

## Supplementary Information

### **Magnetic ZSM-5 zeolite: a selective catalyst for the valorization of furfuryl alcohol to $\gamma$ -valerolactone, alkyl levulinates or levulinic acid**

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**General Methods.** All solvents were dried prior to use by standard procedures. Reagents were purchased at the highest commercial quality and used without further purification. The particle size and morphological studies of the Fe<sub>3</sub>O<sub>4</sub> microspheres and the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-HZSM-5 catalyst were performed by TEM. Transmission Electron Microscopy (TEM) analysis was accomplished using JEOL JEM 2010F at 160kV of accelerating voltage. Microscopic images were obtained by HRTEM TITAN 60-300 with X-FEG type emission gun, operating at 80 kV. This microscope is equipped with Cs image corrector and a STEM high-angle annular dark-field detector (HAADF). The point resolution is 0.06 nm in HRTEM mode. The elemental mappings were obtained by STEM-Energy Dispersive X-ray Spectroscopy (EDS) with acquisition time of 20 min. For HRTEM analyses, the powder samples were dispersed in ethanol and 5 min ultrasonicated. One drop of this solution was placed on a copper grid with holey carbon film. The sample was dried at room temperature. For the statistical particle count, the SEM image of the sample was obtained in a field emission scanning electron microscope FESEM, FEI Nova-Nano SEM-600, The Netherlands.

X-ray diffraction patterns were recorded with a PANalytical X'Pert PRO MPD (PANalytical, Netherlands) diffractometer in the Bragg-Brentano geometry, Co-K $\alpha$  radiation (40 kV, 30 mA,  $\lambda = 0.1789$  nm) equipped with an X'Celerator detector and programmable divergence and diffracted beam anti-scatter slits. The measurement range was  $2\theta:5^\circ - 105^\circ$  with a step size of  $0.017^\circ$ . The identification of crystalline phases was performed using the High Score Plus software (PANalytical) that includes the PDF-4+ database.

The experimental content of aluminum and silicon were determined by x-ray fluorescence (XRF) in a Shimadzu RayNY EDS-720 X-ray spectrometer equipped with an X-ray tube (Rh target) with a 5-50 KV tube voltage and tube current in the range of 1 to 1000  $\mu$ A, a Si(Li) solid state detector with energy resolution of 165 eV at 5.96 KeV K $\alpha$  Mn line cooled with liquid nitrogen. The sample was irradiated in a 3mm<sup>2</sup> spot size under vacuum of  $\sim 10^{-6}$  torr.

Samples were analyzed using an Agilent 6820 gas chromatograph equipped with an Agilent DB-5 capillary column (30 m x 0.32 mm, 0.5  $\mu$ m) under the operation parameters:

temperature of inlet of 100 °C, temperature of flame ionization detector of 250 °C, temperature ramp of the oven from 100 to 250 °C at a rate of 10 °C min<sup>-1</sup>.

