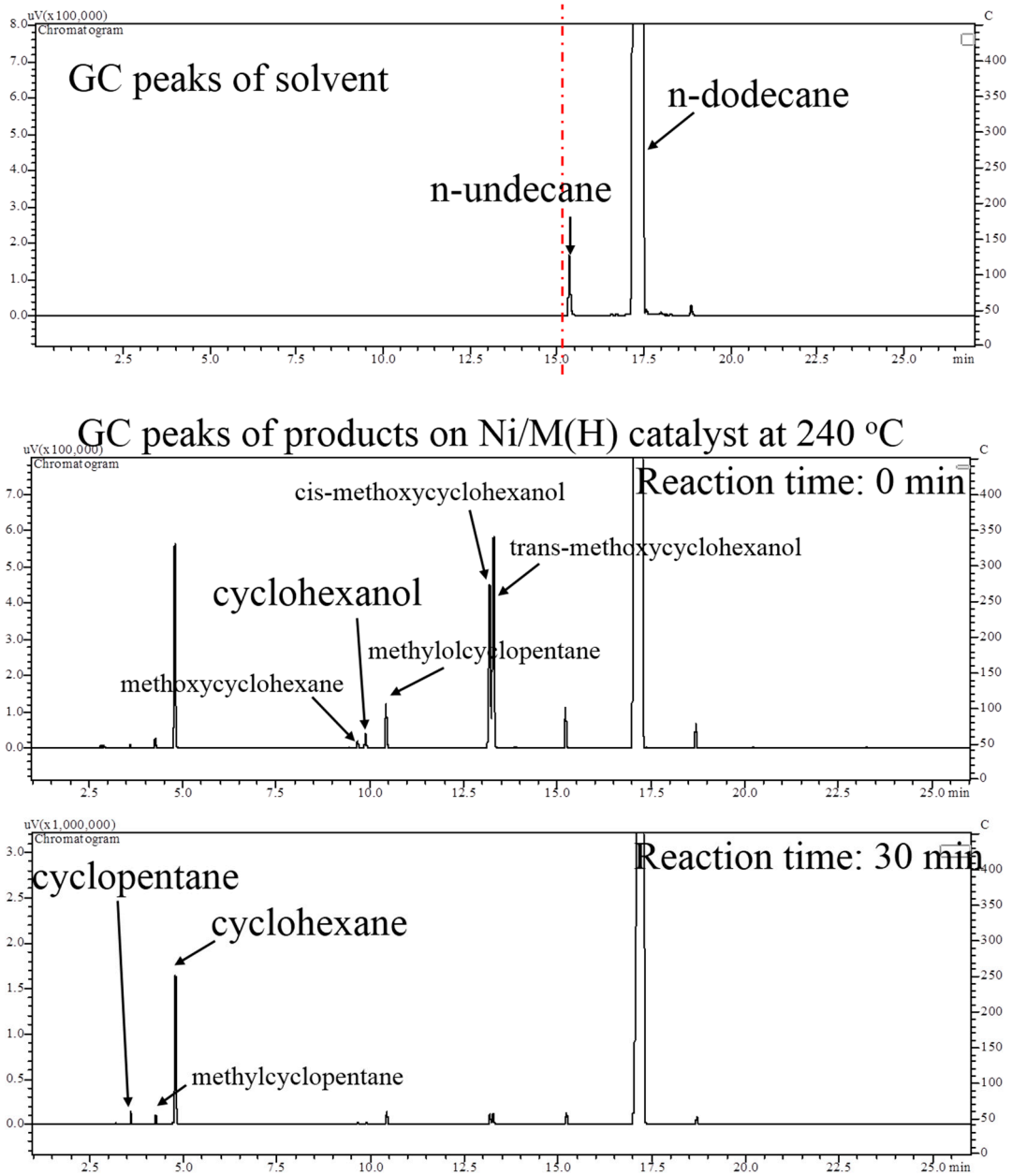

Figure S4. *Cont.*

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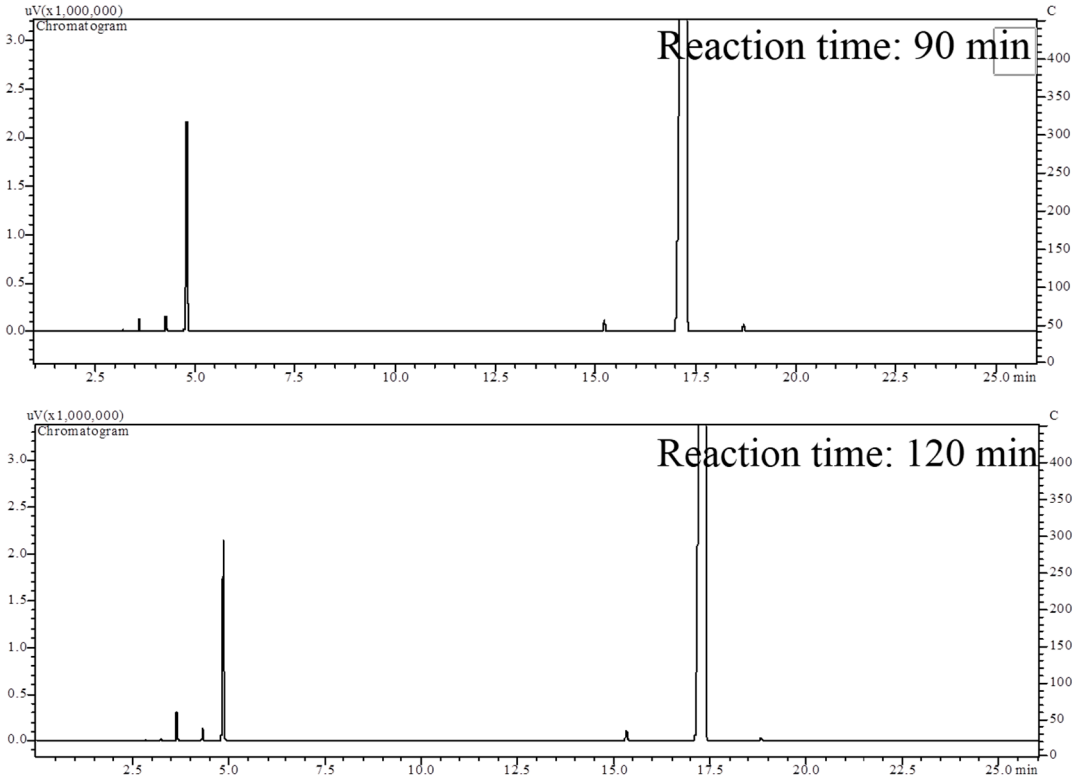

Figure S4. GC analysis of the products for guaiacol HDO at 240 °C with different reaction times on Ni/M(H) 1EG.

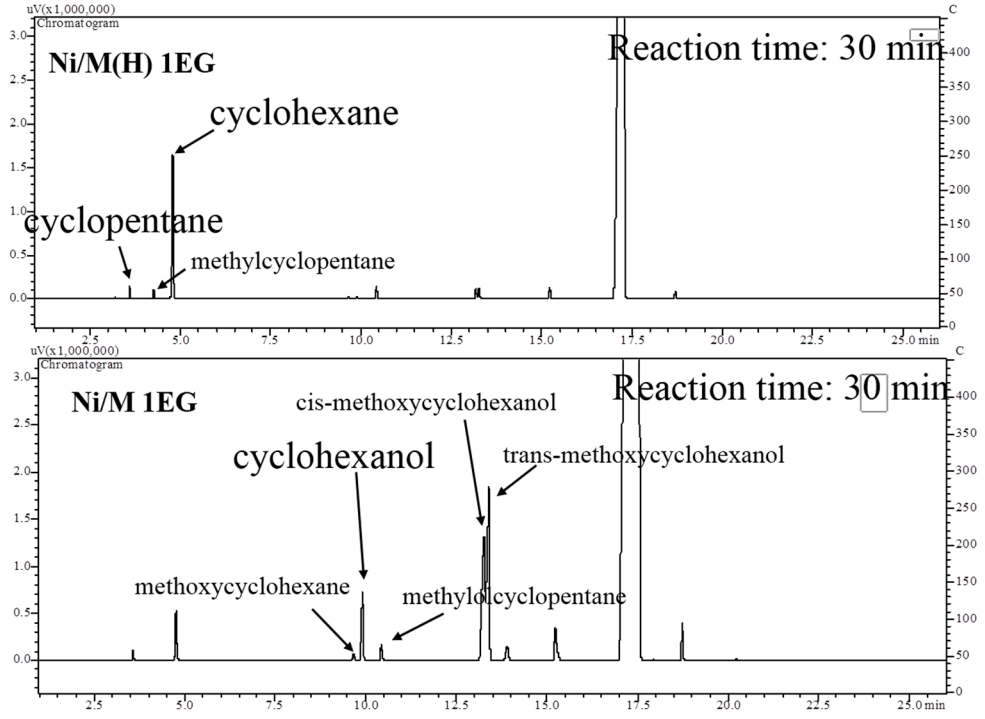

Figure S5. GC analysis of the products for guaiacol HDO at 240 °C for 30 min on Ni/M(H) 1EG and Ni/M 1EG, respectively.

References

1. Poncelet, G., Centeno, M.A., Molina, R. Characterization of reduced α-alumina-supported nickel catalysts by spectroscopic and chemisorption measurements. *Appl. Catal. A* **2005**, *288*, 232–242.