Electronic Supplementary Information (ESI)

Simple effective preparation of highly efficient heterogeneous base catalysts

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1. XRD

MgAl HTC reference sample prepared by the conventional coprecipitation method was a phase-pure HTC material as evidenced by the characteristic reflections at 2Theta ≈ 11.5°, 23.0°, 34.8°, etc. in its XRD pattern (Fig. 1S). The *d003* value (the basal spacing between the layers) calculated from the position of the diffraction peak at 2θ ≈ 11.5° was 7.78 Å which corresponds to the Mg/Al ratio of about 3.[1-4] The calcination of the as-prepared HTC at T=450 °C produced MgAl mixed oxide as evidenced by the appearance of diffraction lines at 2θ ≈ 43.0° and 62.5° (Fig. 1S). The rehydration of the calcined solid at T=25 °C for 20 minutes formed a sample that was a phase-pure reconstructed HTC (Fig. 1S). The calculated *d003* value for this sample was also 7.78 Å, proving that the Mg/Al ratio in HTC platelets did not change during the calcination and rehydration steps.

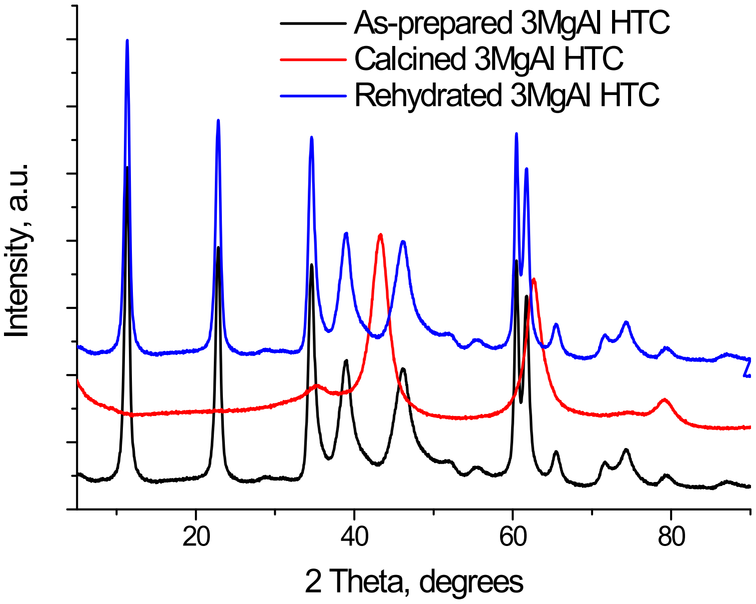


Fig. 1S. XRD patterns of a conventionally prepared 3MgAl HTC sample, a calcined 3MgAl mixed oxide and a rehydrated 3MgAl HTC.

Fig. 2S presents XRD patterns of commercial MgO and Pural SB used as starting Mg and Al reactants as well as of their physical mixture (with the calculated atomic ratio Mg/Al=3) before and after calcination at T=450 °C. According to XRD, Mg and Al commercial sources were phase-pure MgO with a periclase structure and pseudoboehmite, respectively (Fig. 2S). Reflections from both compounds were also present in the XRD pattern of their physical mixture. After the calcination of the physical mixture, XRD reflections from pseudoboehmite disappeared, but the characteristic reflections from γ-Al_2O_3 at 2Theta ≈ 46 ° and 67 ° appeared instead, while those from MgO remained unaltered (Fig. 2S).

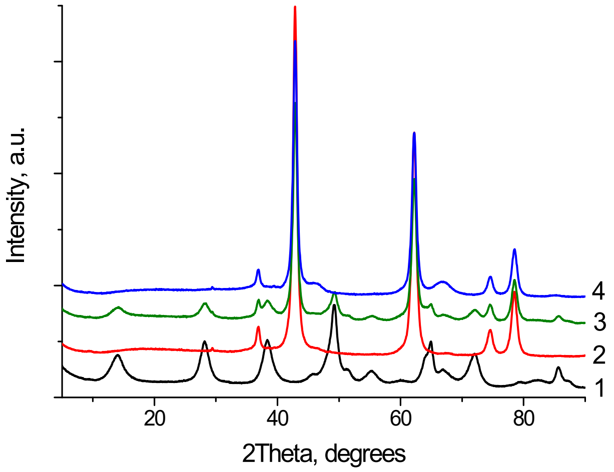


Fig. 2S. XRD patterns of commercial AlOOH (1) and MgO (2) samples taken as starting reactants as well as their physical mixture (atomic ratio Mg/Al=3) before (3) and after calcination at T=450 °C (4).

2. N2 physisorption.

Table 1S. Textural properties of individual oxides, initial 3MgAl physical mixture and rehydrated samples.

