Supporting information to: Microwave-assisted synthesis of magnetic carboxymethyl cellulose-embedded Ag-Fe_3O_4 nanocatalysts for selective carbonyl hydrogenation

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Discussion on the Ag NPs onto reduced Fe microparticles generated by galvanic reduction. Galvanic reduction is a synthesis that uses Fe(0) MNPs as an electron-rich magnetic support to absorb and reduce metal salts on the surface. Our group and others successfully used this method in order to graft metal nanoparticles on Fe(0) MNPs for different reactions: Pd@Fe for the Suzuki cross-coupling reaction[1], Ru@Fe for transfer hydrogenation,[2] Cu@Fe for the Huisgen click condensationa or diazoester cyclopropanation.[3] This method was adapted to make Fe-supported Ag NPs (Ag@Fe), using Fe(0) microparticles coated with Ag under sonication. Fern-like fractal structures could be observed by Scanning Electron Microscopy (SEM), akin to what was observed with Cu coating on Fe in previous works[4]. However in our system the obtained silver structures were not stable enough and the yield dropped quickly at the second recycling test.

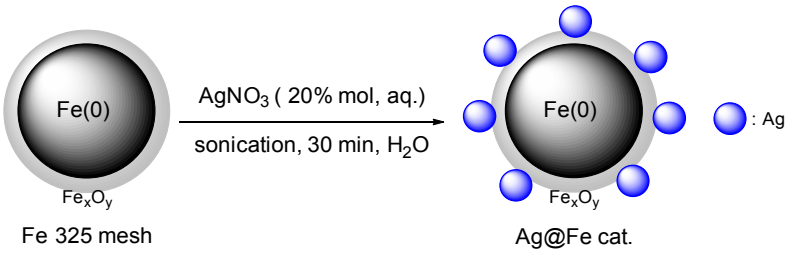

Figure S1. Ag@Fe synthesis.

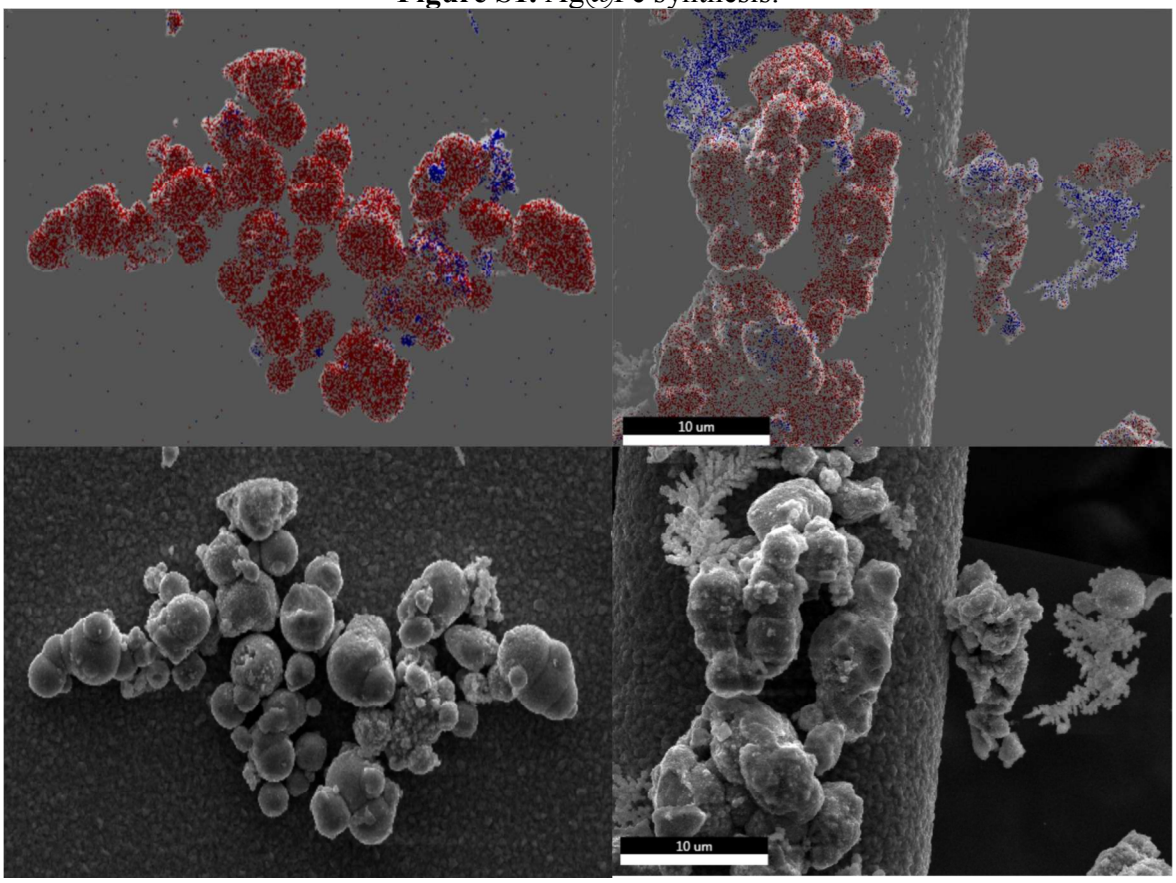

Figure S2. Ag@Fe particles made by galvanic reduction – SEM images (Fe NPs in red, Ag NPs in blue).

These particles proved to be active for benzaldehyde hydrogenation in water. However the catalyst was not recyclable and as shown in Table S1, the yield drops to 20% after only 2 cycles. The high activity shown was probably due to the high surface ratio obtained with the fractal Ag structures, which are fragile and cannot withstand work-ups in air conditions.

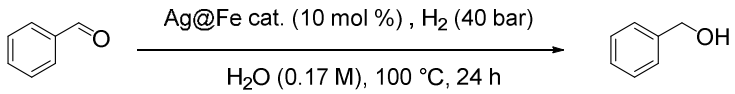

Figure S3. Ag@Fe-catalyzed benzaldehyde hydrogenation.

Cycle	Crude NMR Yield (%)
1	80% yield
2	50% yield
3	20% yield
Reaction conditions: 0.33 mmol benzaldehyde, 10 mol % catalyst, 9 mL H_2O, 40 bars H_2, 100 °C, 24 h	

Table S1. Recycling experiments for Ag@Fe NPs made by galvanic reduction.

Ag@CMC and Ag-Fe_3O_4@CMC characterization.

A typical microwave temperature/pressure/time profile is shown here (power = red, temperature = blue, pressure = green (axis on the right))

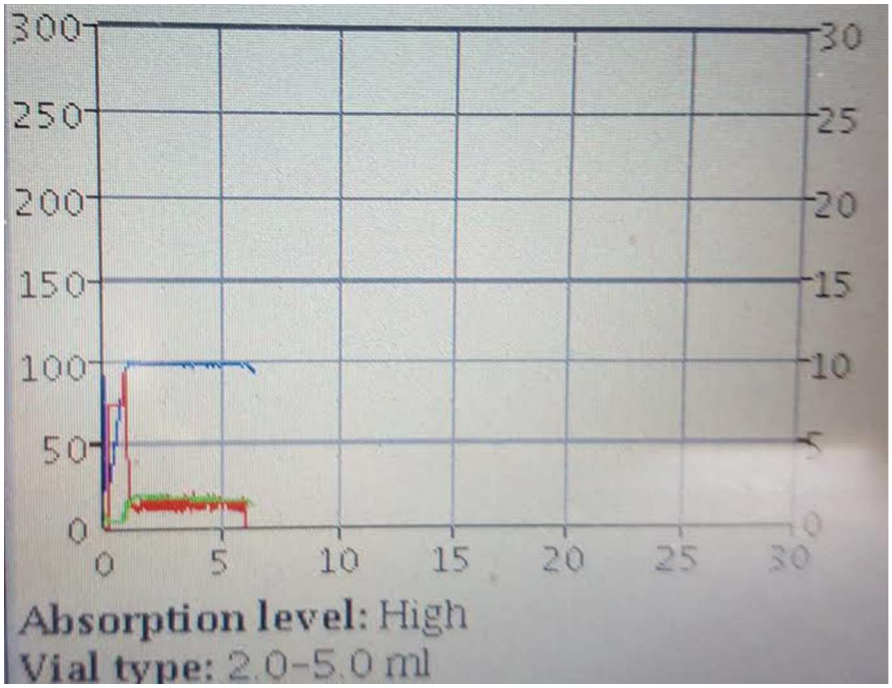

Figure S4. A typical microwave temperature/pressure/time profile (power = red, temperature = blue, pressure = green (axis on the right))

The TEM image size distribution averages were calculated on >300 particles for each metal, except for the Ag aggregates (around 100 particles) mentioned in the main text due to the low number of particles observed.

