

Supporting Information

Determination of the Surface Temperature of Magnetically Heated Nanoparticles using a Catalytic Approach

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Experimental Methods

General laboratory procedures: All air-sensitive procedures were carried out under an argon atmosphere either by using standard Fisher-Porter bottle techniques or in a glovebox. Mesitylene, toluene, decane, hexadecane and tetrahydrofuran were obtained from VWR Prolabo, then purified on alumina desiccant in a Solvent Purification System (Innovative Technology) and degassed by passage of a stream of argon through the solution for 20 minutes. The commercial products, triruthenium dodecarbonyl (99%) and dodecane were obtained from Sigma-Aldrich and used without further purification. Acetophenone was distilled from anhydrous MgSO₄ under reduced pressure and then degassed by passage of a stream of argon. The Fe_{2.2}C@Ru NPs were prepared as previously described,¹ taking special care in removing all excess palmitic acid from the final product to ensure complete insolubility of the NPs. The size and the morphology of the NPs were studied by transmission electronic microscopy (TEM). TEM grids were prepared by deposition of one drop of a colloidal solution containing the NPs on a copper grid covered with amorphous carbon. Conventional bright-field images were performed using JEOL microscopes (Model 1011 and 1400) working at 100 kV and 120 kV respectively. STEM and EDX analyses were performed using a Probe Corrected JEOL JEM-ARM200F Cold FEG equipped with a High Angle EDX detector working at 200 kV. Thermogravimetric analyses (TGA) were performed in a TGA/DSC 1 STAR System equipped with an ultra-microbalance UMX5, a gas switch GC200 and sensors DTA and DSC. XRD measurements were performed on a PANalytical Empyrean diffractometer using Co-K α

radiation ($\lambda=0.1789$ nm) at 35 kV and 45 mA, on powder samples prepared and sealed under argon atmosphere. The specific absorption rate (SAR) value of Fe_{2.2}C@Ru (380 W/g at 47 mT and 93 kHz)¹ was measured by calorimetry experiments following the protocol already described in our previous work,² using a coil with a fixed frequency of 93 kHz. Gas Chromatography–Mass Spectrometry analyses were performed on a PerkinElmer 580 Gas Chromatograph coupled to a Clarus SQ8T Mass Spectrometer.

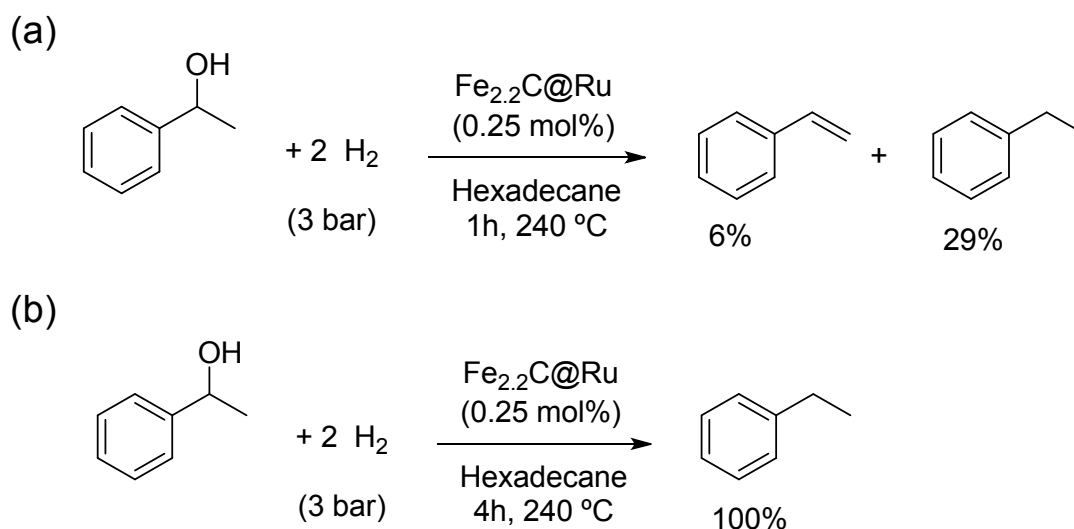
Catalytic experiments: Conventional heating experiments were performed twice using different batches of NPs to ensure the reproducibility. Similarly, magnetic heating experiments in hexadecane and mesitylene were carried out with different batches of FeC@Ru. The apparent temperature and ΔG^\ddagger values thus obtained differed by less than 5%. The results shown in the Results and Discussion section correspond to one same batch of catalyst.

