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How to Modulate Catalytic Properties in Nanosystems: The Case of Iron–Ruthenium Nanoparticles

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Ultrasmall FeRu bimetallic nanoparticles were prepared by codecomposition of two organometallic precursors, {Fe[N(Si-(CH₃)₃)₂]₂ and (η⁴-1,5-cyclooctadiene)(η⁶-1,3,5-cyclooctatriene)ruthenium(0) (Ru(COD)(COT)), under dihydrogen at 150 °C in mesitylene. A series of FeRu nanoparticles of sizes of approximately 1.8 nm and incorporating different ratios of iron to ruthenium were synthesized by varying the quantity of the ruthenium complex introduced (Fe/Ru = 1:1, 1:0.5, 1:0.2, and 1:0.1). FeRu nanoparticles were characterized by TEM, high-resolution TEM, and wide-angle X-ray scattering analyses. Their

Introduction

Iron-based catalysts are of great interest because of their low toxicity and the abundance of iron on Earth. Iron nanoparticles (NPs) have been known to be good catalysts for Fischer-Tropsch synthesis for approximately 100 years.^[1] Recently, the use of iron NPs as catalysts for hydrogenation reactions has emerged. For example, iron NPs supported on graphene were reported to display activity in alkene hydrogenation,^[2] and Morris and co-workers described the application of iron NPs in the asymmetric transfer hydrogenation of ketones.^[3] An interesting general method for the synthesis of soluble iron NPs active in alkene and alkyne hydrogenation has been reported that allows the preparation of Fe NPs supported on MgO.^[4] Independently, our group has developed the synthesis of Fe NPs of various sizes and shapes^[5] and recently published the use of ultrasmall iron(0) NPs as catalysts for the hydrogenation of unsaturated C-C bonds.^[6] These NPs could hydrogenate alkenes and alkynes under mild conditions (10 bar H₂ and room temperature) and also displayed weak activity in the direct hydrogenation of C=O bonds. Our group has a long-standing interest in ruthenium NPs,^[7] which display a rich catalytic chemistry, in particular, for arene^[8] and C=O bonds^[9] hydrogenation.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300907. surface was studied by hydride titration and IR spectroscopy after CO adsorption and their magnetic properties were analyzed by using a superconducting quantum interference device (SQUID). The FeRu nanoparticles were used as catalysts in the hydrogenation of styrene and 2-butanone. The results indicate that the selectivity of the nanoparticle catalysts can be modulated according to their composition and therefore represent a case study on fine-tuning the reactivity of nanocatalysts and adjusting their selectivity in a given reaction.

A challenge in this field is the design of nanocatalysts with precise selectivity. Tuning the selectivity is very important because NPs are expected to play a more extended role in the transformation of multifunctional molecules such as molecules of biological interest. For example, we have recently reported that Ru NPs can be selective for reducing aromatic ketones. In some cases, only the arene ring is hydrogenated and not the ketone function.^[10] However, molecules of biological importance often associate aromatic rings that need to be preserved for their biological activity with functions relatively difficult to reduce such as C=O or C=N bonds. The question is, therefore, the following: can we reverse this selectivity by manipulating the NPs? To answer this question, we decided to look at a combination of two different metals displaying very different catalytic properties, namely iron and ruthenium.

FeRu NPs have proven to be interesting catalysts for various reactions, such as Fischer–Tropsch synthesis,^[11] water gas shift,^[12] and hydrogenation of unsaturated aldehydes and ketones.^[13] In most cases, the catalysts are immobilized on a support and are synthesized by co-impregnation on the solid support or in ionic liquids.^[3,11c,d,14] Other syntheses of FeRu NPs involve microwave irradiation,^[15] hydrazine reduction,^[11a,b] or metal organic chemical vapor deposition.^[16] A synthesis of FeRu bimetallic NPs by a modified polyol method was also recently reported.^[12] By using poly-*N*-vinyl-2-pyrrolidone (PVP) as a stabilizing agent, spherical NPs of approximately 8 nm were obtained. To our knowledge, the synthesis of FeRu bimetallic NPs through an organometallic route is unprecedented.