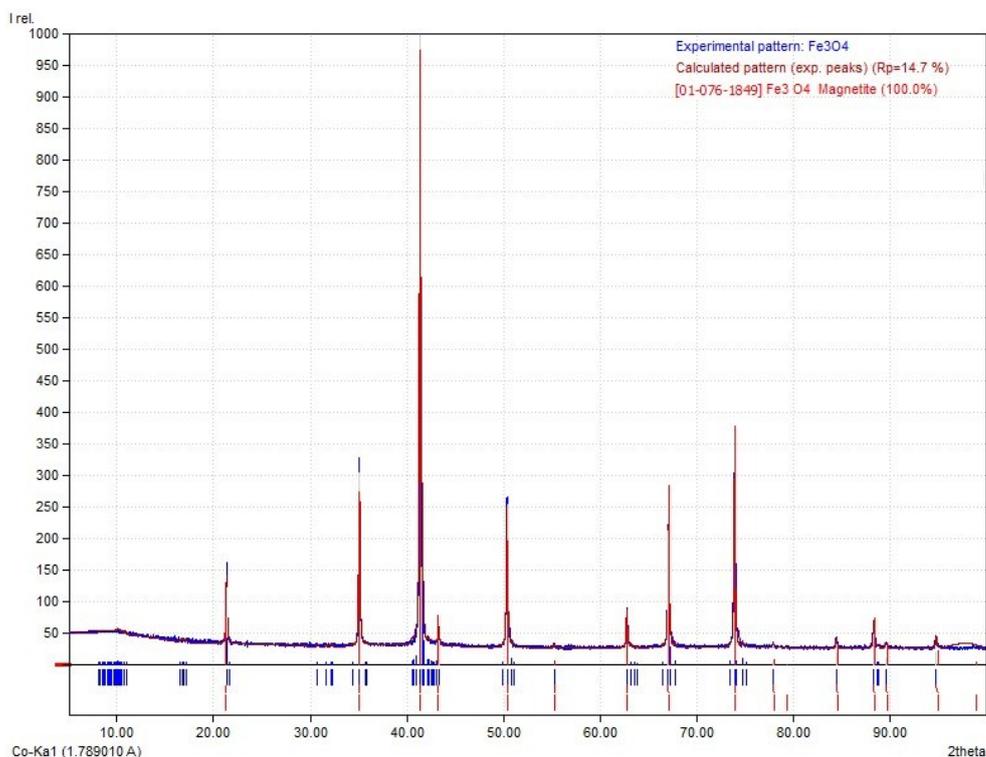
TPD measurements were conducted in a Micromeritics Autochem II 2920 Chemisorption Analyzer equipment with a TCD (Thermal Conductivity Detector) detector. For this, 50 mg of the sample were pre-treated thermally under 30 mL.min<sup>-1</sup> helium flow at a heating rate of 10 °C min<sup>-1</sup> until 600 °C and kept at this temperature for 30 minutes. After this period, the reactor was cooled to 120 °C, and the He flow was kept for 60 minutes. Next, the adsorption of ammonia was performed through the passing of a 15% mixture of NH<sub>3</sub> in He for 30 minutes over the sample. After saturation, the sample was purged with He for 1 hour to remove the excess of ammonia. Finally, the temperature desorption was initiated under a 30 mL min<sup>-1</sup> He flow in a 15 °C min<sup>-1</sup> heating rate until 600 °C. To quantify the acid sites, the area under the curve of the graph of TCD signal x temperature was calculated.

The infrared spectrum of adsorbed pyridine was recorded on a Fourier Transform Infrared spectrophotometer model Prestigi-21 in the range of 1800–1400 cm<sup>-1</sup> wavenumber. For the qualitative acidity determination, 50 mg of sample were subjected to a heat treatment in a tubular furnace at 300 °C and 100 mL min<sup>-1</sup> N<sub>2</sub> flow for 1 h. Gaseous pyridine was then adsorbed on the samples for 1 h at 150 °C with a N<sub>2</sub> gas carrier flow at 100 mL min<sup>-1</sup>. Next, the N<sub>2</sub> flow was kept constant for 1 h at 150 °C for the removal of the physically adsorbed pyridine.

The transmission <sup>57</sup>Fe Mössbauer spectra were recorded employing a Mössbauer spectrometer operating at a constant acceleration mode and equipped with 50 mCi <sup>57</sup>Co(Rh) source. For fitting the collected <sup>57</sup>Fe Mössbauer spectrum, the MossWinn software program was used;<sup>1</sup> prior to fitting, the signal-to-noise ratio was enhanced employing the routines incorporated into MossWinn software program and the statistical procedure developed by Prochazka et al.<sup>2</sup> The isomer shift values were referred to α-Fe at room temperature.