a) Conventional heating. Acetophenone (159 μ L, 1.36 mmol) and dodecane (294 μ L) as GC internal standard were mixed inside a double wall Fisher-Porter bottle, which was then evacuated by 3 cycles of vacuum-argon and taken inside the glovebox. FeC@Ru NPs (5.0 mg, 0.25 mol%) and hexadecane (5 mL) were added and the bottle was pressurized with H₂ (3 bar). The reaction vessel was heated at the desired temperature (200, 210, 220, 230 and 240 °C) within a bath of 1-octadecene and magnetically stirred, the FeC@Ru NPs acting as stirring bar. After 4 hours, the reaction was allowed to cool down at room temperature and a sample was collected for the determination of the conversion of the acetophenone by GC-MS.

b) Magnetic heating. Acetophenone (159 μ L, 1.36 mmol) and dodecane (294 μ L) as GC internal standard were mixed inside a Fisher-Porter bottle, which was then evacuated by 3 cycles of vacuum-argon and taken inside the glovebox. FeC@Ru NPs (5.0 mg, 0.25 mol%) and hexadecane (5 mL) were added and the bottle was pressurized with H₂ (3 bar). The reaction vessel was placed in the center of a magnetic coil and different field amplitudes were applied (22.4, 32.5, 43.9, 60 and 65 mT). After 4 hours, the reaction was removed from the magnetic

coil and allowed to cool down at room temperature. A sample was collected for the determination of the conversion of the acetophenone by GC-MS.

c) Determination of initial rates. Inside the glovebox, FeC@Ru NPs (5.0 mg, 0.25 mol%) was introduced in a double-wall Fisher-Porter bottle, followed by the addition of dodecane (227 μ L, 1 mmol) as GC internal standard, acetophenone (40, 80, 120 or 160 μ L, 0.345, 0.685, 1.03 or 1.36 mmol respectively) and hexadecane (5 mL). The bottle was then sealed and pressurized with H₂ (3 bar). The bottle was heated within a 1-octadecene bath pre-heated at 200 °C and magnetically stirred for 35 min. After this time, the 1-octadecene bath was replaced by a mesitylene bath at room temperature and then placed within a cold water bath, in order to quickly cool the reaction to room temperature. Then the remaining pressure was released and a sample was collected for the determination of the conversion of the acetophenone by GC-MS.



Scheme S1. Hydrodeoxygenation of 1-phenylethanol (1.36 mmol) catalyzed by Fe_{2.2}C@Ru (0.25 mol%) under 3 bar of H₂ at 240 °C after (a) 1 hour and (b) 4 hours of reaction. The yields of styrene and ethylbenzene were calculated from GC-MS analyses using dodecane as internal standard.