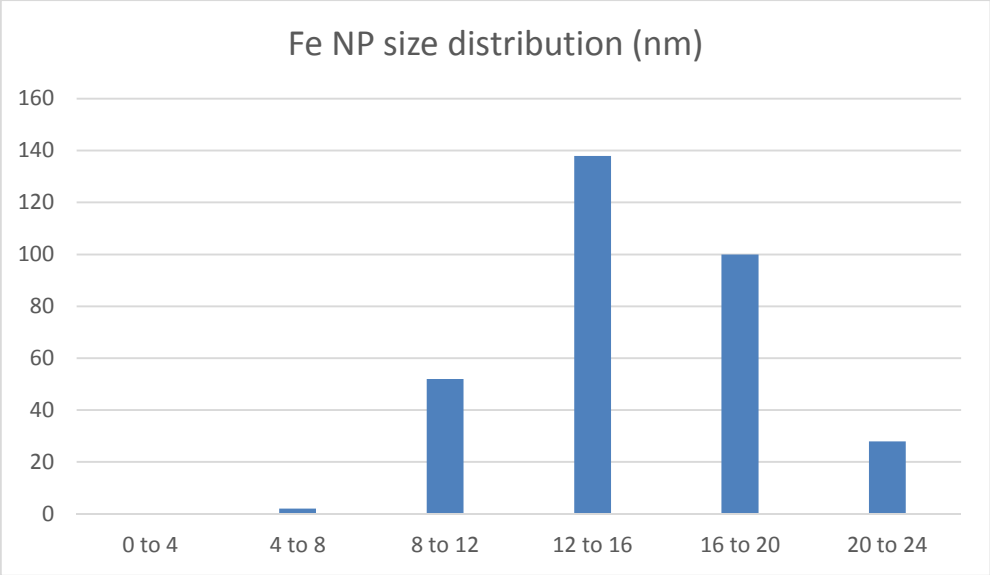

Chart S1. Fe NP size distribution in Ag@Fe_3O_4.

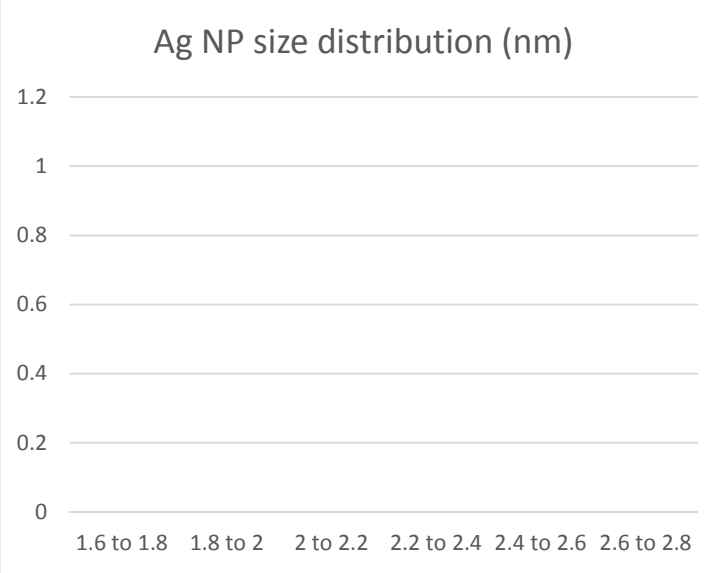

Chart S2. Ag NP size distribution in Ag@Fe_3O_4.

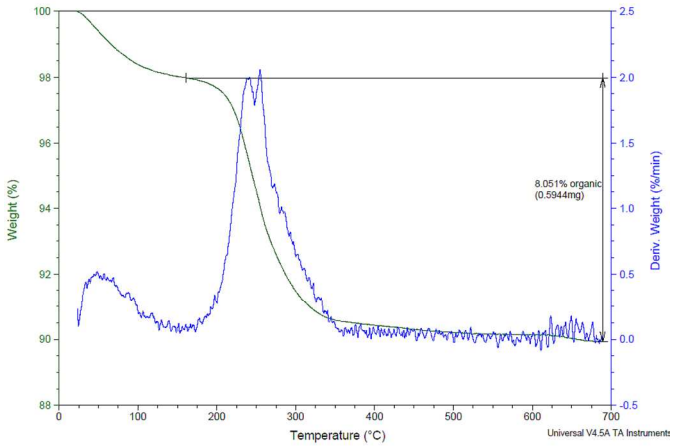

Chart S3. TGA analysis of Ag-Fe_3O_4@CMC.

