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Supporting Information

Magnetic Zeolites: Novel Nanoreactors Through Radiofrequency Heating

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Experimental Section

Synthesis of magnetic nanoparticles: Nanosized $NiFe_2O_4$ nanoparticles were prepared by the citrate precursor method.[1] Iron (III) nitrate nonahydrate, nickel nitrate hexahydrate, citric acid, ethanol, and ammonia solution (Sigma-Aldrich, ACS grade) were used for the preparation of the starting sol. The metal nitrates were dissolved in ethanol in the required molar ratios. Then a solution of citric acid in ethanol was added into the nitrate solution. The resulting solution was stirred for 4 h. The resulting sol was dried at 353 K to get a dry gel which was milled and calcined in air at 1073 K for 1 h (heating rate of 10 K/min) to produce the corresponding nickel ferrite nanoparticles.

The obtained nanoparticles were redispersed in an ethanol-water (80:20 v/v) solution containing 1 mol/L ammonia and 3 mmol/L cetyltrimethylammonium bromide (Sigma-Aldrich) to prepare a solution with a final concentration of 0.135 mg nanoparticles/mL (Solution A). The titania sol was prepared by dissolution of a tetrabutyltitanate-diethanolamine mixture (80:20 v/v, Sigma-Aldrich) in ethanol. The hydrolysis of the sol was performed by dropwise addition of an ethanol-water solution (90:10 v/v) to the titania sol. The resulting mixture was stirred for 24 h and then left under static conditions for another 24 h. Afterwards it was added dropwise to solution A under vigorous stirring. The obtained solids were centrifuged, washed by ethanol twice and then dried in an oven and calcined under air flow at 673 K for 1 h with a heating rate of 1 K/min. According to the elemental analysis data, the titania loading in the TiO_2-$NiFe_2O_4$ nanoparticles was 6 wt.%.

Synthesis of zeolite-encapsulated magnetic nanoparticles: The as-synthesized nickel ferrite nanoparticles were coated with a layer of ZSM-5 zeolite with a procedure which was adapted from the literature.[2,3] The powdered solid was first dispersed in a 1M aqueous solution of tetrapropylammonium hydroxide (TPA-OH) by sonication for 2.5 minutes with an ultrasound probe (Bandelin Sonoplus GM2200, 200 W) at 40% of output power. In order to use as homogeneous a suspension as possible, the sonicated samples were left standing for 1 day and only the supernatant was used for the synthesis of the core@shell samples. The relative amounts of magnetic nanoparticles and TPA-OH solution were 4575 and 50 milligrams, respectively. Aluminium (III) isopropoxide (gentle heating was applied to facilitate dissolution of the aluminium salt), sodium hydroxide, distilled water and tetraethylorthosilicate (TEOS) were added to the magnetic nanoparticle suspension to yield a clear precursor solution (with a brownish colour arising from the presence of the ferrite nanoparticles). Sonication was applied for 2.5 minutes at 40% output power after the addition of the aluminium precursor and again after the silica precursor addition. The resulting zeolite precursor solution had the composition: 1 Al_2O_3:50 SiO_2: 990 H_2O:18 TPA-OH: 0.32 NaOH. This solution was then transferred to a Teflon-lined stainless steel autoclave and hydrothermal synthesis was performed in a convection oven at 438 K for 5 days. The hydrothermal treatment was performed both under static and dynamic conditions. In the former, the autoclaves were left standing in the oven, whereas in the latter the autoclaves were rotated inside the oven at a speed of 20 revolutions/minute in order to ensure a homogeneous crystallization of the zeolite around the ferrite nanoparticles. The as-synthesized samples were filtered, washed with abundant distilled water, and dried in an oven at 333 K overnight. The samples were calcined at 723 K for 12 hours.