Sample	BET surface area, m^2/g	Total pore volume, cm^3/g
As-prepared 3MgAl HTC	26	0.11
Calcined 3MgAl mixed oxide	149	0.36
Rehydrated 3MgAl HTC	3	0.01
MgO	110	0.27
Al_2O_3	280	0.41
3MgAl	167	0.3
3MgAl-C	172	0.35
S25-5m	91	0.21
S25-20m	78	0.18
S25-2h	83	0.18
S25-1d	82	0.18
S25-3d	86	0.21
S25-5d	84	0.19
S25-7d	84	0.22
S75-5m	89	0.21
S75-20m	78	0.18
S75-2h	86	0.19
S75-1d	64	0.15
S75-3d	47	0.13
S25-5d	45	0.12
S25-7d	61	0.15

3. FTIR

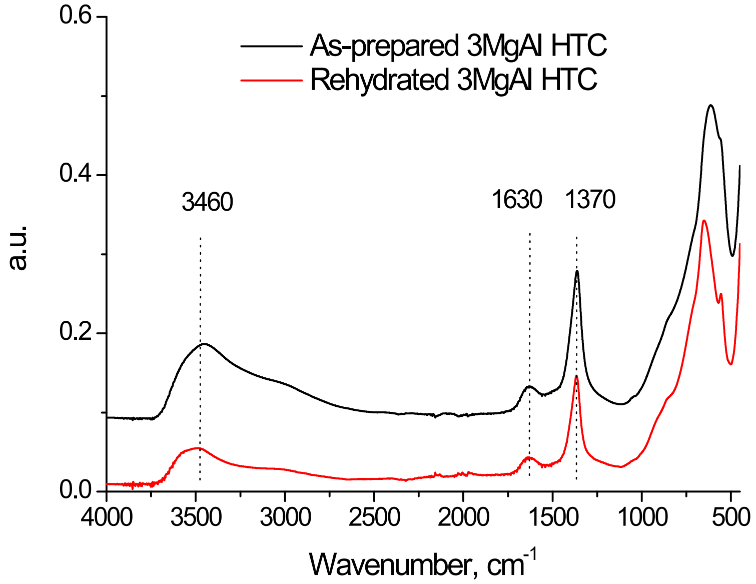


Fig. 3S. The FTIR spectrum of a conventionally prepared 3MgAl HTC sample.

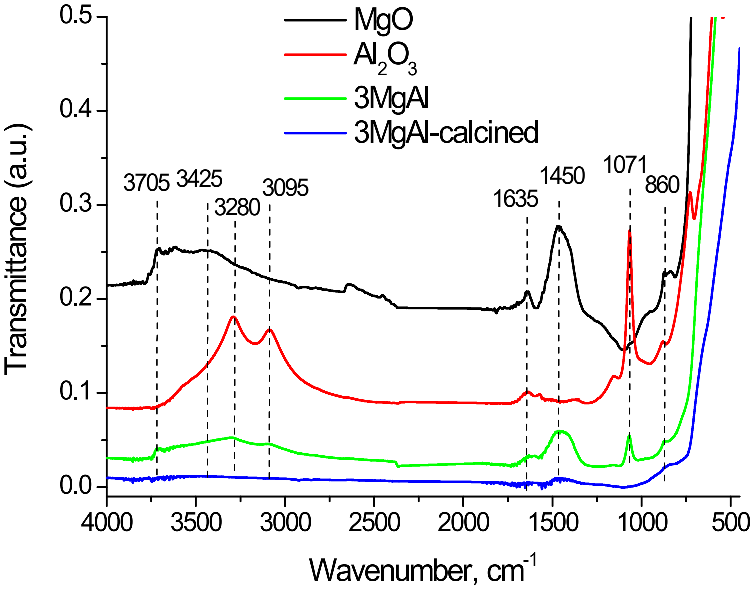


Fig. 4S. The FTIR spectra of starting MgO and Al_2O_3 components and their physical mixture (Mg/Al=3) before and after calcination at T=450 °C.

FTIR spectrum of MgO was consistent with data reported for similar materials.[5-7] The peaks between 431 cm^{-1} to 1080 cm^{-1} were assigned to Mg-O stretching vibrations.[8,9] It was reported earlier[10] that both H_2O and CO_2 molecules are easily chemisorbed onto MgO surface when exposed to open air. Indeed, for the absorbed water molecules, the peak of the O-H vibration was observed at 3420 cm^{-1}, but the small intensity of this FTIR band suggested that the surface of the commercial MgO sample was hydroxylated scarcely. In contrast, the FTIR spectrum of MgO evidenced presence of a broad band at around 1430-1460 cm^{-1} characteristic for CO_3^{2-} anions due to the interaction of the MgO surface with CO_2 from air.[6,7] Additionally, a small peak at 3700 cm^{-1} could be characteristic of residual surface Mg-OH groups in the MgO sample.[6,11]