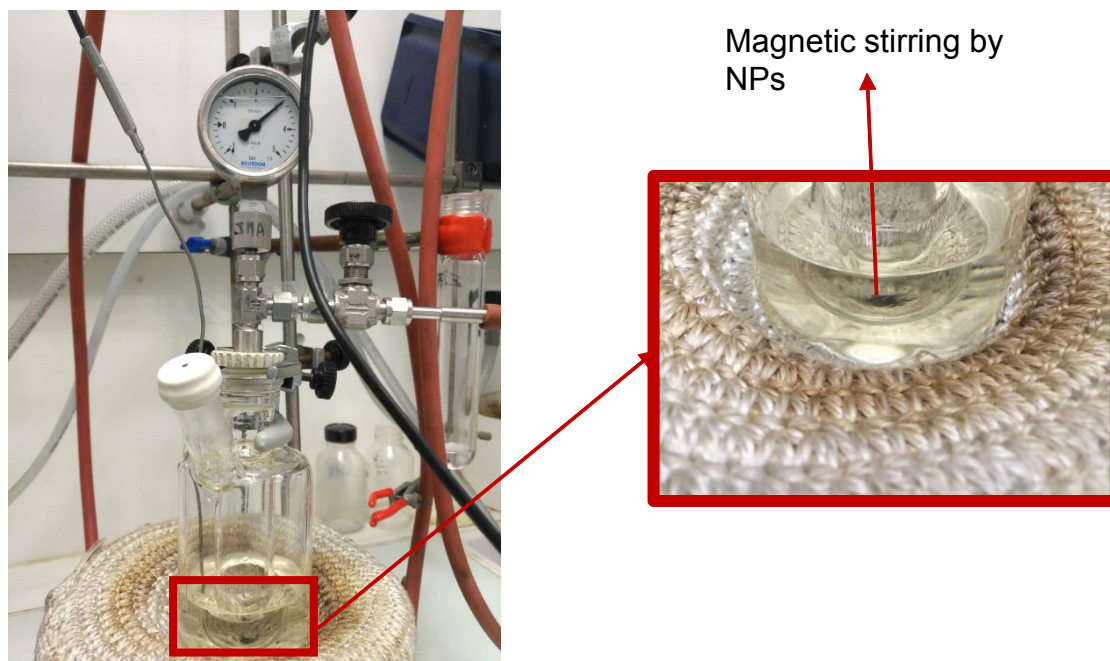


Figure S1. Experimental setting used for the catalytic experiments with conventional heating. The pictures show the double wall Fisher-Porter bottle containing 1-octadecene bath in the external cavity and the components of a catalytic run inside the pressurized vessel.

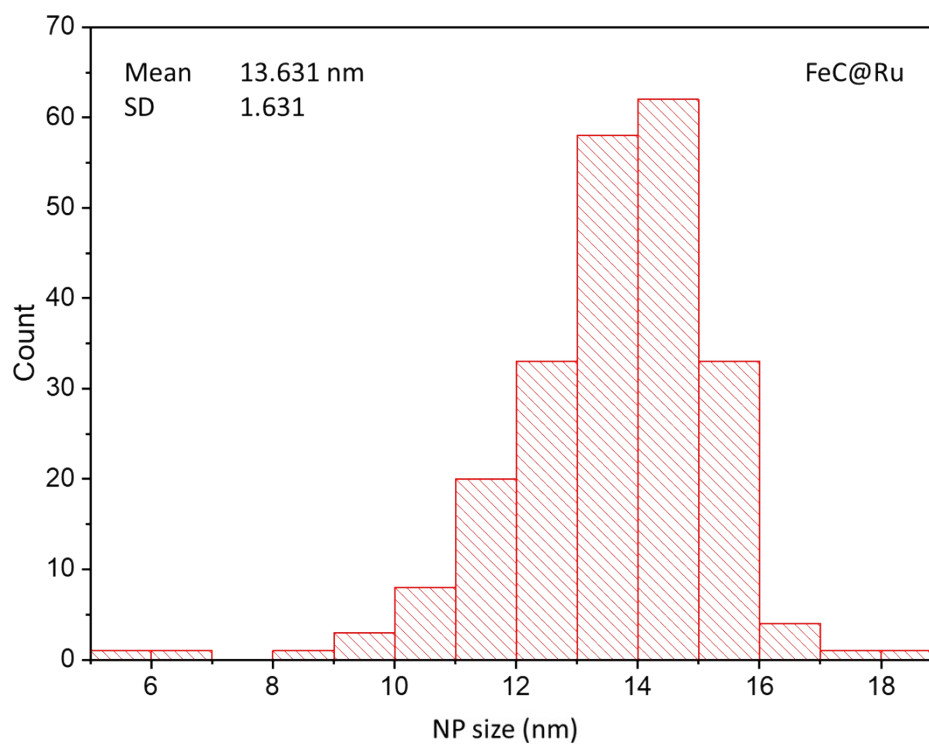


Figure S2. Size distribution of $\text{Fe}_{2.2}\text{C}@Ru$ nanoparticles, determined from TEM images.