Characterization: The samples prepared in this study were characterized by transmission electron microscopy (TEM) using a JEOL JEM-120 microscope. The composition of the magnetic nanoparticles was measured by Energy Dispersive Spectroscopy (EDS) coupled to the TEM equipment (OXFORD instruments model INCA energy TEM100). The external morphology of the samples was also analyzed by field emission scanning electron microscopy (FE-SEM, Merlin VP Zeiss) in order to assess the quality and extent of the zeolite coating around the ferrite nanoparticles. The N_2 adsorption isotherms were obtained at 77 K using an ASAP2020 apparatus (Micromeritics). The magnetization curves were recorded at 293 K with a vibrating sample magnetometer (Oxford Instruments). The X-ray diffraction patterns were obtained in the 10-80º 2θ range at a rate of 0.02º min^{-1} with a diffractometer (Pan Analytical Empyrean). The specific absorption rate under Radiofrequency (RF) heating was determined using a 1 kW induction heating system operated at 300 kHz (Ambrell EasyHeat®).

The catalytic activity in the isomerization of citronellal was measured in a quartz reactor (i.d. 9.5 mm). The reactor was placed inside a 6-turn induction coil connected to the 300 kHz induction heating system. The gas and liquid flows were fed in co-current mode from the top. A solution of citronellal (40-80 mM) in 1,4-dioxane was fed to the reactor with an HPLC pump (Shimazdu LC-20AT, liquid flow rate 0.1 mL/min). A He flow of 3.0 ml/min (STP) was fed with a mass flow controller (Brooks). The gas flow provides a more uniform distribution of the liquid and prevents bed densification which improves hydrodynamics in the reactor as demonstrated in our previous work.[4,5].

Prior to the assembly of the structured reactor, the magnetic core@shell particles were purified applying a high-power magnet to a suspension of the powdered solid in water. This was done in order to ensure that the catalyst bed was composed of magnetic ferrite@zeolite particles. A bed of glass beads mixed with magnetic particles of nickel ferrite was placed at the initial section of the catalyst bed to provide uniform flow distribution and preheat the reaction mixture to the desired temperature. In order to maintain an isothermal temperature profile inside the reactor, the catalyst bed was placed between two beds of nickel ferrite particles as this configuration was found to be efficient in maintaining isothermal conditions, as reported in our previous work.[5,6] Based on these studies, the configuration of the catalyst bed was chosen so that the volumetric heating rate was equal to the rate of heat loss to the environment via conduction and convection. This allowed a near isothermal condition in the entire catalytic bed to be maintained. The structured bed (nickel ferrite/catalyst/nickel ferrite) was kept in the middle part of the reactor with two porous polyether ether ketone (PEEK) plates. The movable optical fibre temperature sensor (FISO FPI HR) was placed inside a thin glass well along the centre line of the catalyst bed to monitor the bed temperature. The temperature of the reactor was controlled within 0.5 K with a LabVIEW software. The reaction products were analysed on a gas chromatograph (Shimadzu GC-2010) equipped with a CP-Sil column and a Flame Ionization Detector (FID) detector.

1. P. Gao, X. Hua, V. Degirmenci, D. Rooney, M. Khraisheh, R. Pollard, R.M. Bowman, E.V. Rebrov, *J. Magn. Magn. Mater.,* 2013, **348**, 44.
2. E.G. Derouane, *J. Molec. Catal. A,* 1998, **134**, 29.
3. B.J. Schoeman, J. Sterte, J.-E. Otterstedt, *Zeolites,* 1994, **14**, 110.

4. J. García-Aguilar, I. Miguel-García, Á. Berenguer-Murcia, D. Cazorla-Amorós, *ACS Appl. Mater. Interfaces,* 2014, **6**, 22506.
5. J. Fernandez, S. Chatterjee, V. Degirmenci, E.V. Rebrov, *Green Process. Synth.,* 2015, **4**, 343.
6. S. Chatterjee, V. Degirmenci,, F. Aiouache, E.V. Rebrov, *Chem. Eng. J.* 2015 ,**243**, 225.