FTIR spectrum of the commercial Al source with boehmite structure was also in accordance with results obtained for similar materials. It showed two distinct stretching vibrations from (O)Al-OH at 3270-3280 and 3075-3100 cm^{-1}.[12,13] An intense band at 1071 cm^{-1} and a shoulder at 1150 cm^{-1} were assigned to the symmetric and asymmetric bending modes of the (Al)O-H groups respectively.[12] The FTIR spectrum of the MgO+Al_2O_3 mixture represented the superposition of the signals observed in the FTIR spectra of the individual oxides. Accordingly, the calcination of the mixture resulted in the decomposition of surface OH groups and the removal of surface water molecules what was reflected in a loss in the intensity of the FTIR signals. Nevertheless, a small band in the range of 1420-1460 cm^{-1} attributed to CO_3^{2-} groups was still observed in the spectra of calcined MgO+Al_2O_3 sample what was in accordance with a previous result.[6]

4. SEM

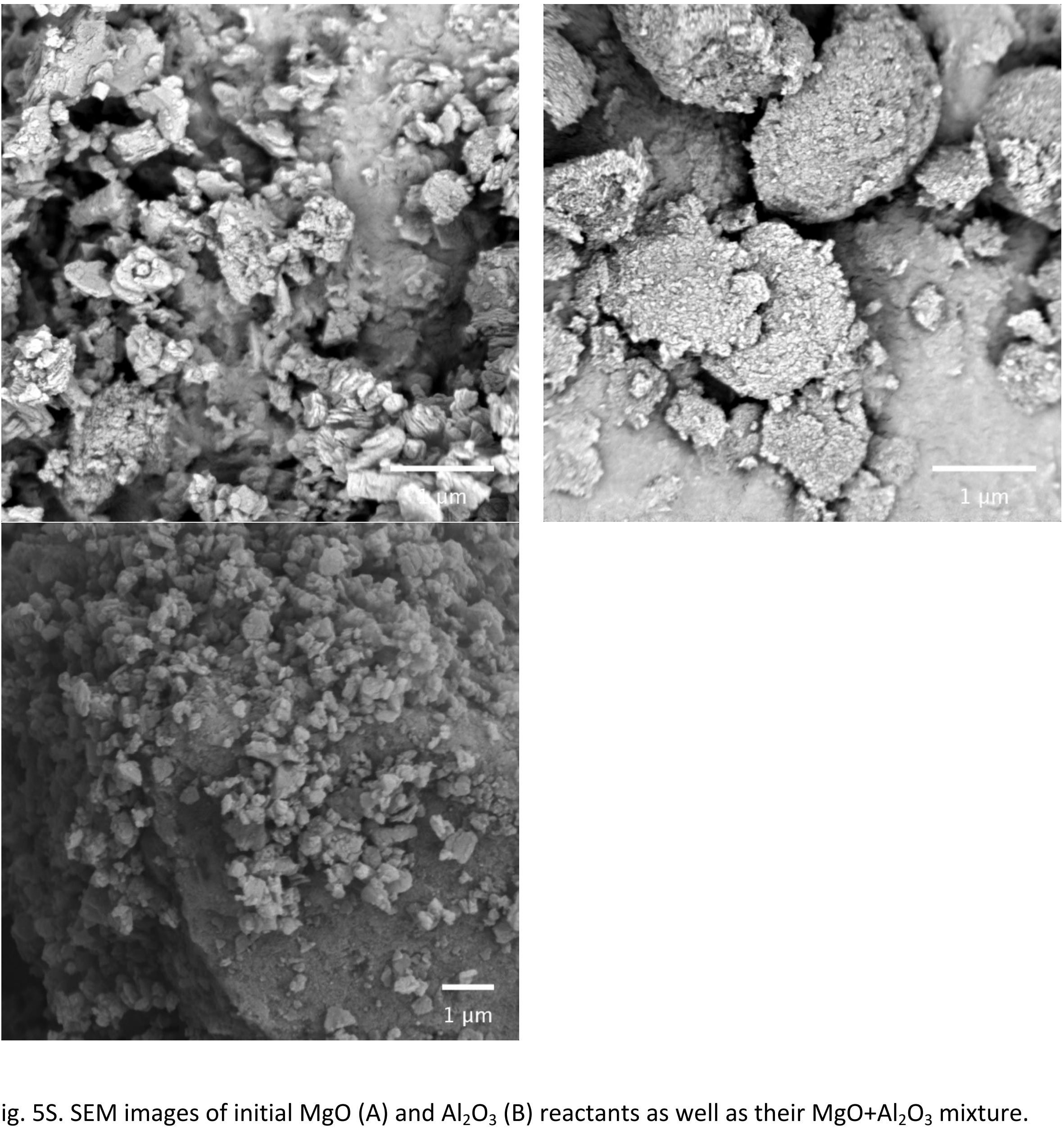


Fig. 5S. SEM images of initial MgO (A) and Al_2O_3 (B) reactants as well as their MgO+Al_2O_3 mixture.