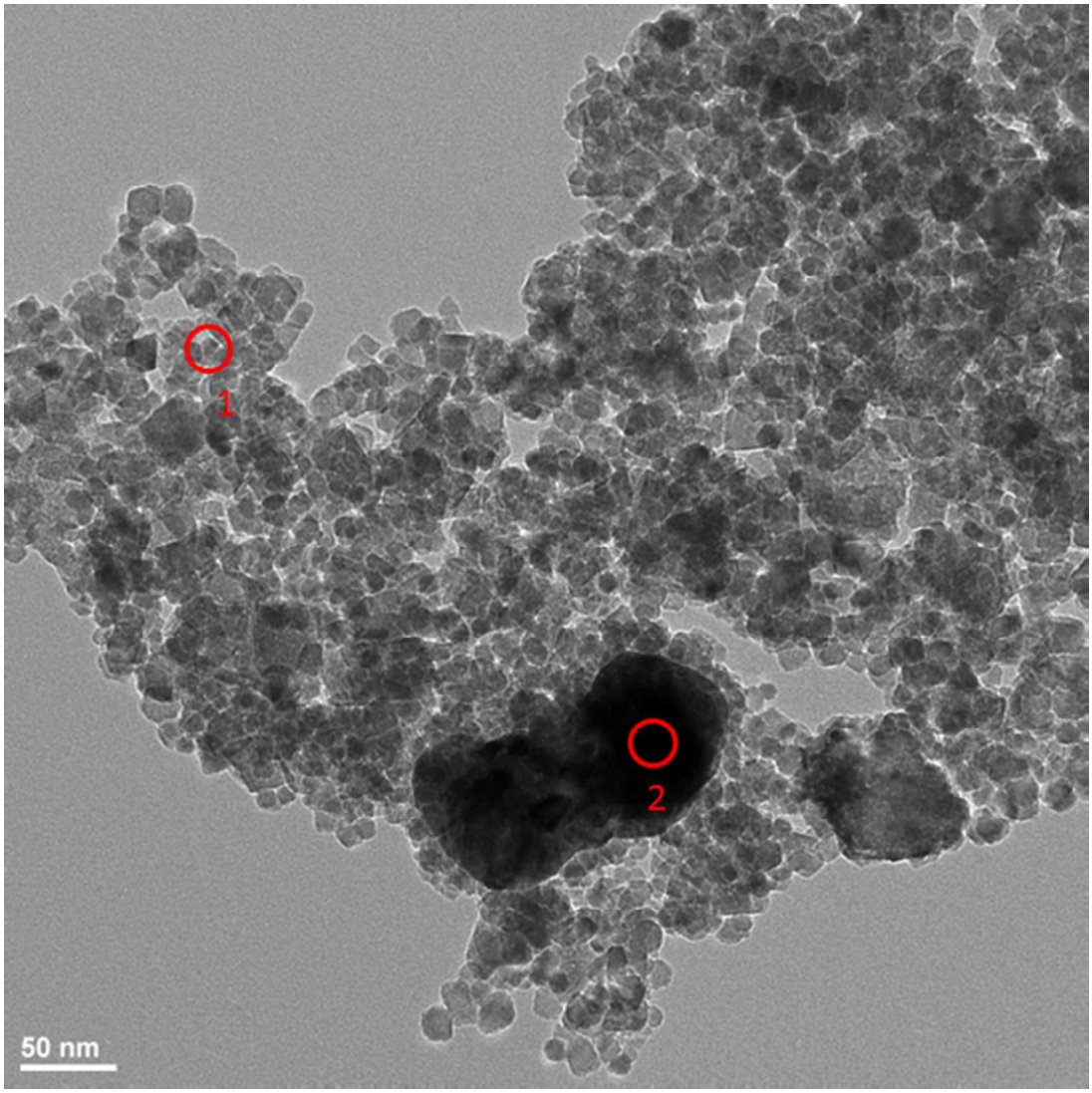

Figure S5. TEM image of Ag-Fe_3O_4@CMC.

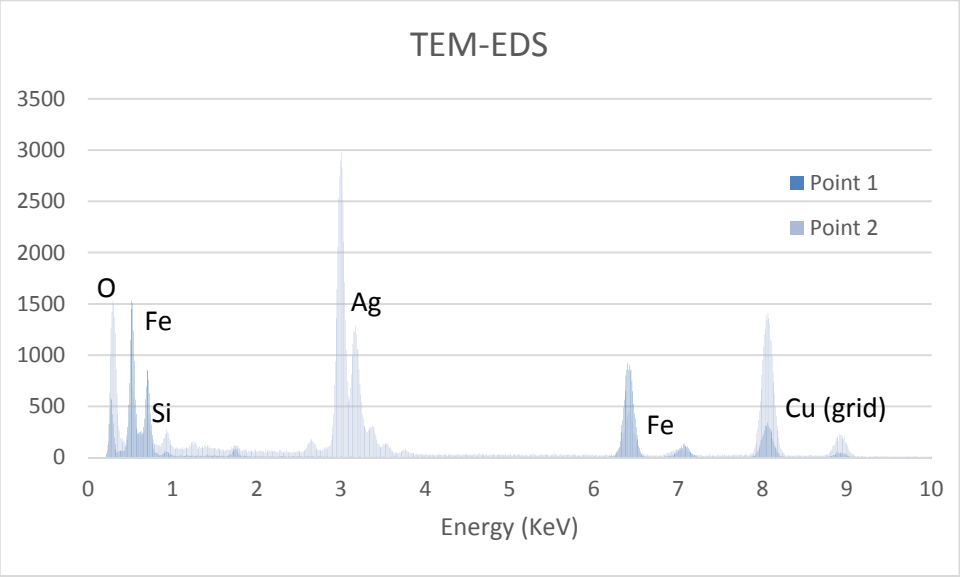

Chart S4. EDS analysis of Figure S5.

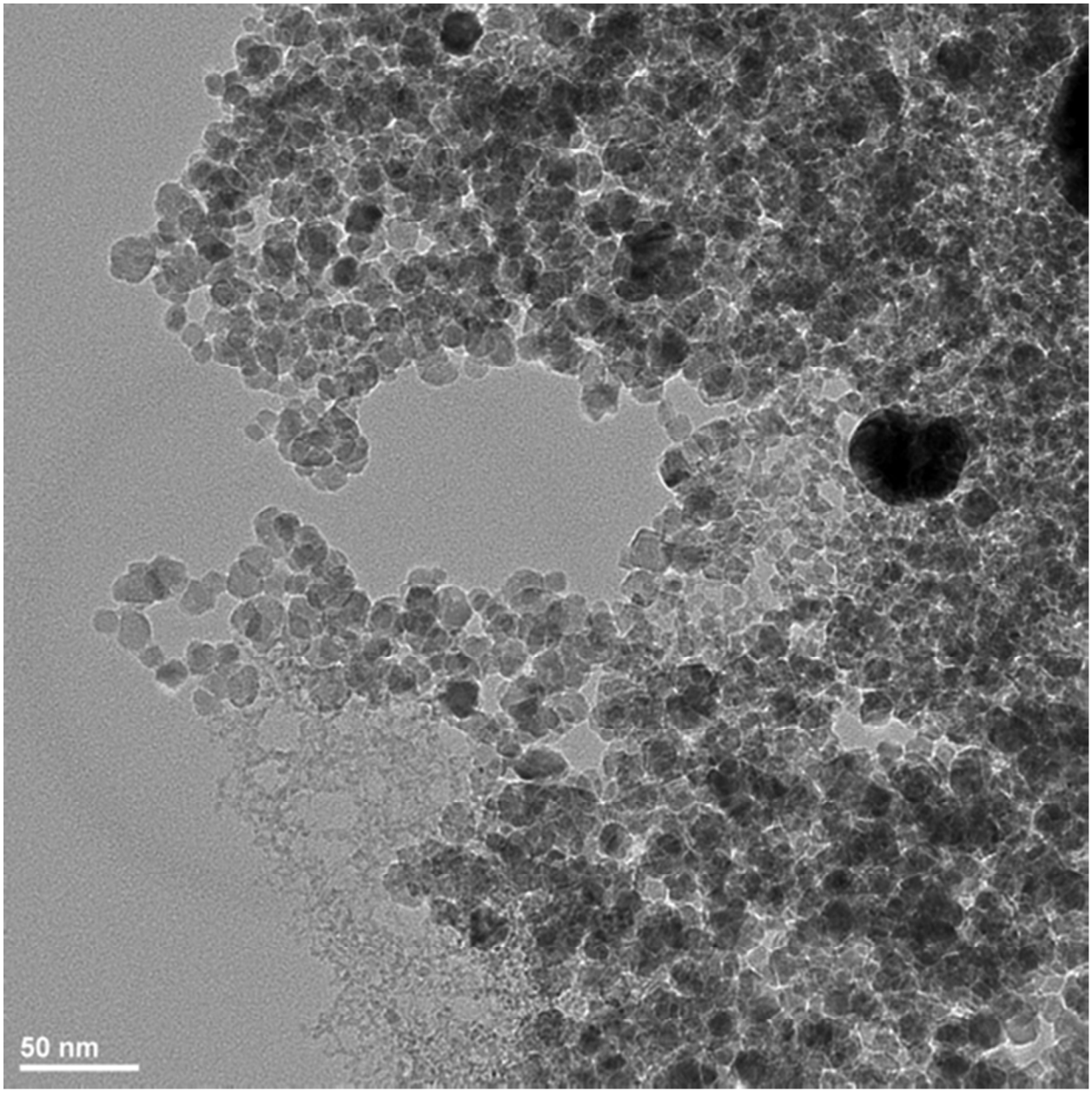

Figure S6. TEM image of Ag-Fe_3O_4@CMC.