Herein we report the synthesis and full characterization of FeRu bimetallic NPs with different ratios of iron to ruthenium by co-decomposition of two organometallic precursors, $\{Fe[N(Si(CH_3)_3)_2]_2\}_2$ and Ru(COD)(COT), under H₂ pressure. We

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Results and Discussion

Structural properties

FeRu NPs with different molar Ru/Fe ratios were synthesized to study the effect of ruthenium concentration on their catalytic properties. These properties were compared to those of both Ru NPs and ultrasmall iron(0) NPs described in a previous paper.^[6] For this purpose, a mesitylene solution containing various relative concentrations of {Fe[N(Si(CH₃)₃)₂]₂} and (η^4 -1,5-cyclooctadiene)(η^6 -1,3,5-cyclooctatriene) ruthenium(0) [Ru(COD)-



Figure 1. TEM images of FeRu bimetallic NPs with a) 1, b) 0.5, c) 0.2, and d) 0.1 equiv. of ruthenium (scale bar = 100 nm).

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iron to ruthenium did not influence the morphology of the resulting NPs.

High-resolution transmission electron microscopy (HRTEM) as well as scanning transmission electron microscopy (STEM) imaging combined with energy-dispersive X-ray analysis (EDX) were used to analyze the structure and composition of the resulting NPs. In Figure 2 the HRTEM images of NPs with differ-



Figure 2. HRTEM images of FeRu NPs with a) 0.5 equiv. Ru and b) 0.2 equiv. Ru.

ent molar Ru/Fe ratios are displayed. It is clear from this analysis that the FeRu NPs do not have a well-defined crystalline structure.

STEM/EDX analyses allow the cartography of the particles composition. The resulting signal-to-noise ratios were, however, too low to obtain reliable STEM/EDX data on the particles, owing to their small size and the presence of free ligands on the TEM grid. To determine whether bimetallic NPs can be formed in these conditions, we decided to increase the size of NPs by adding a ligand, hexadecylamine (HDA). For these NPs, one equivalent of ruthenium and three equivalents of HDA were added to the iron precursor. In Figure 3 the TEM, HRTEM,

(COT)] (1 Ru:1 Fe, 0.5 Ru:1 Fe, 0.1 Ru:1 Fe; Fig-0.2 Ru:1 Fe, ure 1 a-d, respectively) was treated under 3 bar of dihydrogen at 150°C overnight. In all cases, the samples were analyzed by elemental analysis after precipitation and washing with toluene to determine the composition of the NPs (see the Supporting Information). The values found (Fe/Ru = 1:0.09, 1:0.16, 1:0.49, 1:1) matched the initial composition of the solutions (Fe/Ru = 1:0.1, 1:0.2, 1:0.5, and 1:1).

TEM images obtained after evaporation of the solution only revealed one population of spherical NPs displaying a size between 1.6 and 1.9 nm (Figure 1). The molar ratio of



Figure 3. a) TEM, b) HRTEM, and c) STEM/EDX images of FeRu (1:1) NPs synthesized in the presence of HDA with the cartographies of d) iron and e) ruthenium. Scale bars (c, d, e) = 40 nm.

and STEM/EDX images are shown characterizing the FeRu NPs synthesized in the presence of HDA. Interestingly, these NPs presented a different morphology: a wormlike irregular shape. We have previously demonstrated that HDA promotes the coalescence of Ru NPs to lead to a wormlike morphology as a result of weak coordination of HDA on the metal surface.^[17] The mean diameter of the worms is approximately 2–3 nm, which allows characterization by STEM/EDX. The cartography of elements revealed that Fe and Ru are both present in the same particles and confirmed the bimetallic nature of the FeRu NPs.

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Owing to the small size of these NPs, X-ray diffraction measurements only provided broad peaks, which did not allow a clear understanding of the structure of our NPs. Therefore, wide-angle X-ray scattering (WAXS) analyses were performed, which provided more information (see Figure 4).



Figure 4. WAXS analyses of FeRu NPs with b) 0.2, c) 0.5, and d) 1 equiv. of Ru, e) in the presence of HDA, and their comparison with a) the experimental function obtained for pure Fe NPs^[18,19] and f) the function computed from the Fe 1Ru 1 structure (expanded by 3% for comparison purposes). r = Coherence length.