5. TEM

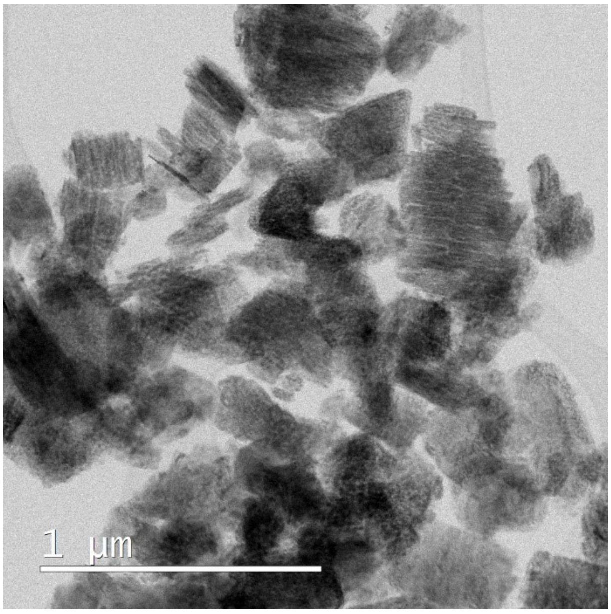
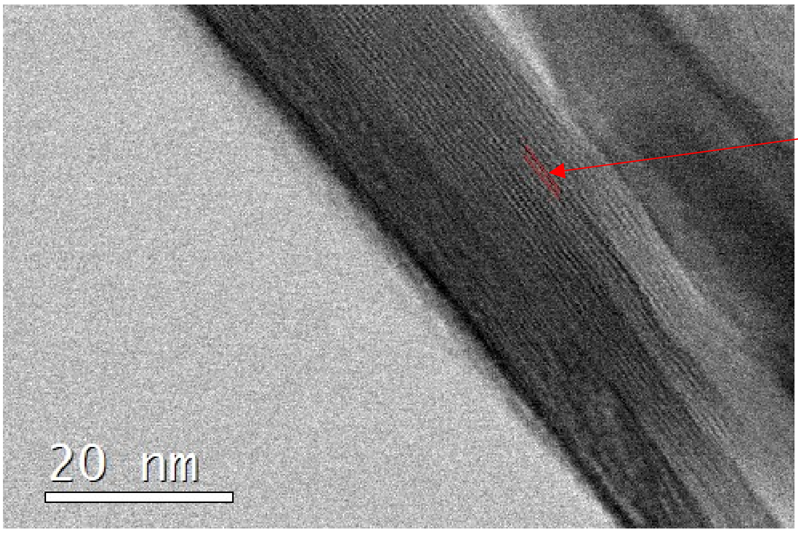
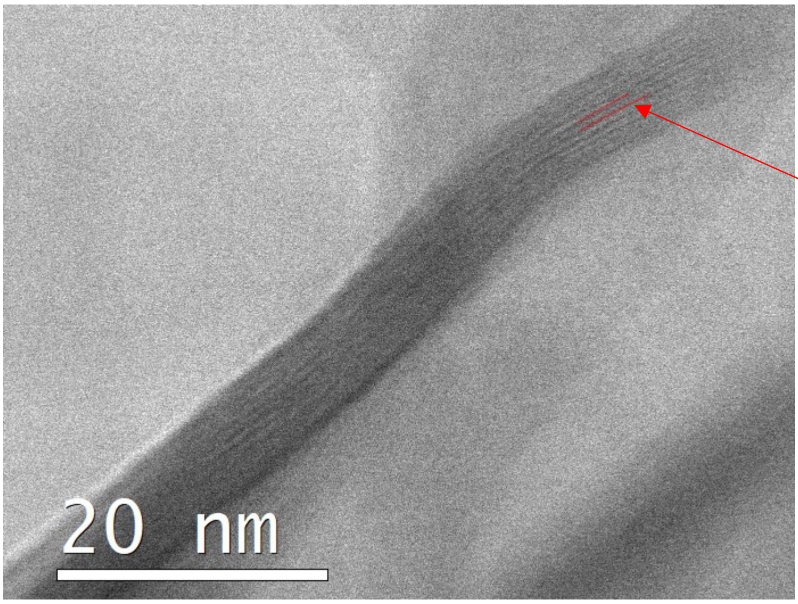


Fig. 6S. TEM image of initial $MgO+Al_2O_3$ mixture.



interlayer spacing ≈0.5 nm



interlayer spacing ≈0.8 nm

Fig. 7S. The different TEM images of S75-2h sample. The images allow suggesting that both LDH phase (interlayer spacing ca. 0.8 nm) and $Mg(OH)_2$ (interlayer spacing ca. 0.5 nm) could be present in the samples prepared by the hydration of $MgO+Al_2O_3$ physical mixture.