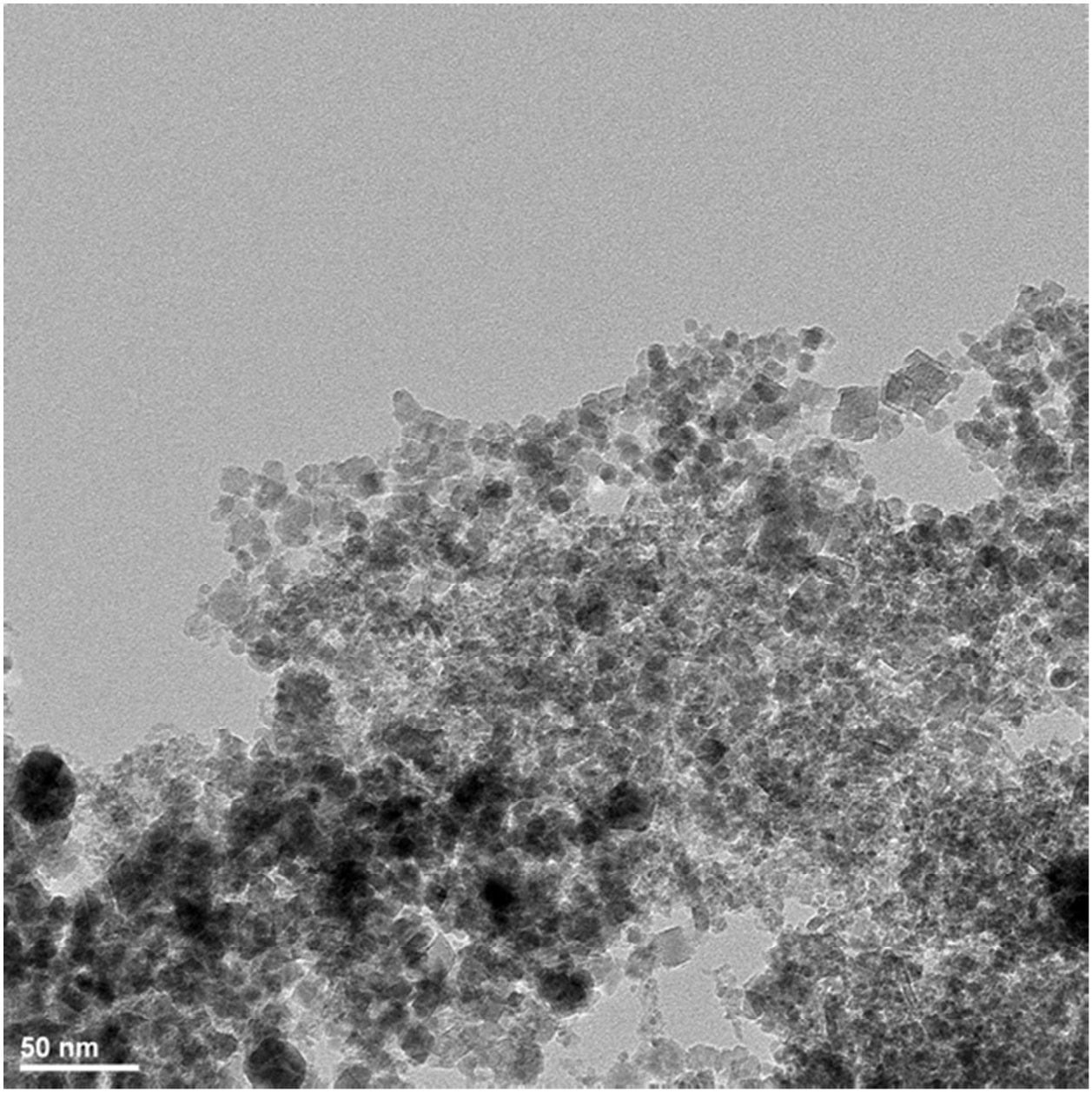

Figure S7. TEM image of Ag-Fe_3O_4@CMC.

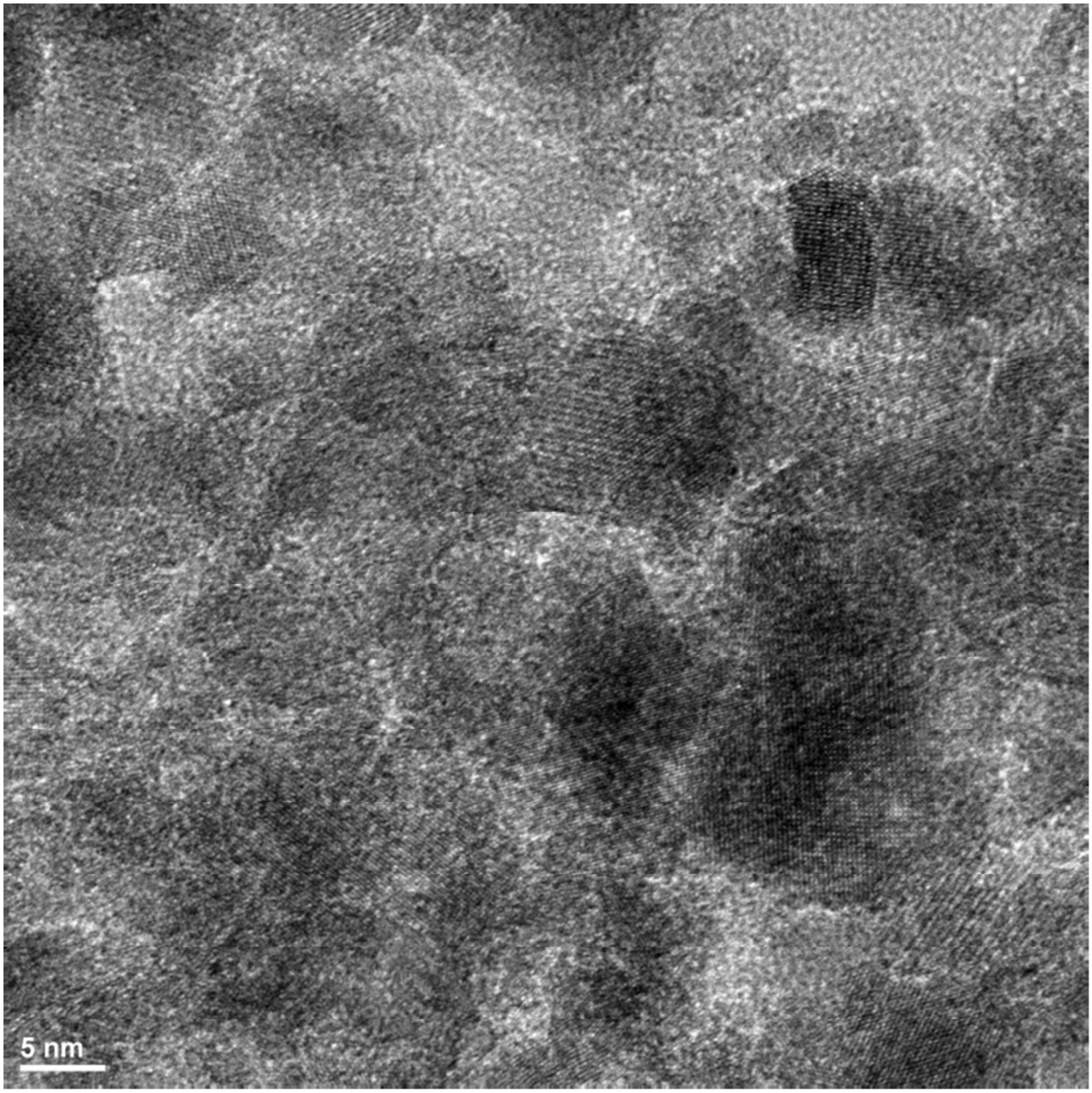

Figure S8. TEM image of Ag-Fe_3O_4@CMC.