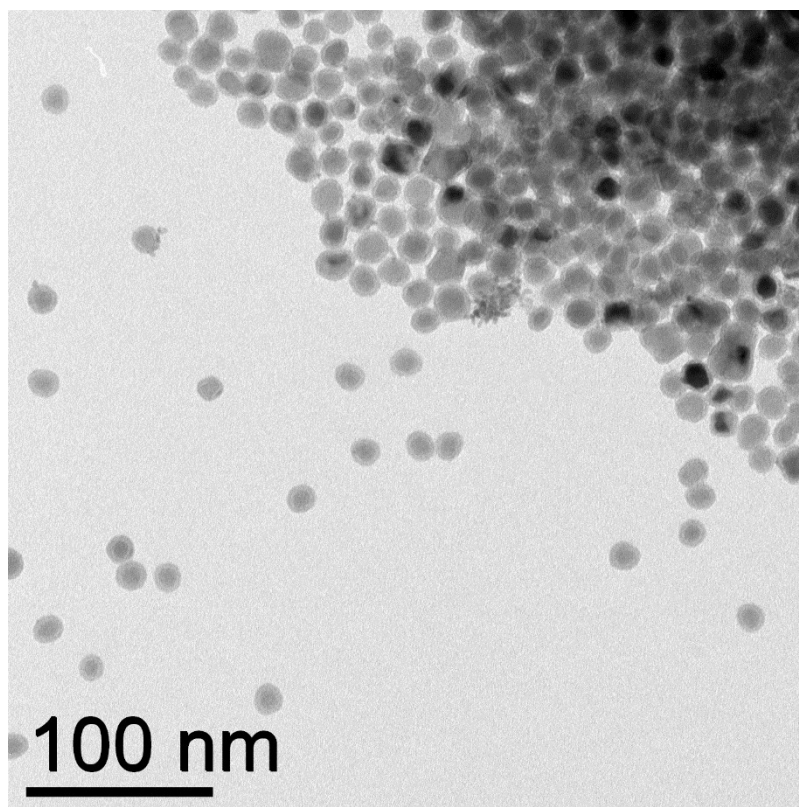


Figure S3. Representative TEM image of $\text{Fe}_{2.2}\text{C}@Ru$ nanoparticles.

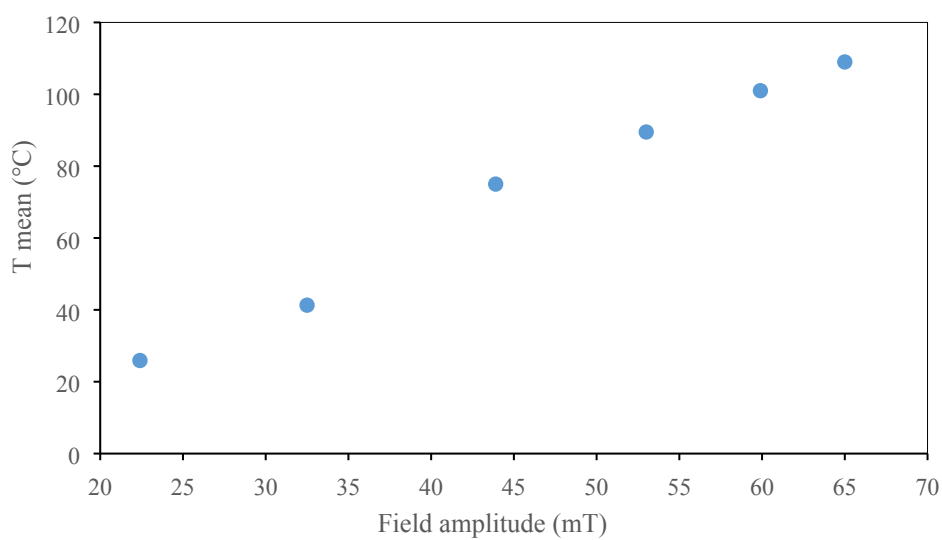


Figure S4. Correlation between the mean temperature of the solution (T_{mean} , measured by an infrared camera) and the field amplitude during the HDO of acetophenone catalyzed by $\text{Fe}_{2.2}\text{C}@Ru$ NPs.