6. Catalysis

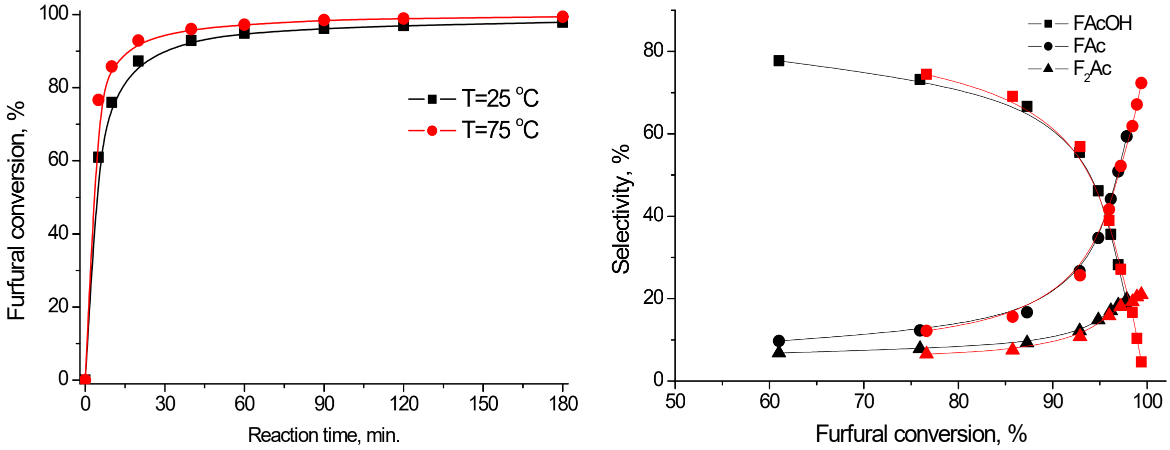


Fig. 8S. A). The dependence of furfural conversion on reaction time observed for rehydrated catalysts prepared from a conventional 3MgAl HTC. The mass of 3MgAl mixed oxide taken for a rehydration step = 0.9g, rehydration temperature – 25 °C and 75 °C, rehydration time – 20 minutes. Reaction conditions: $T_{reac.}$=25 °C, Furfural mass =11.6g, Acetone mass=39 g, F:Ac=1:5 (mol.), RPM – 250. B). Selectivity to reaction products. Black color – $T_{reh.}$=25 °C, red color - $T_{reh.}$=75 °C.

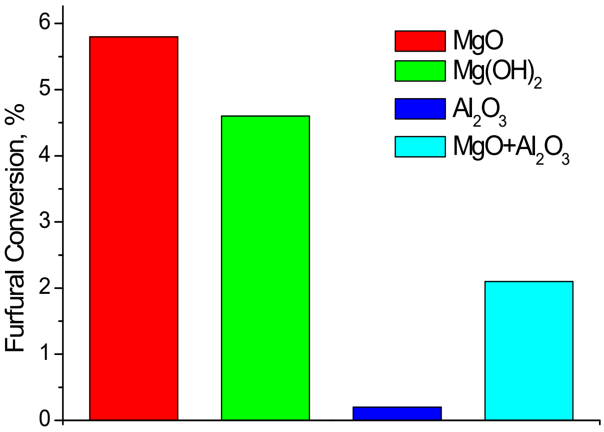


Fig. 9S. Furfural conversion observed over MgO, Al_2O_3 and their mixture (atomic ratio Mg/Al=3). Reaction conditions: catalyst mass - 0.9g, $T_{reac.}$=25 °C, $t_{reac.}$=180 min., Furfural mass =11.6g, Acetone mass=39 g; F:Ac=1:5 (mol.), RPM – 250.