The observed coherence length, which corresponds to the size of crystalline domains, is close to 1.5 nm for FeRu NPs prepared in the absence of HDA. It exceeds 2 nm for the NPs prepared in the presence of HDA. These values are in good agreement with the observations made by TEM/HRTEM analyses. The structure of the particles prepared in the presence of HDA (FeRu/HDA) appears very similar to that of both bulk Fe1Ru1 alloy and pure hexagonal close-packed (hcp) ruthenium. Thus, the obtained radial distribution function (RDF) of FeRu/HDA is close to the one computed from a model based on the structure of Fe1Ru1. The coherence length is above 2 nm and a significant deviation from the perfect hexagonal structure can be observed at increasing distances. The average bond length estimated on the RDF is, however, larger than the one in the Fe1Ru1 alloy (0.2624 nm) by a 3% expansion factor, which makes the average bond length in FeRu/HDA almost identical to the value in pure ruthenium (0.2705 nm). In previous WAXS studies on different bimetallic NPs,^[19] scaling of all the interatomic distances on the parameter of the species of higher atomic number has been shown to be a direct proof of segregation in the particles. In the present case, such scaling strongly indicates that FeRu/HDA NPs, although bimetallic as observed by STEM/EDX, are actually not alloyed but organized as Ru@Fe core-shell particles.

For the other samples, a much smaller and nearly constant amplitude could be observed. In addition, RDF patterns are very similar for all compositions with no significant shift of the first interatomic distance, indicating an average bond length nearly independent from the Ru/Fe ratio. This pattern is also very close to the one previously observed for pure Fe particles prepared by using similar conditions.^[18] All these results strongly suggest that most of the order in the FeRu PVP samples, as observed by using X-ray scattering, is derived from the same small particles in all four cases, namely Fe NPs adopting the manganese beta structure, all with a coherence length of approximately 1.5 nm. This structure does not exclude a bimetallic character of the particles, which would explain the discrepancy between the nearly constant coherence length and the different sizes observed by TEM. Considering the large atomic number of Ru compared to that of Fe and the lack of distances clearly related to the bigger Ru atoms, these results exclude any kind of extended structure involving Ru, for example, Janus-like organization.

In summary, the WAXS studies evidence the presence of a well-ordered core-shell structure Ru@Fe in the presence of HDA and a more disordered but also core-shell structure of the type Fe@Ru in the absence of HDA, with a core structure similar to the one observed for pure iron NPs. The origin of this discrepancy is not clear but is probably related to the accessibility of Ru surface to HDA during the initial steps of the growth of Ru NPs, which then coalesce as in the case of pure Ru NPs.^[17] In the case of the particles prepared in the absence of HDA, the core is clearly essentially composed of Fe NPs on which Ru is adsorbed in a disordered way. One explanation for this surprising reversal of reactivity could be the fact that Ru-(COD)(COT) reacts in the absence of added amine with aromatic solvents at elevated temperature under H₂ to give stable (arene)(COD) ruthenium(0) species much more stable than Ru-(COD)(COT). $\ensuremath{^{[20]}}$ If an excess of HDA is present in the solution, it coordinates on ruthenium, hence preventing the formation of the ruthenium-arene complex. This demonstrates once more the importance of the organometallic chemistry present in solution prior to the formation of NPs.^[21] For the purpose of our catalytic studies, we did not consider the Fe/Ru/HDA system, which is too different, and concentrated on the NPs obtained in the absence of additional ligand. It is, however, necessary to gain more evidence for the presence of increasing quantities of Ru on the surface of the Fe NPs. For this purpose, surface and magnetic studies were performed.