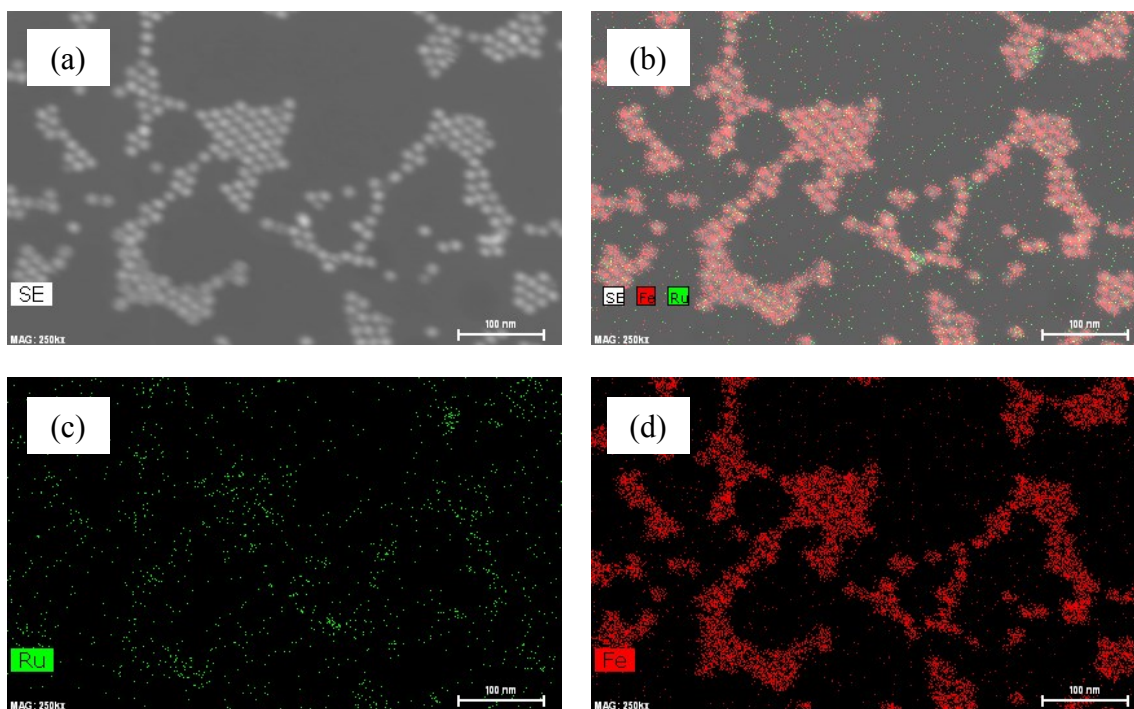


Figure S5. STEM images of Fe_{2.2}C@Ru nanoparticles before being used in catalysis, showing a) HAADF (high angle annular dark field) image, b) HAADF and EDX mapping of both Fe and Ru superimposed, c) EDX mapping of ruthenium, and d) EDX mapping of iron.