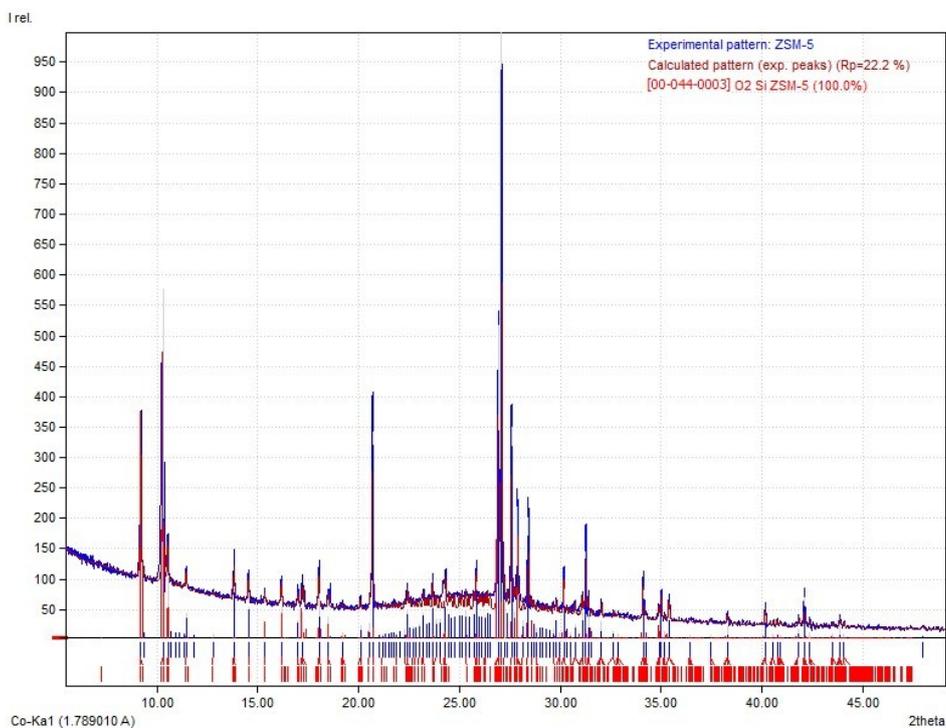
ICP-OES measurements were conducted in a Thermo Fisher Scientific, iCAP 6300 Duo, with a CID (Charge Injection Device) detector.

**Characterization of the magnetite microspheres and the magnetically recoverable catalyst.** The x-ray diffractogram used to calculate the average crystallite size through



Scherrer's equation is depicted in Figure S1 (blue line), as well as the data from JCPDS card number 01-076-1849 (red line). Likewise, the experimental data of the x-ray diffractogram of the ZSM-5 zeolite and that of JCPDS card number 00-044-0003 are depicted in Figure S2.

**Figure S1** Experimental x-ray diffractogram of Fe<sub>3</sub>O<sub>4</sub> (in blue) and data from JCPDS card number 01-076-1849 (in red).



**Figure S2** Experimental data of the x-ray diffractogram of the ZSM-5 zeolite and the JCPDS card number 00-044-0003.

Figure S3 shows a TEM image in which it is possible to observe the magnetite nanoparticles that form the microspheres. In the image, some of the particles were highlighted in order to facilitate the observation of their size.