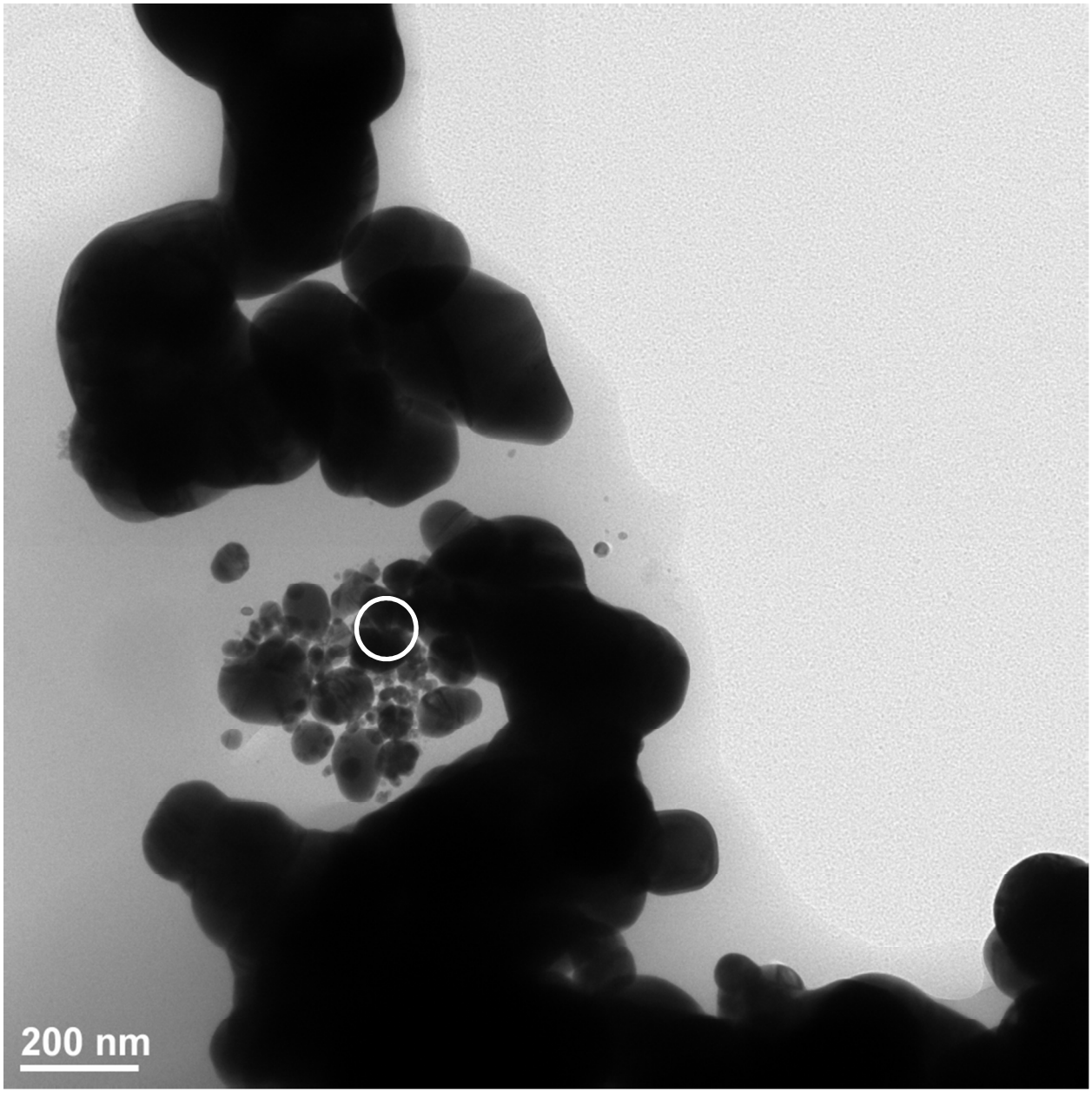

Figure S9. TEM image of $AgNO_3$ and CMC after a hydrogenation reaction (Table 3 of the main text). The position with the circle was measured by EDS in Chart S5. EDS analysis of Figure S9.

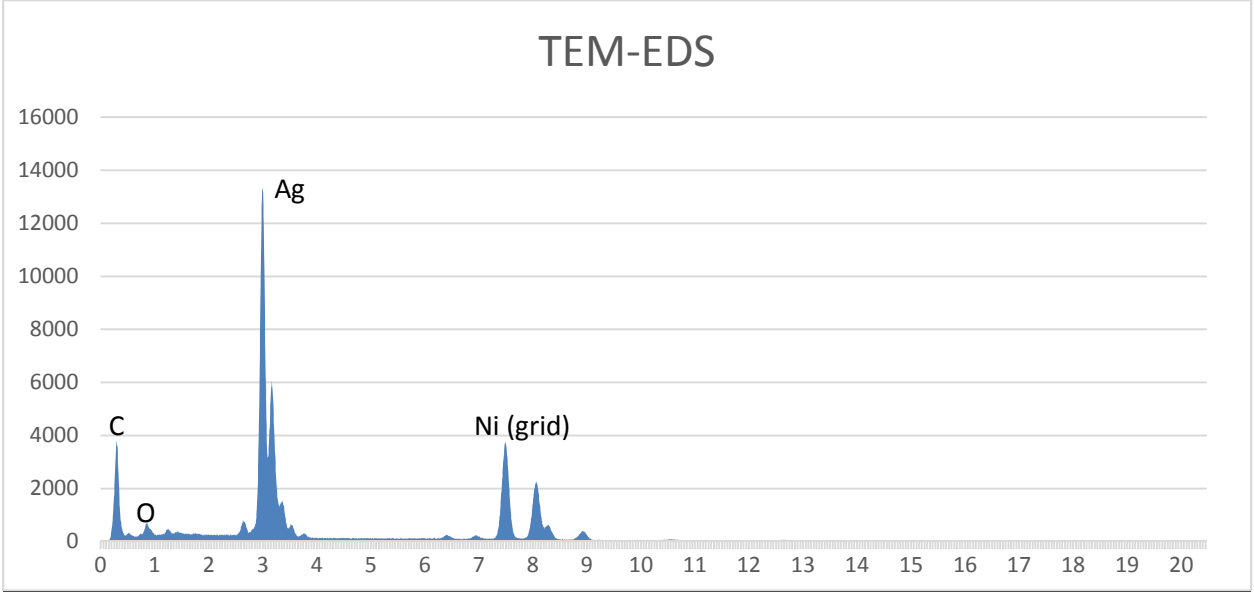

Chart S5. EDS analysis of Figure S9.