Surface state studies

We performed first the titration of hydrides present at the surface of the FeRu NPs. The general procedure for the quantification of hydrogen atoms adsorbed onto the surface of metallic NPs through hydrogenation of 2-norbornene has been previ-

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ously described.^[22] This procedure allows not only the determination of the number of hydrides present on the surface of a given nanoparticle but also the demonstration that the surface of the particle is not oxidized, because, especially for iron, any trace of oxidation would immediately lead to the disappearance of all hydrides. The procedure is the following: three freeze-pump cycles were performed on each fresh colloidal solution of bimetallic FeRu NPs to eliminate the dihydrogen present in the solvent. Then, one equivalent of olefin (2-norbornene) was added. After 24 h of magnetic stirring at room temperature, samples were analyzed by gas phase chromatography. With the conversion of 2-norbornene into norbornane and the estimated percentage of surface atoms of Ru and Fe of the particle (we considered 70% for a mean size of 1.7 nm), the number of hydrides per surface metal atom can be estimated. Results are reported in Table 1.

Table 1. Number of hydrides per surface metal atom of some FeRu bi- metallic NPs.				
NPs	Number of surface hydrides per surface metal atom			
FeRu (1:1)	0.40			
FeRu (1:0.5)	0.40			
FeRu (1:0.1)	0.46			

We found approximately 0.4 hydrides per surface metal atom for all the FeRu NPs studied. This is a lower limit because the freeze–pump cycles lead to the elimination of a number of hydrides from the NPs surface. These results demonstrate, nevertheless, the nonoxidized character of these FeRu NPs and, hence, their potential in catalytic hydrogenation reactions.

To have a better understanding of the surface state of our bimetallic FeRu NPs, experiments of CO absorption were also performed, because the CO stretch can give information on the nature of the metal present on the surface (see the Supporting Information).^[23]

For this study, solid samples of FeRu NPs were placed in a Fischer–Porter bottle under CO (3 bar) for 2 h. After this time, the powder was analyzed by IR spectroscopy. Very broad CO stretches were detected at 1927 cm⁻¹ and 1946 cm⁻¹ for FeRu NPs of a molar ratio of 0.1 Ru:1 Fe and 0.5 Ru:1 Fe, respectively. These values are again in agreement with the absence of oxidation of the NPs surfaces and are intermediate between those resulting from CO adsorption on pure Fe (1899 cm⁻¹) and pure Ru/PVP NPs (\approx 1945 cm⁻¹) or close pure Ru/PVP.^[24] Furthermore, the CO band frequency varies as a function of the Ru content as expected. This is in excellent agreement with the proposal of the bimetallic nature of the NPs and the presence of Ru on their surfaces.

Magnetic properties

Magnetic studies are a very sensitive tool to monitor the formation of bimetallic NPs, previously used, for example, to follow the formation of RuCo NPs.^[25] Magnetization measurements were performed on a Quantum Design model MPMS 5.5 superconducting quantum interference device (SQUID) magnetometer. They were performed on dried powders and the samples were sealed under argon atmosphere to preserve the NPs from any uncontrolled oxidation. In Figure 5 the hysteresis curves are shown relative to the



Figure 5. Hysteresis curves measured at 2 K of bimetallic FeRu NPs with different molar ratios of iron to ruthenium. $\mu_0 H(T) =$ Applied magnetic field intensity.

series of FeRu NPs and measured at 2 K. The absolute magnetization was deduced from the iron(0) total content determined by microanalysis using the inductively coupled plasma mass spectrometry technique (ICP). Bimetallic FeRu NPs exhibit a ferromagnetic behavior at 2 K. The measured saturation magnetizations (M_s) are lower than that of bulk iron (210 Am²kg⁻¹ at 2 K).^[26] FeRu NPs saturation magnetizations vary between 187 and 18 Am²kg⁻¹ at 2 K following the increase of the ruthenium molar ratio as expected for a dilution effect of nonmagnetic Ru atoms.^[27]

Catalytic properties

Having proven the bimetallic nature of the FeRu particles, their catalytic performance was investigated in the hydrogenation of styrene and 2-butanone (Scheme 1) and compared with the



Scheme 1. Hydrogenation of styrene catalyzed by FeRu bimetallic NPs.

catalytic performance of monometallic iron and ruthenium NPs. We chose these two unsaturated substrates to evaluate the potential of our NPs for the hydrogenation of a terminal alkene and an arene (with styrene) and of a keto function (with 2-butanone). Reference Ru NPs were synthesized by

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adding two equivalents of bis(trimethylsilyl)amine (HMDS, the ligand of the bimetallic NPs) on Ru(COD)(COT) in mesitylene and by stirring the mixture under 3 bar of H_2 at room temperature overnight.