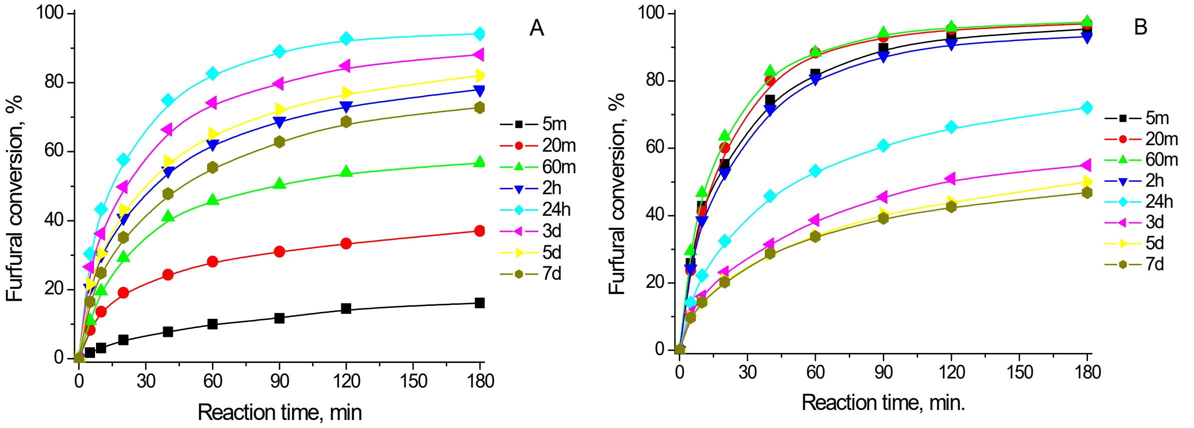


Fig. 10S. The change of furfural conversion on reaction time observed over MgAl samples hydrated for 5 minutes to 7 days at T=25 °C (A) and 75 °C (B). Reaction conditions: $T_{reac.}$=25 °C, Furfural mass =11.6g, Acetone mass=39 g, F:Ac=1:5 (mol.), RPM – 250.

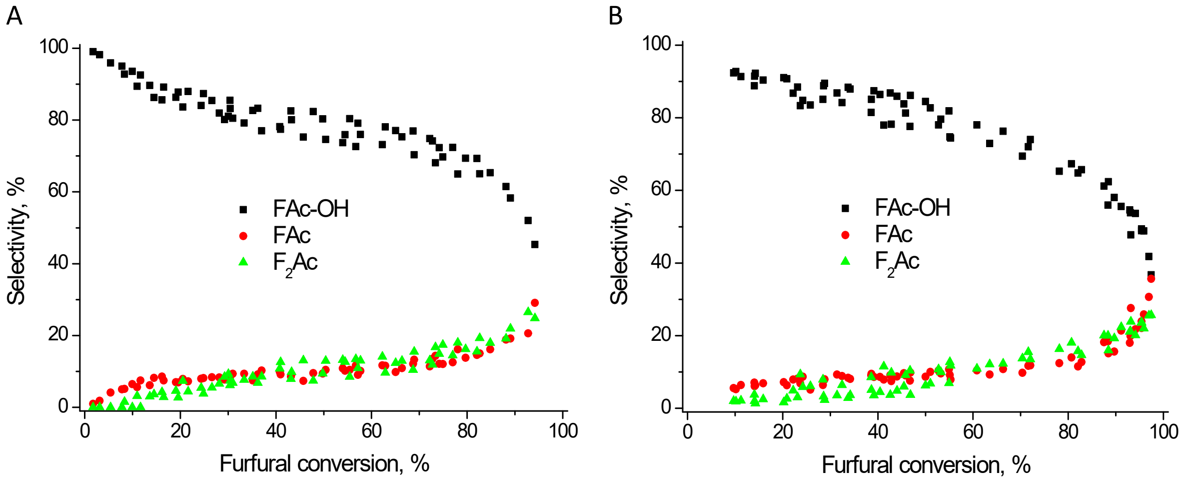


Fig. 11S. Combined results on selectivity to reaction products observed over MgAl catalysts hydrated at T=25 °C (A) and T=75 °C (B).