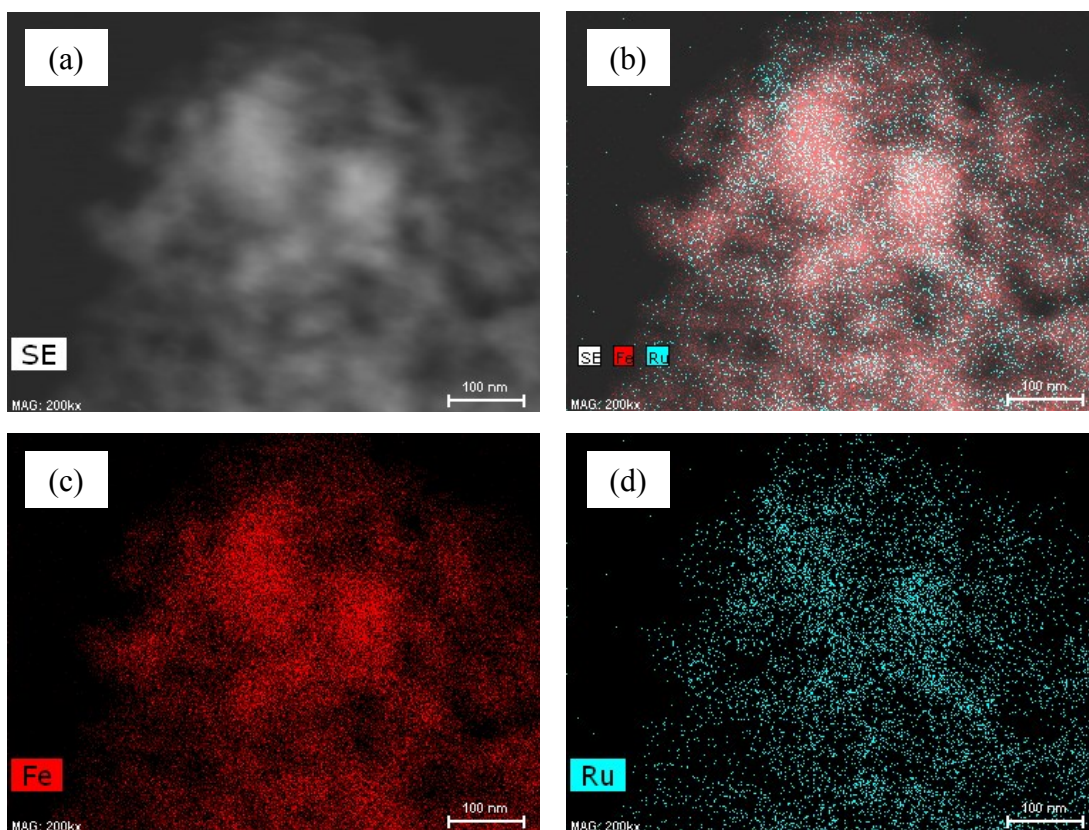


Figure S6. STEM images of $\text{Fe}_{2.2}\text{C}@\text{Ru}$ nanoparticles recovered from a catalytic experiment under magnetic induction at a field of 65 mT during 4 hours, showing a) HAADF (high angle annular dark field) image, b) HAADF and EDX mapping of both Fe and Ru superimposed, c) EDX mapping of iron, and d) EDX mapping of ruthenium.