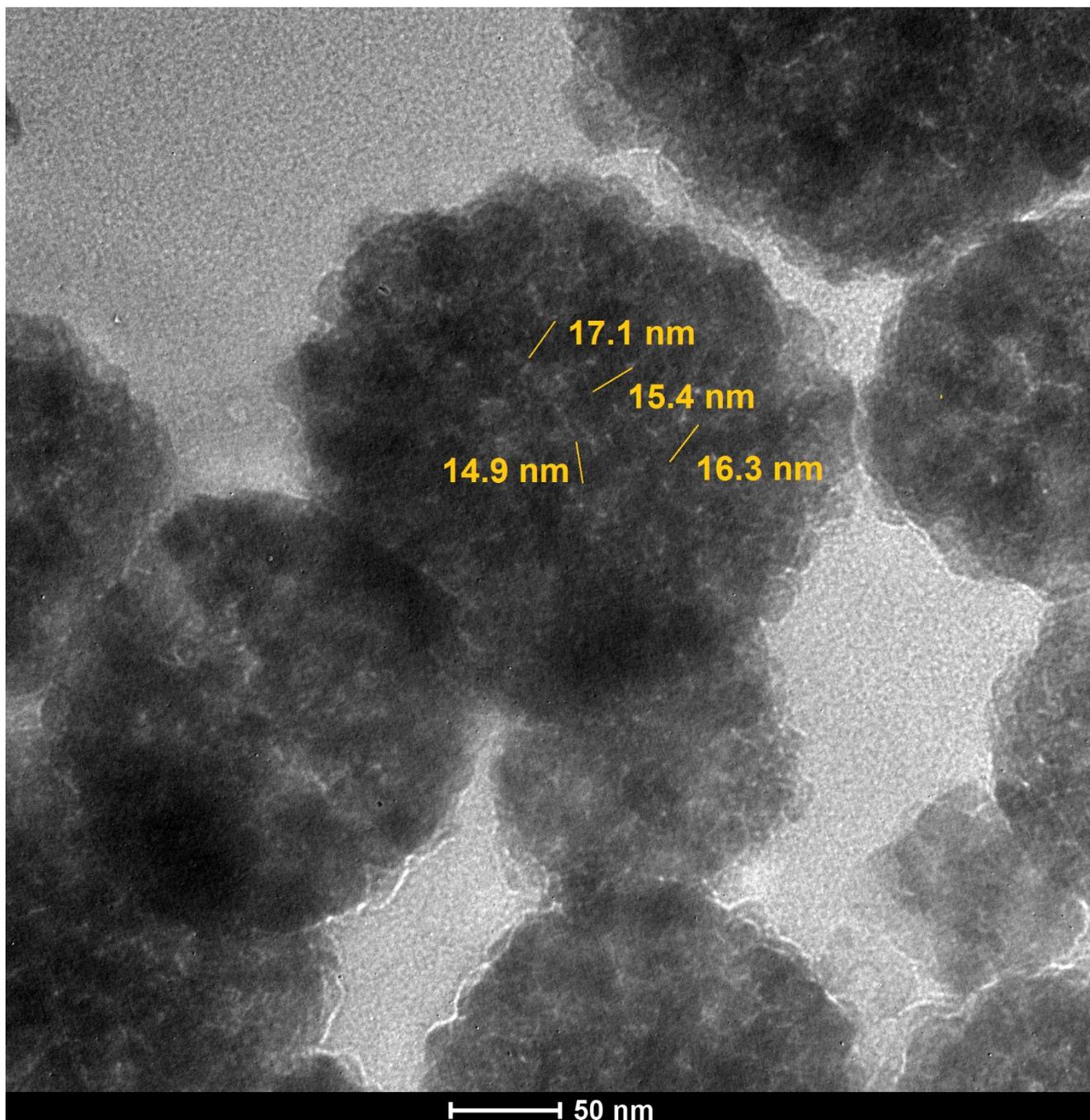


Figure S3. TEM image of the magnetic microspheres.

Figure S4 shows the SEM image used to conduct a statistical particle count, and the particle size distribution was plotted as a histogram (Figure S5).