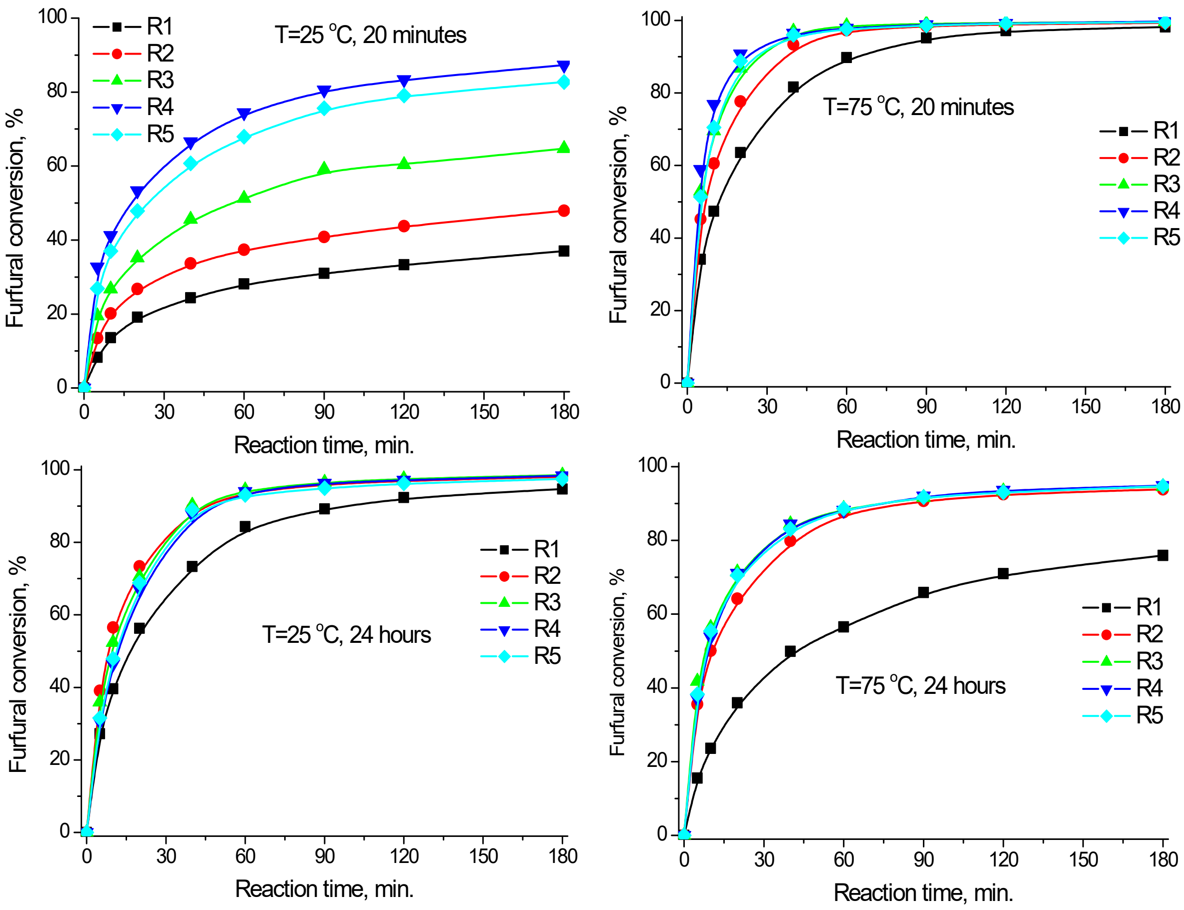


Fig. 12S. The performance of differently hydrated catalysts in repeating (hydration-reaction-calcination) cycles.