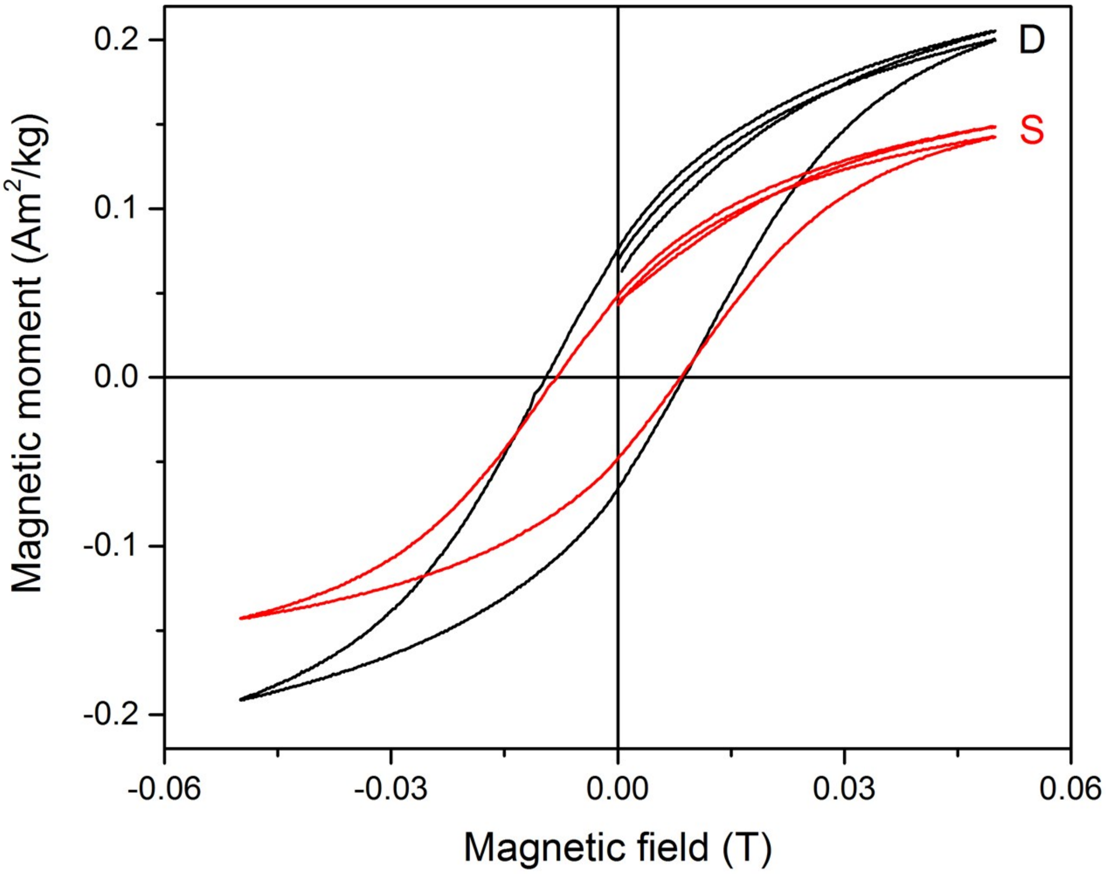

Figure S1. Magnetization versus field curves for magnetic zeolite samples. D-Dynamic, S-Static.