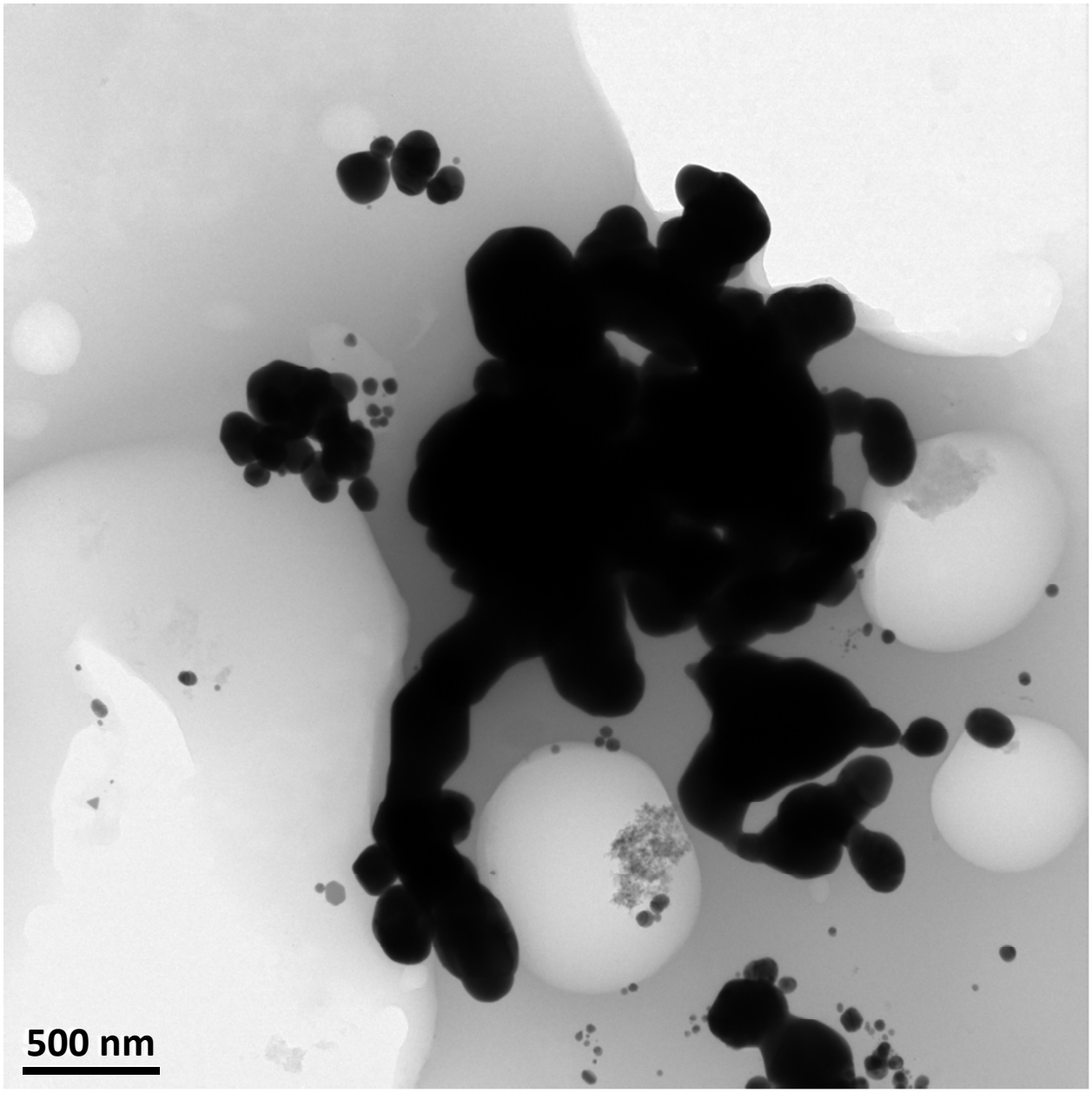

Figure S10. TEM image of $AgNO_3$ and CMC after a hydrogenation reaction (Table 3 of the main text).

TEM shows that Ag NPs can be also formed in situ in the hydrogenation reaction by adding $AgNO_3$ and CMC (Figure S9 and Figure S10). The high polydispersity and the aggregation discard the hypothesis of these Ag NPs being formed under the TEM electron beam. An EDS analysis confirmed the nature of the Ag NPs(Chart S5. EDS analysis of Figure S9.).

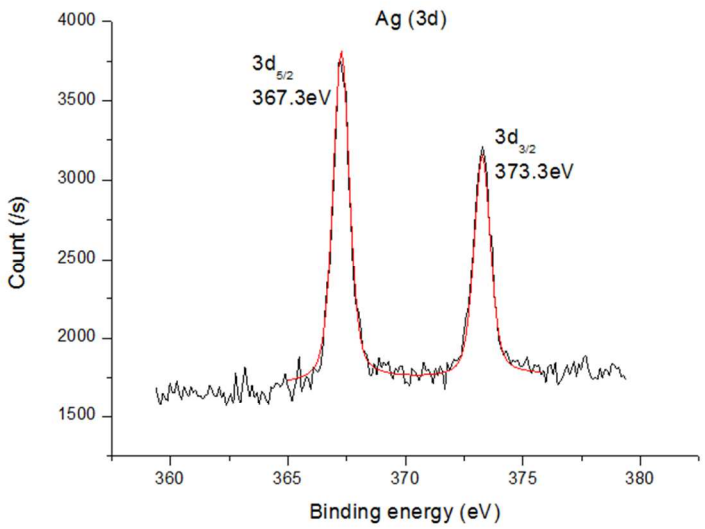

Chart S6. XPS spectrum of Ag.

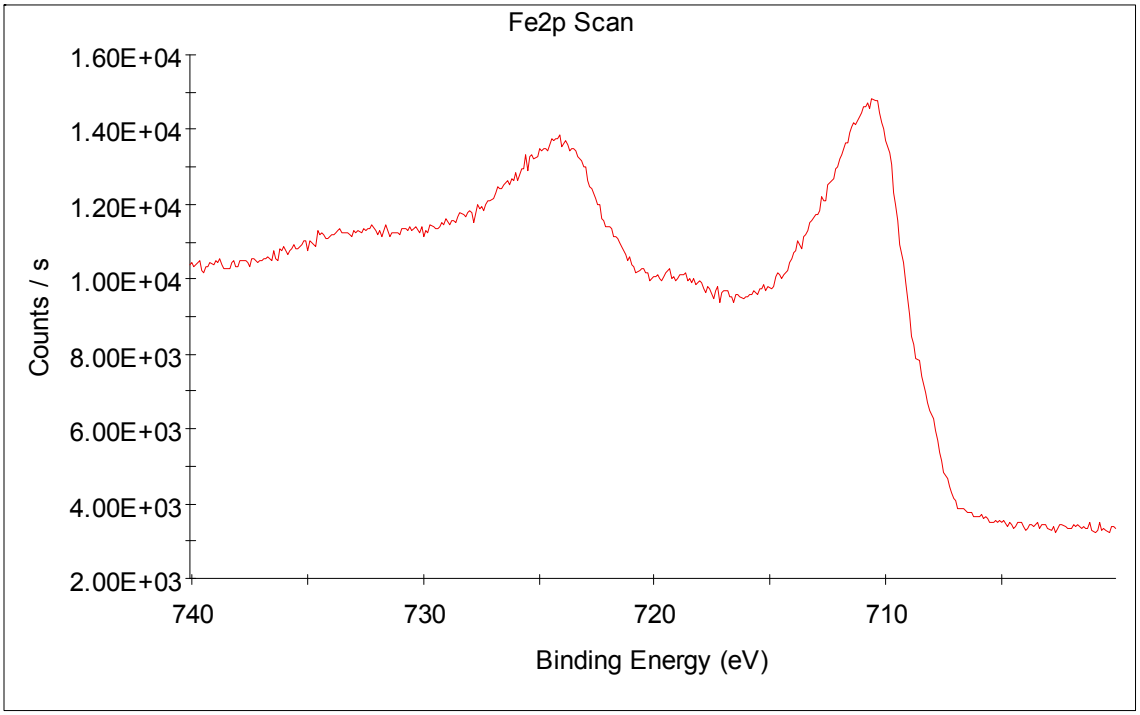

Chart S7. XPS spectrum of Fe.