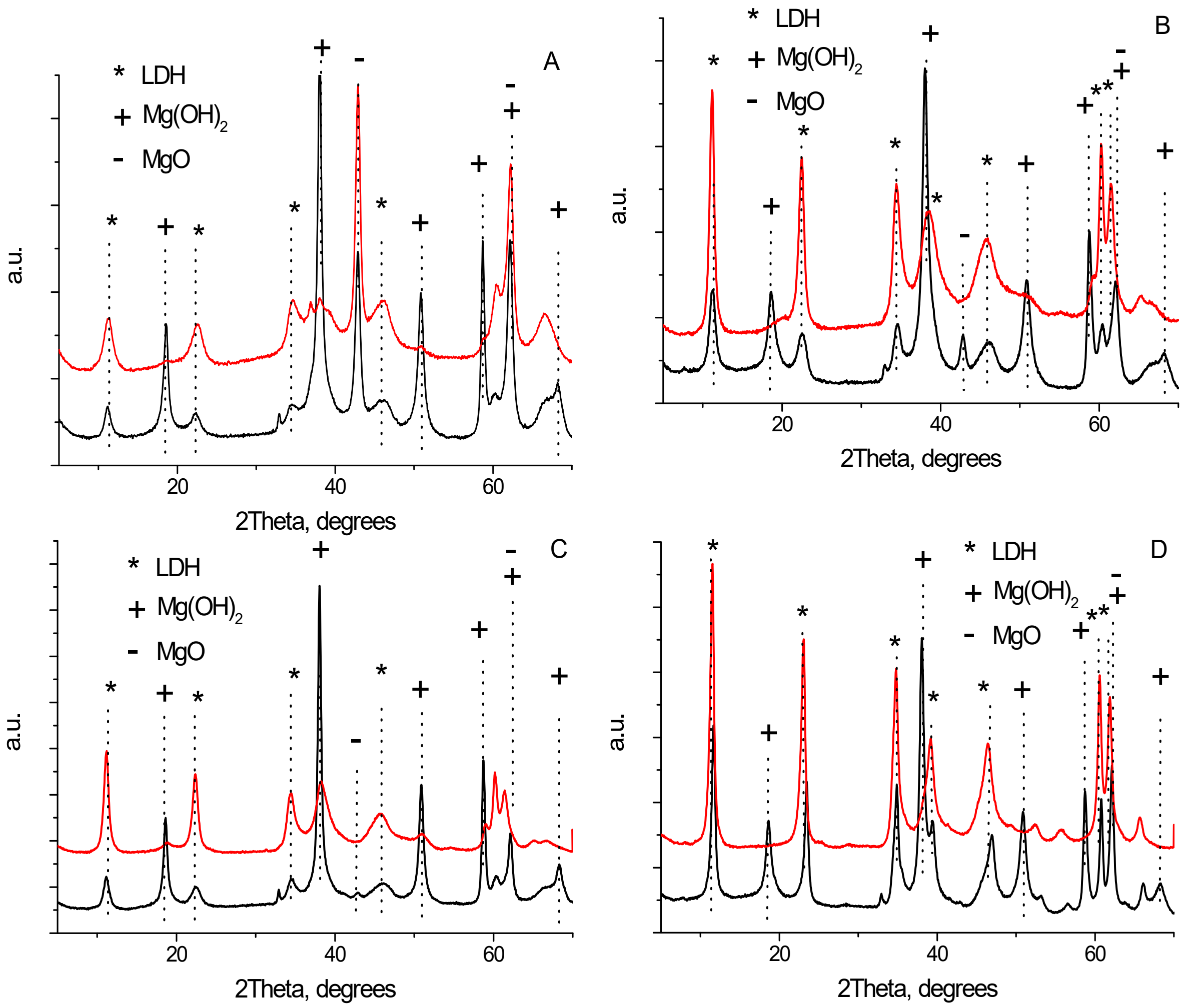


Fig. 13S. The XRD patterns of hydrated MgAl samples after the first (black) and the sixth (red) hydration steps. A). S25-20m-Rm series; B). S75-20m-Rm series; C). S25-24h-Rm series; D). S75-24h-Rm series.

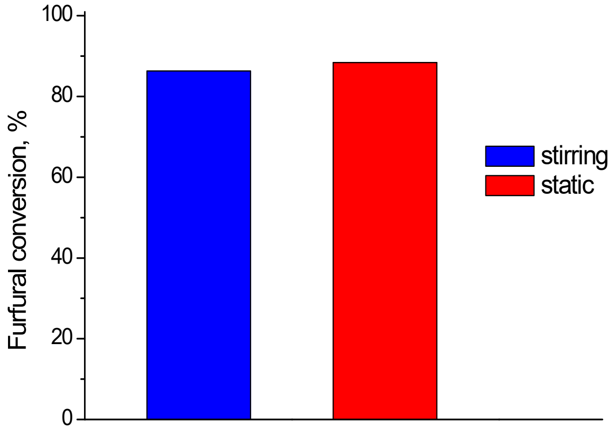


Fig. 14S. The catalytic performance of hydrated samples prepared at stirring and static modes. Hydration T = 75 °C, time - 20 minutes. Furfural conversion after 60 minutes.

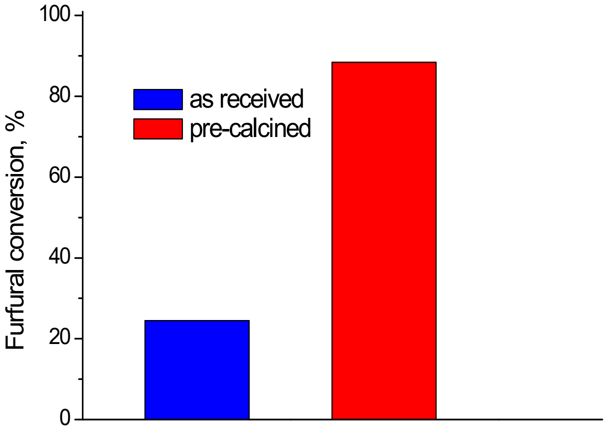


Fig. 15S. The effect of a pre-calcination step before the hydration of the $MgO+Al_2O_3$ mixture on the performance of resulting samples. Hydration T = 75 °C, time - 20 minutes. Furfural conversion after 60 minutes.

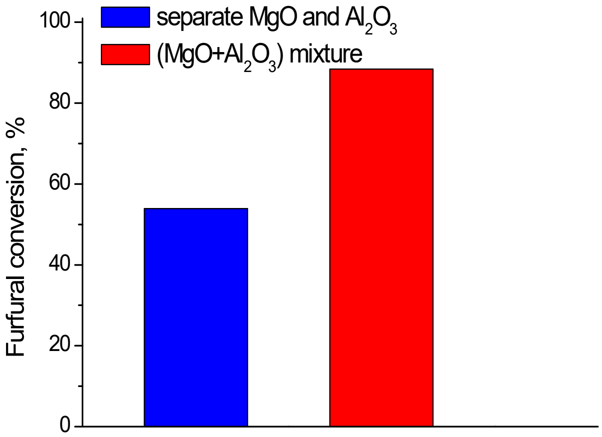


Fig. 16S. The effect of mixing the components of the $MgO+Al_2O_3$ mixture on the performance of resulting samples. Hydration T = 75 °C, time - 20 minutes. Furfural conversion after 60 minutes.

References

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