As discussed in a previous work,^[6] ultrasmall Fe⁰ NPs selectively hydrogenated styrene to give ethylbenzene without touching the phenyl ring in the conditions used (3 bar $H_{2^{\prime}}$ room temperature). Moreover, Fe⁰ NPs were inactive for the hydrogenation of 2-butanone in the conditions used herein (in our previous work, a 7% conversion was observed at an H_2 pressure of 10 bar).

In the case of the use of pure ruthenium NPs as the catalysts, styrene was completely converted into ethylcyclohexane and 2-butanone was completely converted into 2-butanol with high yield, in both cases after 20 h under an H_2 pressure of 3 bar at room temperature and by using 5 mol% of Ru (Tables 2 and 3).

Table 2. Styrene hydrogenation under 3 bar H_2 at room temperature during 24 h using 5 mol% of NPs as the catalyst and mesitylene as the solvent: influence of the NPs metallic composition on the reaction selectivity.

Entry	NPs	Styrene conv. ^[a] [%]	Ethylbenzene ^[a] yield [%]	Ethylcyclohexane yield ^[a] [%]
1	Fe⁰	>99	>99	0
2	Ru⁰	>99	0	>99
3	FeRu (1:1)	>99	75	1
4	FeRu (1:0.5)	>99	90	0
5	FeRu (1:0.2)	>99	95	0
6	FeRu (1:0.1)	>99	91	0

[a] Determined by using GC with *n*-dodecane as an internal standard.

Table 3. 2-Butanone hydrogenation under 3 bar H_2 at room temperature during 24 h using 5 mol% of NPs as the catalyst and mesitylene as the solvent: influence of the molar ratio of iron to ruthenium on the reaction activity.

Entry	NPs	2-Butanone conv. ^[a] [%]	2-Butanol yield ^[a] [%]		
1	Fe ⁰	0	0		
2	Ru ^o	>99	>99		
3	FeRu (1:1)	>99	70		
4	FeRu (1:0.5)	>99	92		
5	FeRu (1:0.2)	78	68		
6	FeRu (1:0.1)	67	44		
[a] Determined by using GC with <i>n</i> -dodecane as an internal standard.					

The bimetallic FeRu NPs displayed basically the same reactivity as the Fe⁰ NPs, that is, hydrogenation of the vinyl group but not of the arene moiety. Only in the case of high ruthenium loading, we observed some hydrogenation to ethylcyclohexane. This is consistent with the fact that hydrogenation of arenes occurs on a nanocrystal face, which, in the present case, needed to be exclusively of ruthenium. Statistically, this situation is not met for the present RuFe NPs. However, these bimetallic NPs could hydrogenate 2-butanone into 2-butanol with a conversion increasing as a function of the increased number of Ru equivalents in the mild conditions used (3 bar H_2 , room temperature, 24 h, 5 mol% NPs). In principle, only one surface ruthenium atom is necessary to hydrogenate the C=O bond. NPs at very low ruthenium loading (0.1 Ru:1 Fe) selectively hydrogenated both styrene into ethylbenzene and butanone into butanol (Table 2, entry 6; Table 3, entry 6). Although the reaction conditions were far from optimum, these results are interesting in that the selectivity of the hydrogenation reaction could be easily tuned by doping iron NPs with ruthenium metal.

Conclusions

FeRu nanoparticles were synthesized by a simple chemical route consisting of the co-decomposition of $\{Fe[N(Si(CH_3)_3)_2]_2\}_2$ and Ru(cyclooctadiene)(cyclooctatriene) under an H₂ pressure of 3 bar at 150 °C overnight. Thus, ultrasmall FeRu nanoparticles of approximately 1.8 nm were obtained. Structural characterization methods (TEM, high-resolution TEM, scanning transmission electron microscopy combined with energy-dispersive X-ray analysis, and wide-angle X-ray scattering analysis) proved the bimetallic composition of the nanoparticles. A magnetic study on a superconducting quantum interference device demonstrated the ferromagnetic behavior of the FeRu nanoparticles and showed that their magnetization decreased with the ruthenium content of the particles. Surface state studies (hydride titration and IR spectroscopy on CO-exposed nanoparticles) revealed that the FeRu nanoparticles were not oxidized and, therefore, suitable for hydrogenation reaction.