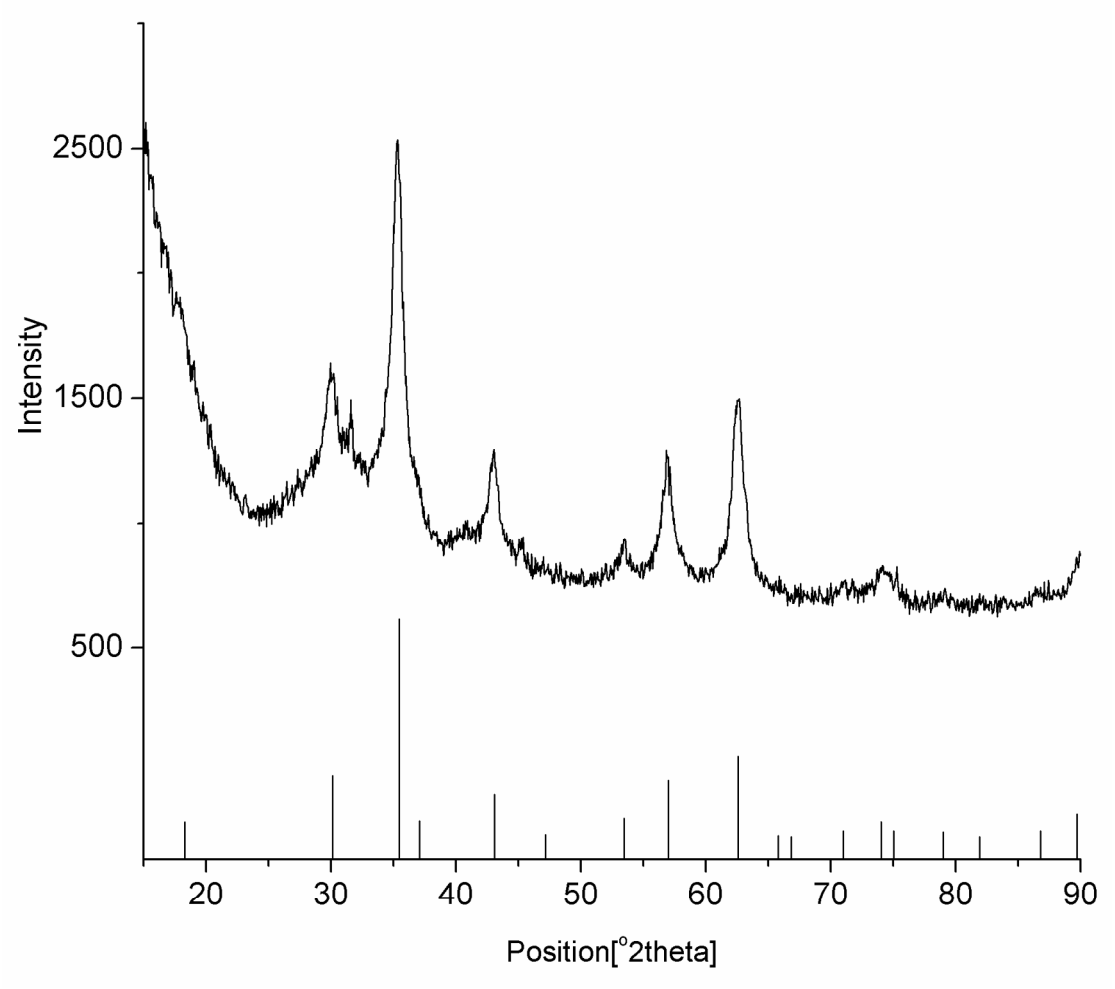

Chart S8. XRD pattern of Fe_3O_4@CMC (top) and face-centered Fe_3O_4 XRD pattern (JCPDS no. 65-3107, bottom).

Fe_3O_4@CMC synthesis (39 mg/mmol m_{CMC}/n_{Fe} ratio). In a 5 mL microwave vial, the iron salts were loaded: $FeSO_4 \cdot 7H_2O$ (53 mg, 0.20 mmol), $FeCl_3 \cdot 6H_2O$ (102 mg, 0.40 mmol) and H_2O (0.9 mL). The solution was stirred a few seconds until it turns into a homogeneous orange translucent solution. Then CMC (0.7 mL, 7mg) suspension was added under heavy stirring and NaOH (1.88 mL, 1.25 M) was added drop by drop to the solution, at which point black NPs formed quickly. It was stirred for an additional 5 min under room temperature before being capped and put to microwave at 100 °C for 1 h.

Cycle	Crude NMR Yield (%)[a]
1	95% yield

2	95% yield
3	95% yield
4	95% yield
5	95% yield
6	56% yield
Reaction conditions: 0.33 mmol benzaldehyde, 6.5 mol % catalyst, 9 mL H_2O, 40 bars H_2, 100 °C, 24 h **[a]NMR Yield was calculated as an average of three measurements from separate batches.**	

Table S2. Ag@Fe_3O_4 recyclability results for benzaldehyde hydrogenation in water.

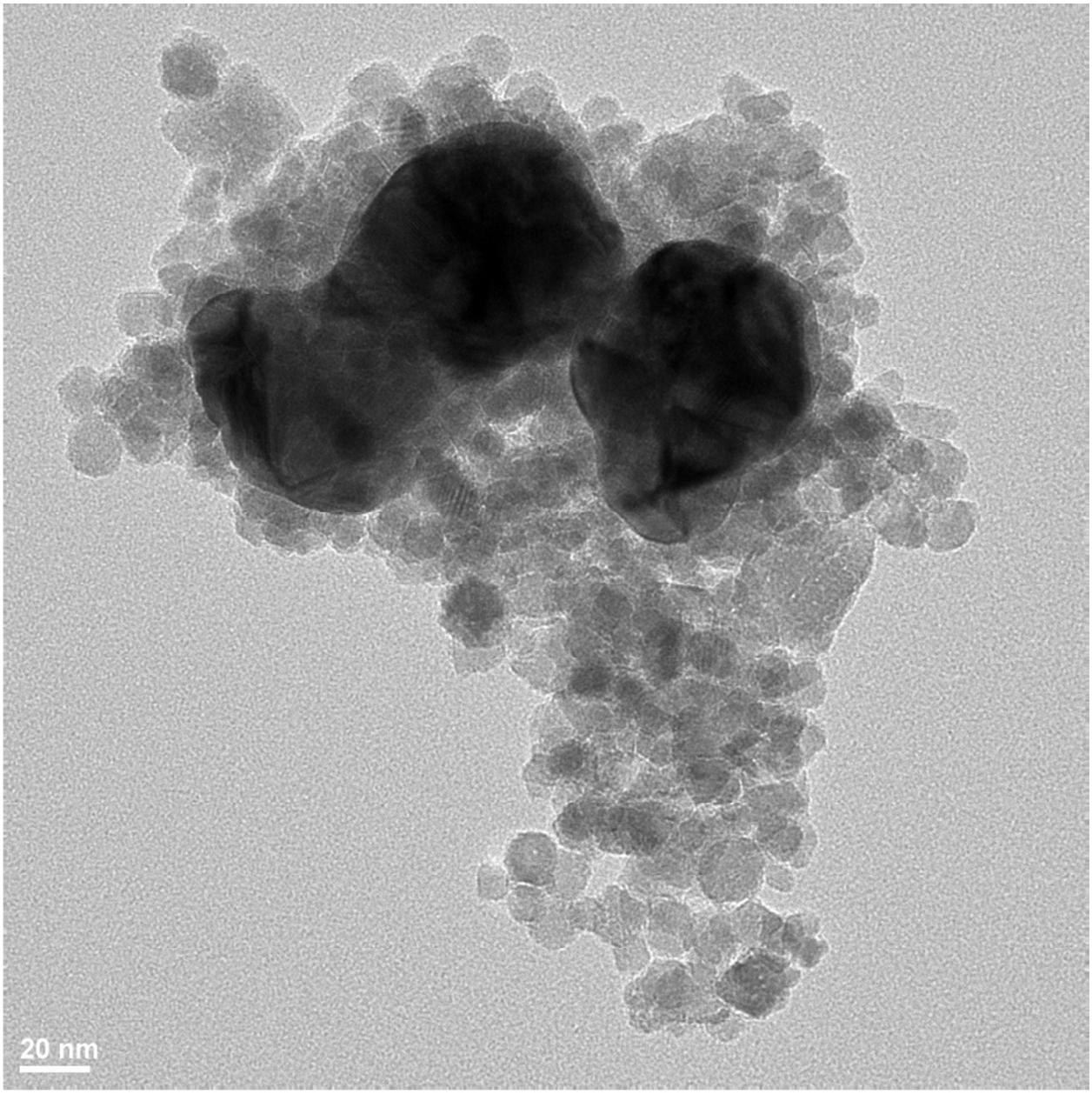

Figure S11. TEM image of Ag-Fe_3O_4@CMC after 6 catalytic cycles.