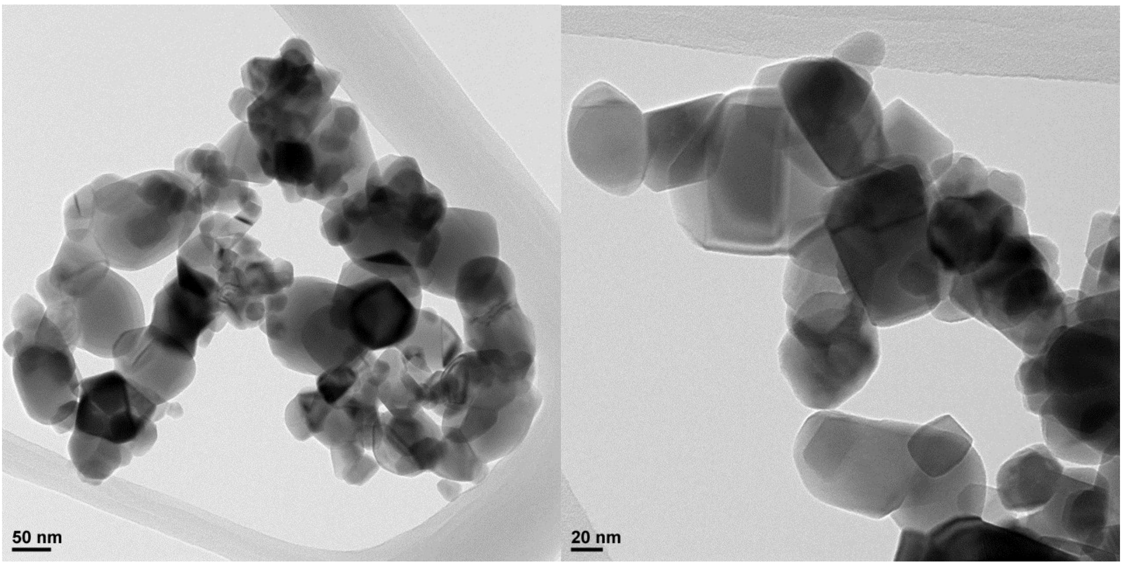

Figure S2. TEM micrographs TiO_2-coated ferrite nanoparticles synthetized in this study.