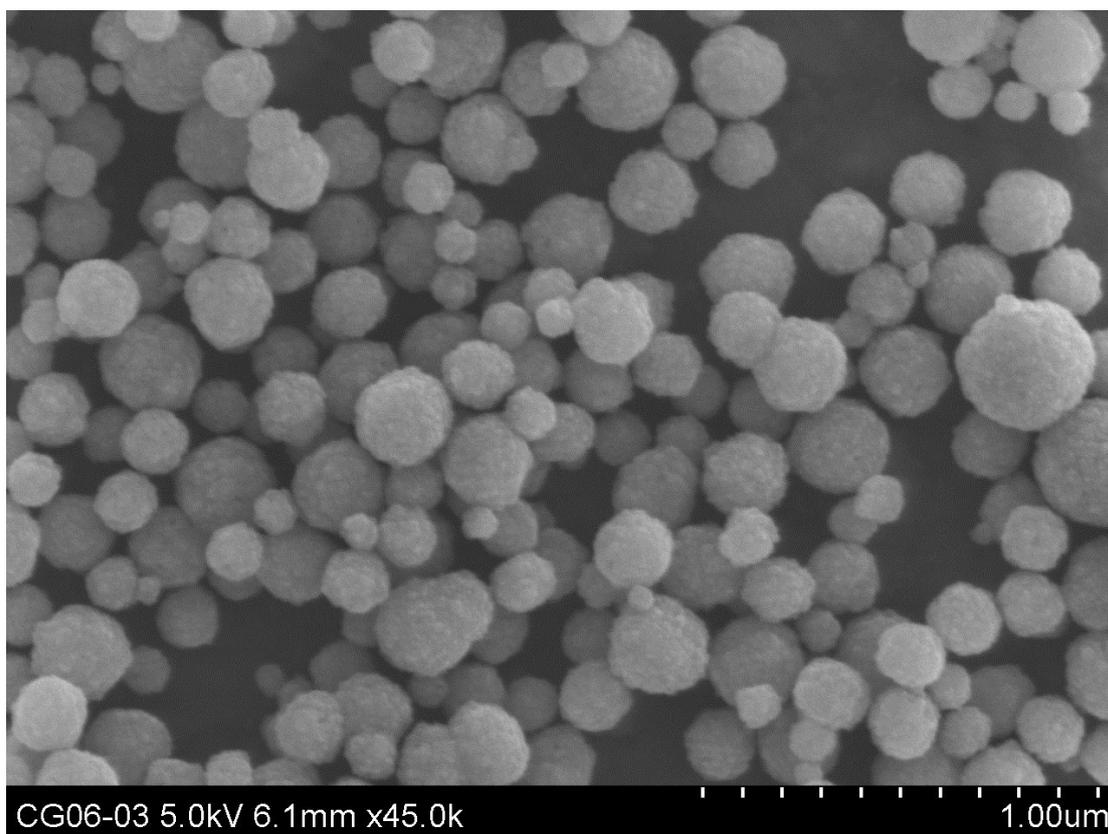
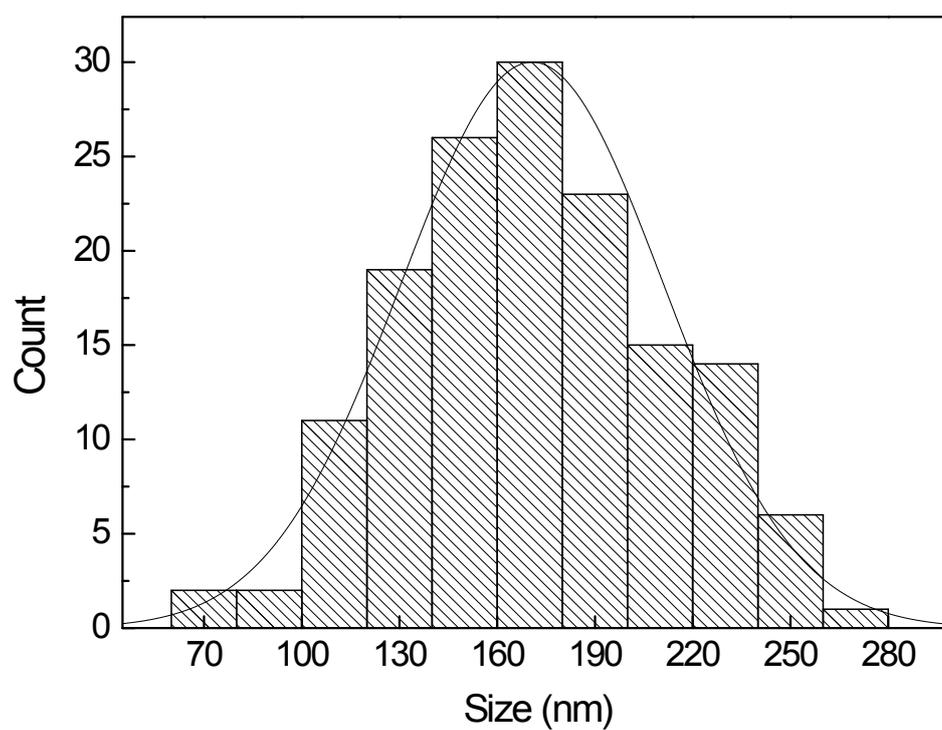
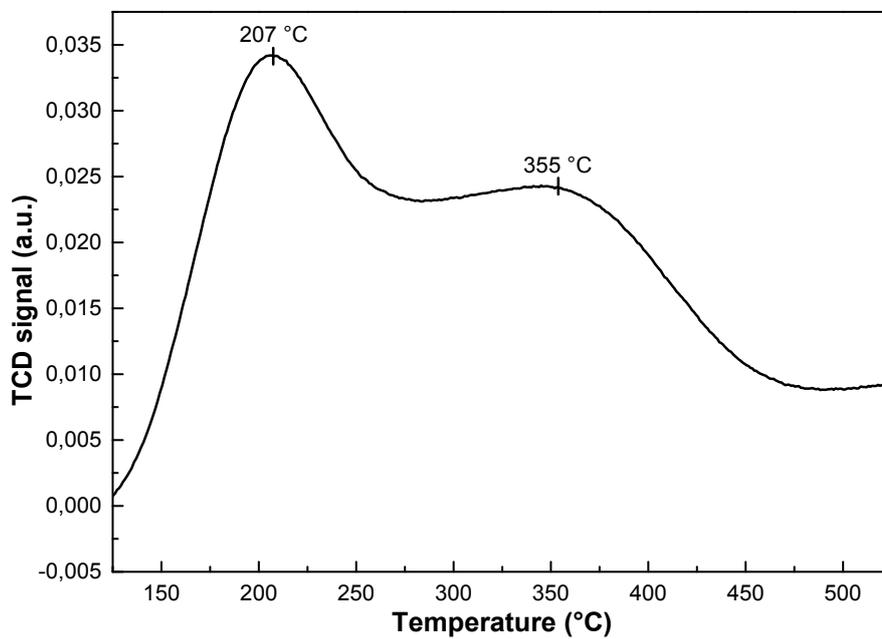


Figure S4 SEM image used in the construction of the size distribution histogram.