The catalytic properties of bimetallic FeRu nanoparticles in the hydrogenation of styrene and 2-butanone were investigated to elucidate the influence of the presence of the two metals on the hydrogenation reactions. FeRu nanoparticles could selectively hydrogenate styrene to ethylbenzene and catalyzed the hydrogenation of 2-butanone to 2-butanol with good yields. Therefore, the present work is a case study on fine-tuning the reactivity of nanocatalysts and adjusting their selectivity for a given reaction. The next step will be to apply this methodology to the reduction of more complex molecules.

Experimental Section

Preparation of FeRu bimetallic NPs

The FeRu NPs were prepared in the same conditions as those used for the synthesis of ultrasmall Fe⁰ NPs.^[6] The method consisted of the simultaneous decomposition of {Fe[N(Si(CH₃)₃)₂]₂} (1 mmol, 376.5 mg) and (η⁴-1,5-cyclooctadiene)(η⁶-1,3,5-cyclooctatriene)ruthenium(0) [Ru(COD)(COT)] in mesitylene (20 mL) under a H₂ pressure of 3 bar at 150 °C overnight. The quantity of the ruthenium complex was adjusted to the desired molar ratio of iron to ruthenium (1, 0.5, 0.2, and 0.1 equiv. of Ru corresponding to 1 mmol, 315.4 mg; 0.5 mmol, 157.7 mg; 0.2 mmol, 63.1 mg; and 0.1 mmol, 31.5 mg of Ru(COD)(COT)). After the reaction time, the solution turned from dark green to black in each case. The solution was

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then dried under vacuum to remove the solvent and to give a black powder in all cases.

Preparation of FeRu bimetallic NPs in the presence of hexadecylamine

FeRu NPs with a molar ratio of iron to ruthenium equal to 1 were synthesized in the presence of HDA. ${Fe[N(Si(CH_3)_3)_2]_2}_2$ (0.5 mmol, 188.3 mg), [Ru(COD)(COT)] (0.5 mmol, 157.7 mg) and HDA (1.5 mmol, 362.2 mg) were mixed together in mesitylene (10 mL) under an inert atmosphere. The mixture was then pressurized to three bars of dihydrogen and heated at 150 °C overnight. At the end of the reaction, a black precipitate and a green supernatant were observed. After removing of the supernatant, the black precipitate was washed with toluene and then dried under vacuum to give a black powder.

Characterization

FeRu bimetallic NPs were characterized by TEM. Conventional images were obtained by using JEOL1011 and JEOL1400 microscopes operated at 100 kV and 120 kV, respectively. HRTEM and STEM images were obtained by using a JEOL2100F microscope operated at 200 kV and equipped with a high-angle annular dark-field detector and an EDX spectrometer. Crystallographic characterizations were conducted by WAXS performed at CEMES–CNRS. Samples were sealed in 1 mm diameter Lindemann glass capillaries. Data collection was performed by using a dedicated two-axis diffractometer with graphite-monochromated MoK_{α} radiation (λ = 0.7107 Å). Magnetic studies were recorded on a SQUID (MPMS Quantum Design 5.5). IR spectra were recorded on a Perkin–Elmer GX2000 spectrometer in the wavelengths range of 4000–400 cm⁻¹.

Catalytic hydrogenation reactions

The as-prepared solutions of NPs in mesitylene were used directly for catalysis. The concentration of the catalyst solution was 5 mol% and the amount of the substrates used (styrene and 2-butanone) was 2 mmol. The reactions were conducted in a Fischer– Porter vessel under H₂ (3 bar) at RT during 24 h. At the end of the reaction, the Fischer–Porter vessel was depressurized and the internal standard (*n*-dodecane) was added to the reaction mixture for analysis by gas chromatography (GC Perkin–Elmer Clarus 500).

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Keywords: electron microscopy · iron · hydrogenation · nanoparticles · ruthenium

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