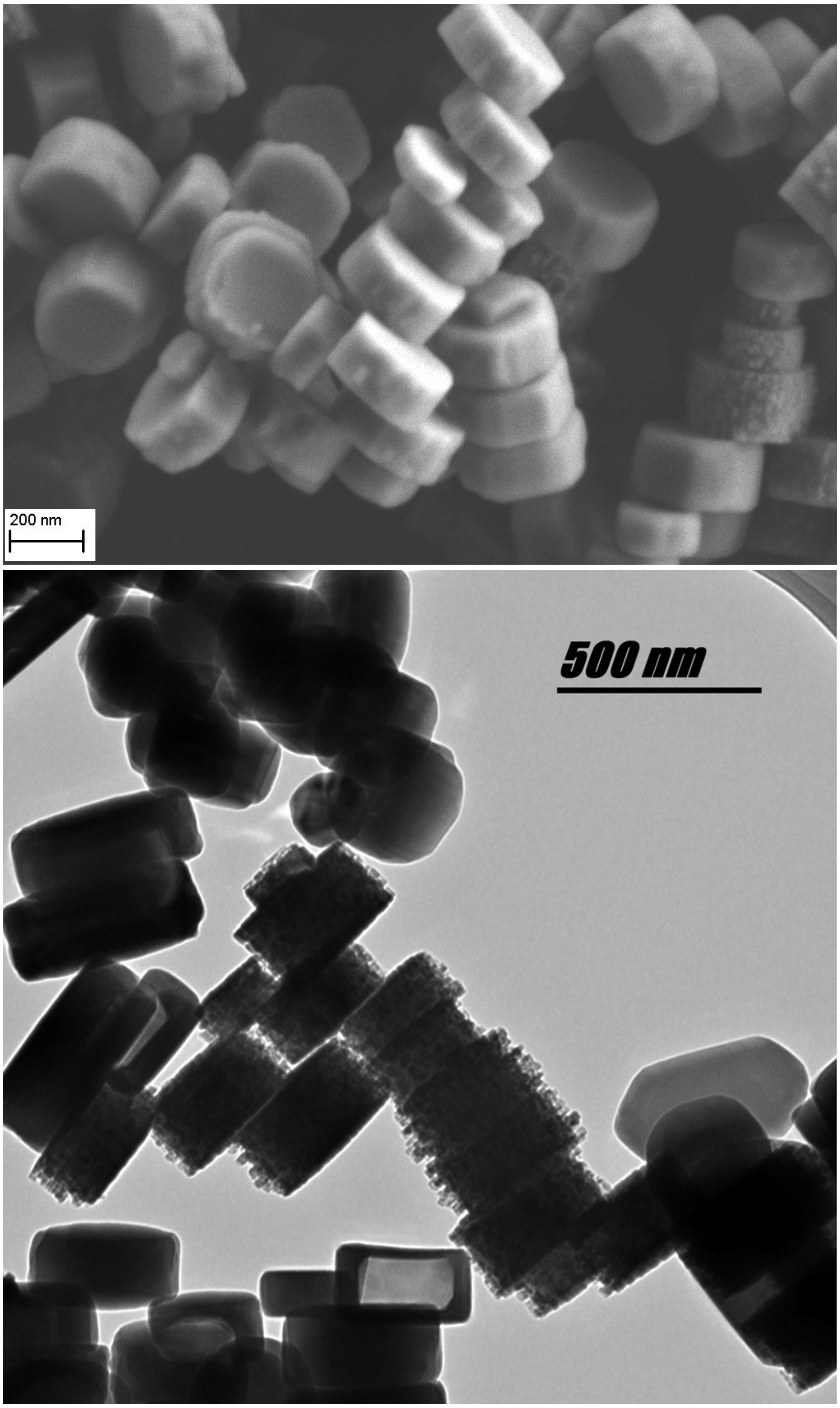

Figure S3. FE-SEM (top) and TEM (bottom) pictures of the ferrite@zeolite nanoparticles synthetized under static conditions at 438 K for 5 days.

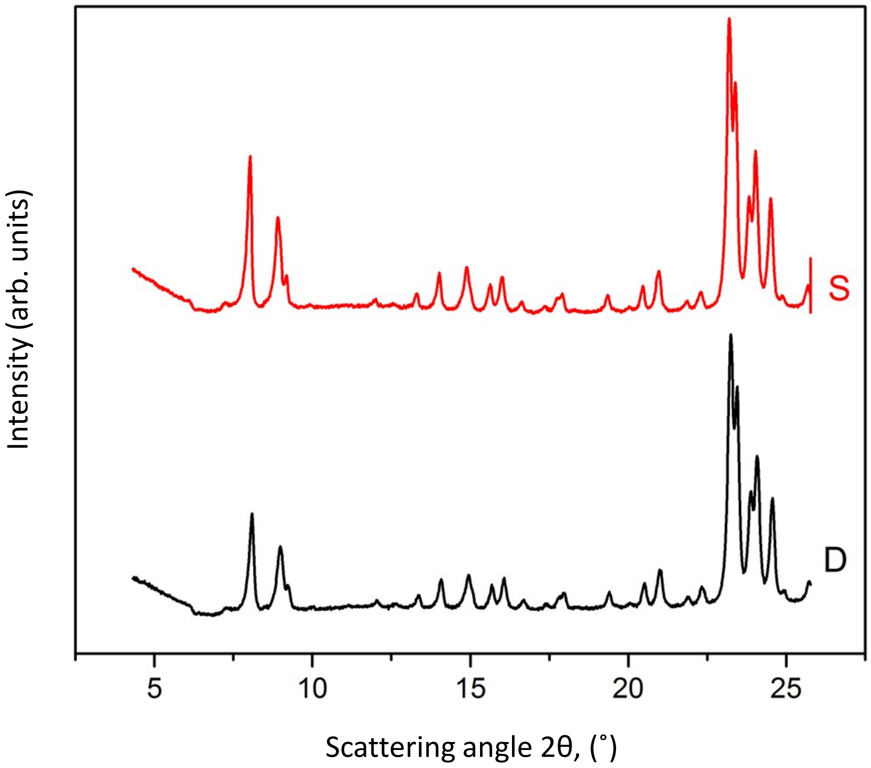

Figure S4. Powder x-ray diffraction patterns of magnetic zeolite. D-Dynamic, S-Static.