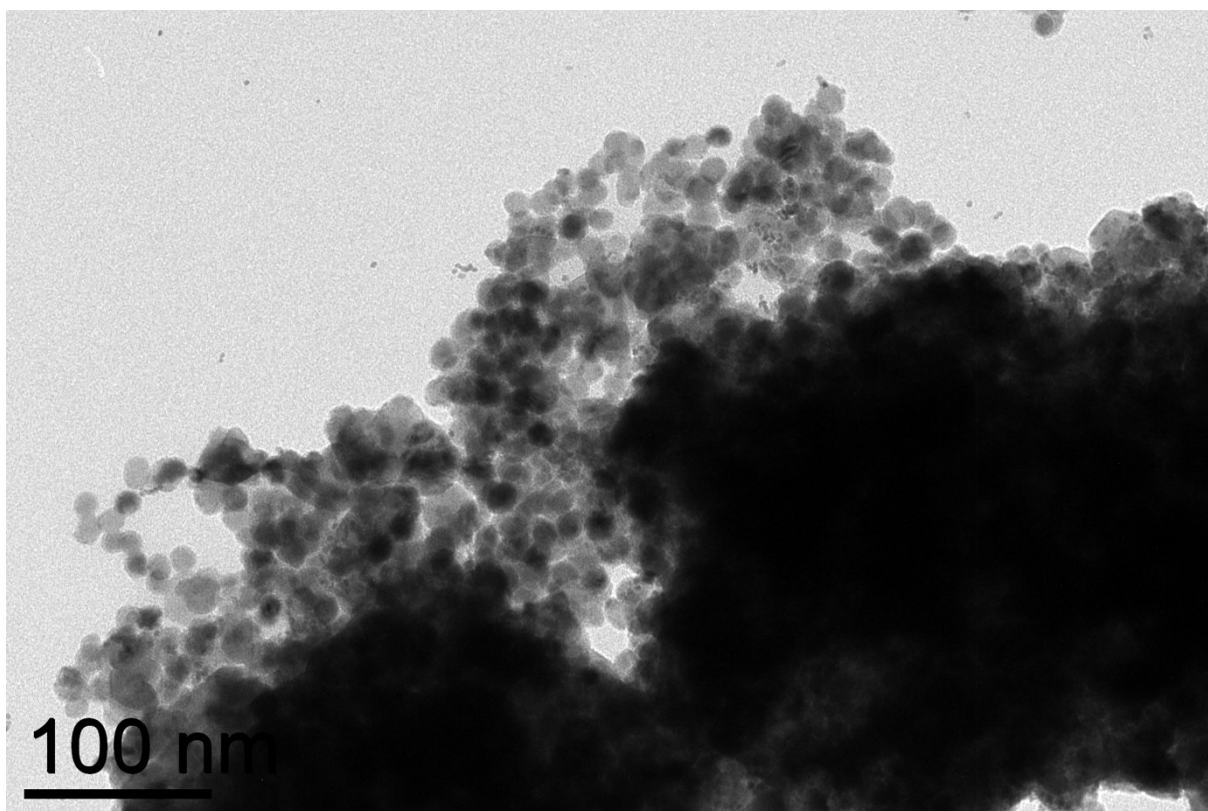


Figure S7. TEM image of $\text{Fe}_{2.2}\text{C}@\text{Ru}$ nanoparticles recovered from a catalytic experiment under magnetic induction at a field of 44 mT during 4 hours.

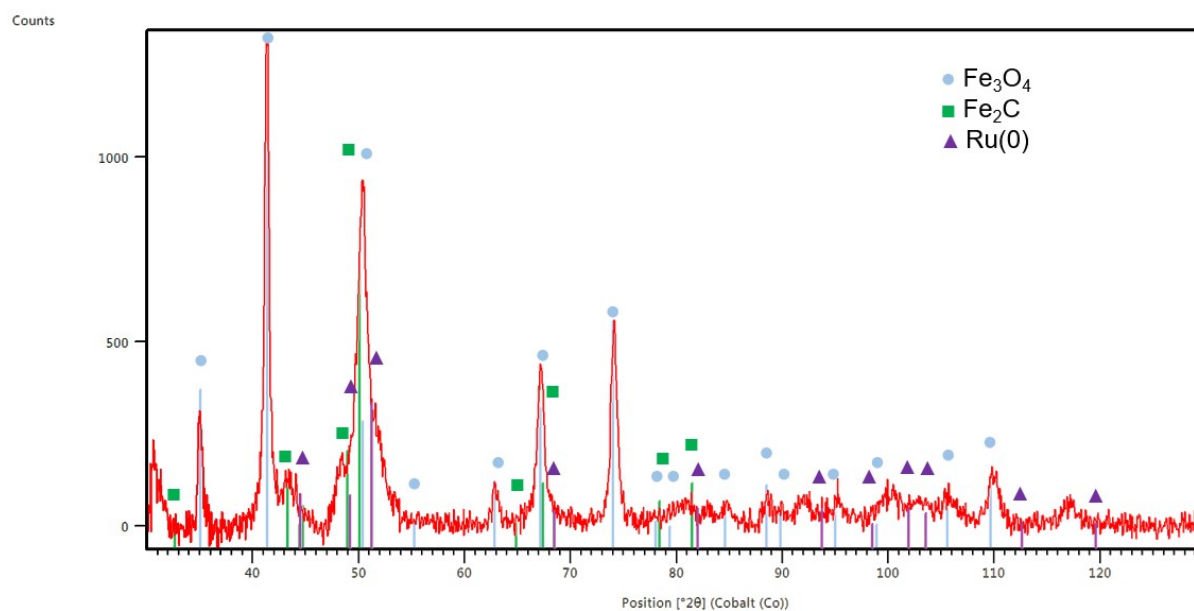


Figure S8. XRD diffractogram of $\text{Fe}_{2.2}\text{C}@\text{Ru}$ NPs recovered from a catalytic experiment under magnetic induction at a field of 65 mT during 4 hours.

References

¹ J. M. Asensio, A. B. Miguel, P.-F. Fazzini, P. W. N. M. van Leeuwen, B. Chaudret, *Angew. Chem. Int. Ed.*, 2019, **58**, 11306.

² A. Bordet, L-M. Lacroix, P.-F. Fazzini, J. Carrey, K. Soulantica, B. Chaudret, *Angew. Chem. Int. Ed.*, 2016, **55**, 15894.