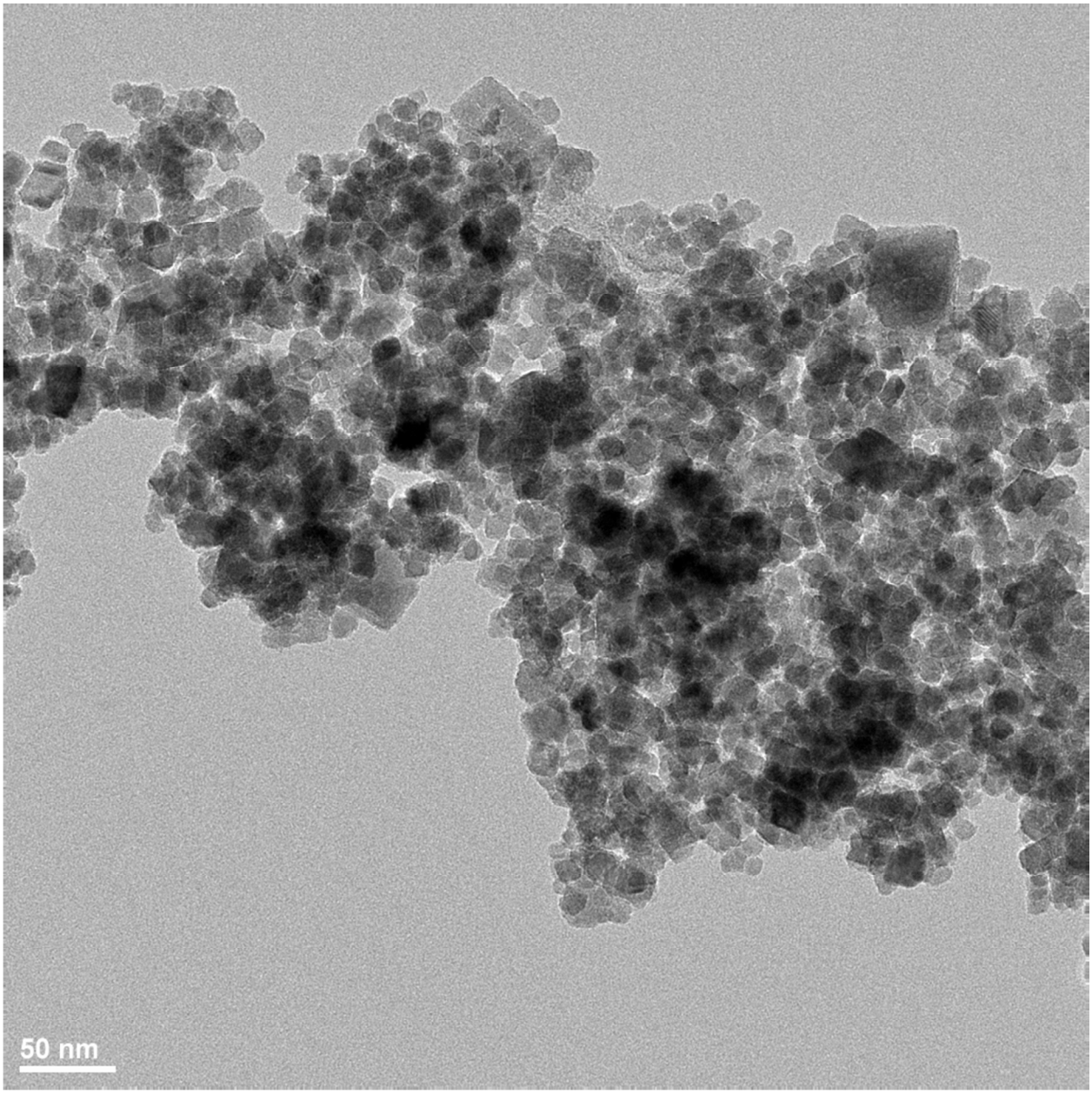

Figure S12. TEM image of Ag-Fe_3O_4@CMC after 6 catalytic cycles.

TEM images of the catalyst after 6 catalytic cycles show an absence of small Ag NPs, though silver is still present in the sample in the form of big aggregates (Figure S11). Due to the small amount of these aggregates and their high discrepancy in shape and size a size distribution, a proper size distribution histogram could not be done. The size distribution of the Fe_3O_4 NPs was obtained (Chart S9 (21,8 ± 8,3 nm).

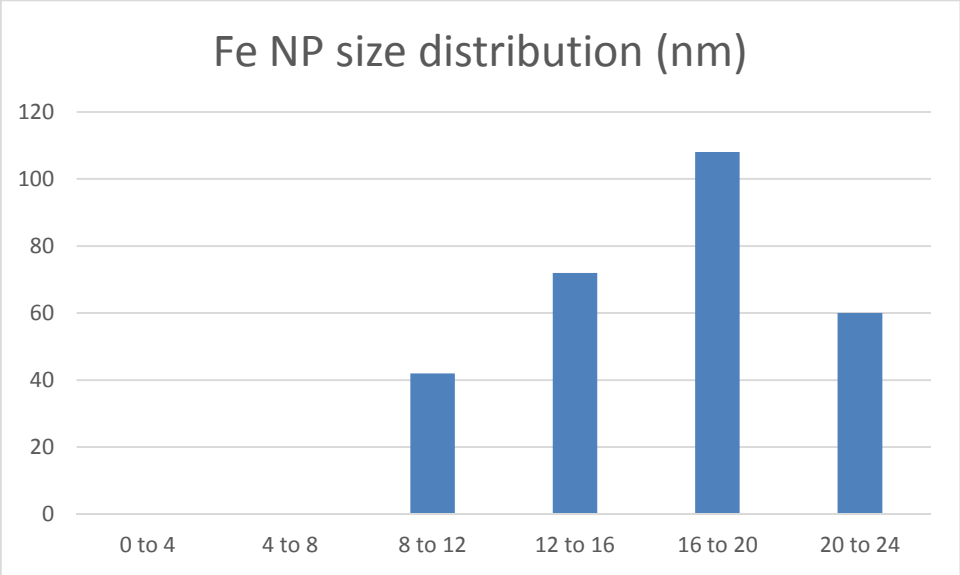

Chart S9. Fe NP size distribution in the catalyst after 6 cycles.

1. Zhou, S.; Johnson, M.; Veinot, J. G. C., Iron/iron oxide nanoparticles: a versatile support for catalytic metals and their application in Suzuki-Miyaura cross-coupling reactions. *Chem. Commun.* **2010,** *46* (14), 2411-2413.
2. Hudson, R.; Chazelle, V.; Bateman, M.; Roy, R.; Li, C.-J.; Moores, A., Sustainable Synthesis of Magnetic Ruthenium-Coated Iron Nanoparticles and Application in the Catalytic Transfer Hydrogenation of Ketones. *ACS Sustainable Chem. Eng.* **2015,** *3* (5), 814-820.
3. Hudson, R.; Li, C.-J.; Moores, A., Magnetic copper-iron nanoparticles as simple heterogeneous catalysts for the azide-alkyne click reaction in water. *Green Chem.* **2012,** *14* (3), 622-624.
4. Masnadi, M.; Yao, N.; Braidy, N.; Moores, A., Cu(II) Galvanic Reduction and Deposition onto Iron Nano- and Microparticles: Resulting Morphologies and Growth Mechanisms. *Langmuir* **2015,** *31* (2), 789-798.