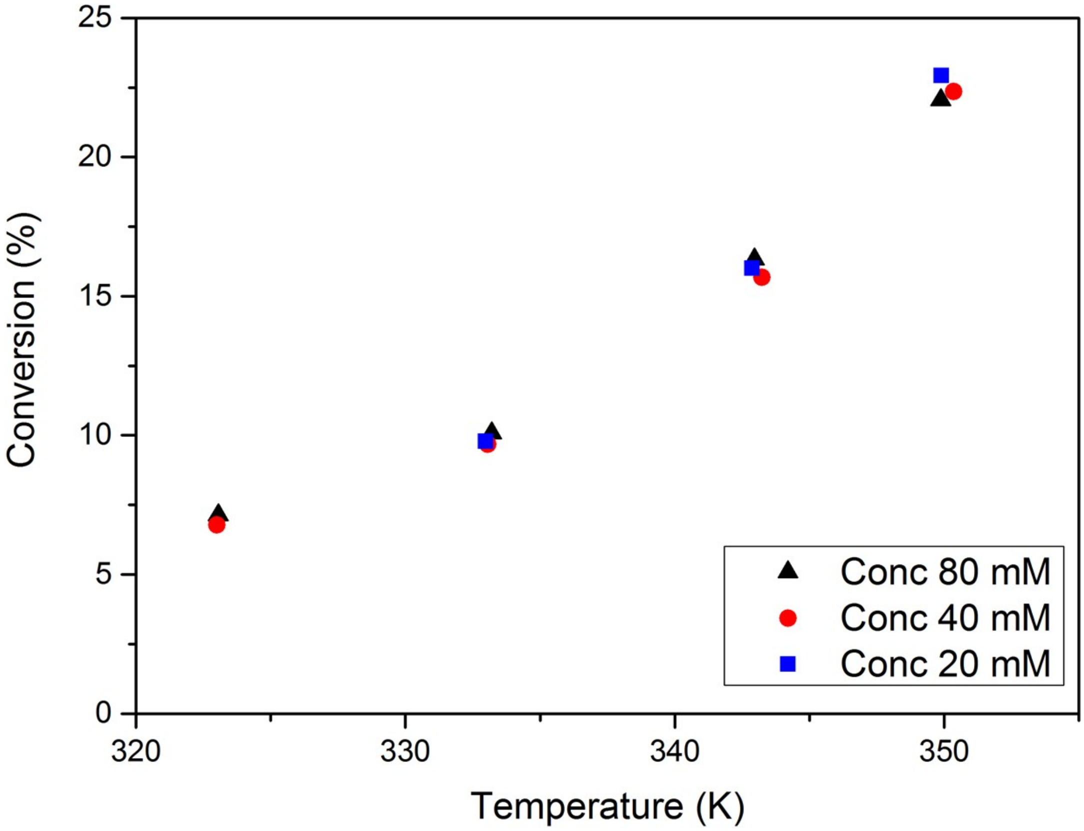

Figure S5. Light-off curves for citronellal isomerisation. Catalyst weight: 82.2 mg. Liquid flow rate: 0.1 ml/min. Gas flow rate: 3.0 ml/min (STP).

Table S1. Surface area and pore volume obtained for the samples presented in this study from their respective N_2 adsorption isotherms at 77 K.

Sample	A_{BET}[m^2/g]	V_{pores}* [cm^3/g]
Static	310	0.14
Dynamic	355	0.15

[*] Obtained using the Dubinin-Radushkevich (DR) method.

Table S2. Comparison for reaction rate results of magnetic composite and physical mixture.

Initial concentration [mmol/L]	Reaction rate Magnetic composite [mol/(s g)] x 10^8	Reaction rate Physical mixture [mol/(s g)] x 10^8
20	1.2	1.3
40	2.6	2.6
80	5.4	5.5