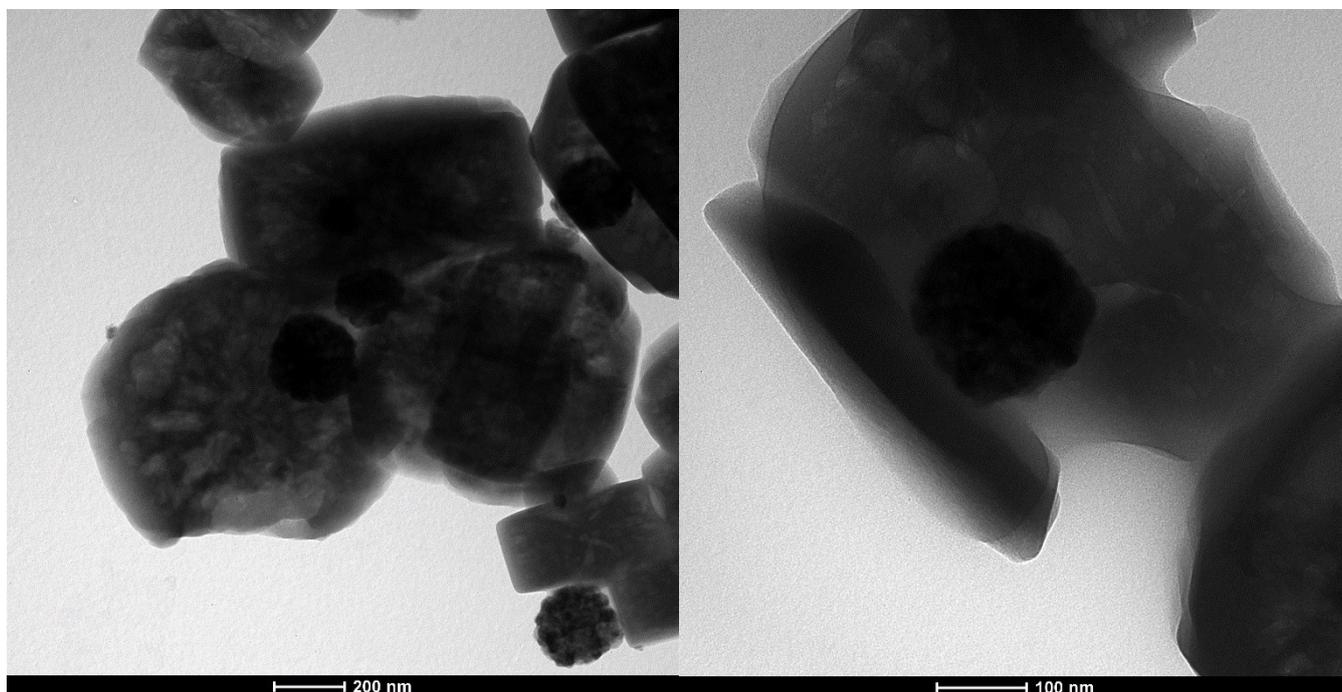


**Figure S5** Histogram showing the size distribution of the particles showed in Figure S4.

The graph showing the temperature programmed desorption of  $\text{NH}_3$  over  $\text{Fe}_3\text{O}_4$ -HZSM-5 is depicted in Figure S6.



**Figure S6** Temperature programmed desorption of  $\text{NH}_3$  over  $\text{Fe}_3\text{O}_4$ -HZSM-5.



**Figure S7** TEM images of the catalyst after the recovery from the reaction medium using a magnetic field.

## References

- 1 Z. Klencsar, E. Kuzmann and Vertes, *A. J. Radioanal. Nucl. Chem.* **1996**, *210*, 105-118.
- 2 R. Prochazka, P. Tucek, J. Tucek, J. Marek, M. Mashlan and Pechousek, *Meas. Sci. Technol.* **2010**, *21*, 025107.