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Bimetallic Fe_xPt_{100-x} Nanoparticles Immobilized on Supported Ionic Liquid Phases as Hydrogenation and Hydrodeoxygenation Catalysts: Influence of the Metal Content on Activity and Selectivity

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ABSTRACT

Iron-platinum nanoparticles of tunable Fe:Pt ratios were immobilized on an imidazolium-based supported ionic liquid phase (SILP). The resulting Fe_xPt_{100-x}@SILP materials were characterized and applied in catalysis. Electron microscopy confirmed the formation of small, well-dispersed, bimetallic nanoparticles in all the investigated materials. Magnetometry measurements evidenced a clear influence of the Fe:Pt ratio on the oxidation state of Fe in Fe_xPt_{100-x}@SILP. In particular, Fe appeared in the metallic state at x≤40, whereas partial oxidation was observed at x≥60. The catalytic properties of Fe_xPt_{100-x}@SILP materials were probed using the hydrogenation and hydrodeoxygenation of benzylic ketones as a model reaction. The Fe:Pt ratio of the nanoparticles was found to have a critical influence on the observed activity and selectivity, with clear synergistic effects. In particular, by diluting Pt with Fe sites, the ability of Fe_xPt_{100-x}@SILP catalysts to hydrogenate 6-membered aromatic rings was shut down for x≥40, while C=O hydrogenation activity was preserved. In addition, Fe₄₀Pt₆₀@SILP showed excellent hydrodeoxygenation activity and selectivity with acetophenone derivatives in the absence of acid additives. This remarkable reactivity, out of reach for monometallic Pt@SILP, is attributed to the enhanced oxophilicity of Fe in FePt catalysts favoring C=O activation and cleavage.

KEYWORDS

bimetallic nanoparticles, supported ionic liquid phases, platinum, iron, hydrogenation, hydrodeoxygenation, catalysis, magnetism

INTRODUCTION

Most of the industrial hydrogenation processes are conducted in the presence of heterogeneous catalysts. Noble metal catalysts such as Adams catalyst¹ or palladium black² are in use for more than

100 years due to their high activity and reusability. However, improvements in terms of selectivity and functional groups tolerance require continuous advancement in catalyst design for different fields of chemistry, as *e.g.* fine chemicals synthesis, pharmaceutical or agrochemical industry. In addition, the diversification of carbon feedstock associated to the rise of renewable resources represents a challenge, making the development of new catalytic systems of crucial importance.³ Different strategies were developed to tune the selectivity of heterogeneous catalysts by modification of electronic or/and steric properties of the active surface.⁴ Particularly, the design of bimetallic nanoparticles (NPs) has attracted tremendous attention since synergetic interactions between different metals showed to unlock selectivities that cannot be reached with monometallic catalysts.⁵⁻⁹ For example, the alloying of noble metals with 3d metals provided selectivity control in the hydrogenation or hydrodeoxygenation (HDO) of various functionalities including alkynes, aldehydes and ketones, carboxylic acids, nitroaromatics, amides, etc.¹⁰⁻¹⁹ In this context, the controlled preparation of well-defined nanoparticles varying systematically the composition of the two distinct metal components is of great importance. Based on an organometallic approach for the assembly of nanoparticles on molecularly modified surfaces,²⁰ our groups reported recently the versatile synthesis of $\text{Fe}_x\text{Ru}_{100-x}$, $\text{Co}_x\text{Ru}_{100-x}$, and $\text{Co}_x\text{Rh}_{100-x}$ NPs on supported ionic liquid phases supports (SILPs). The application of these $\text{M1}_x\text{M2}_{100-x}@SILP$ materials in catalysis evidenced the remarkable influence of the nature of the “diluting” 3d metal M1 and its relative ratio to the noble metal M2 on the overall hydrogenation performance.²¹⁻²³ In particular, synergistic effects were observed for the hydrogenation of aromatic ketones, with an enhancement of C=O hydrogenation activity for bimetallic NPs, while aromatic ring hydrogenation was completely shut down for specific metal ratios.

In order to further explore the potential of bimetallic NPs, we set our goal to systematically investigate NPs composed of Fe and Pt of defined compositions. $\text{Fe}_x\text{Pt}_{100-x}$ NPs have been widely studied in the past decade, in particular for their excellent magnetic properties.²⁴⁻²⁶ In catalysis, $\text{Fe}_x\text{Pt}_{100-x}$ NPs have been mainly explored for the selective hydrogenation of conjugated aldehydes.²⁷⁻²⁹ For example, Bai and co-workers synthesized and characterized Pt-based nanowires, which they applied to the hydrogenation of cinnamaldehyde.³⁰ While monometallic Pt catalysts hydrogenated both C=C and C=O double bonds to produce 3-phenyl-propanol, bimetallic FePt materials hydrogenated only the aldehyde functionality, leaving the C=C untouched. Applications in oxygen reduction reaction,^{31,32} hydrogenation of unsaturated hydrocarbons³³ and nitroaromatics^{34,35} were also punctually reported. However, to the best of our knowledge, systematic investigations of the reactivity of supported $\text{Fe}_x\text{Pt}_{100-x}$ NPs of tunable composition for the reduction of ketones are missing. They are nevertheless highly desirable, since the known enhanced electrophilic properties of Fe in $\text{Fe}_x\text{Pt}_{100-x}$ alloys^{36,37} may provide access to reactivities that are out of reach for previously reported [noble metal-3d metal] bimetallic alloys.

Herein, we present the synthesis, characterization, and application of bimetallic $\text{Fe}_x\text{Pt}_{100-x}$ NPs of finely tunable Fe:Pt ratio immobilized on an imidazolium-based SILP support. The resulting $\text{Fe}_x\text{Pt}_{100-x}@SILP$ materials were characterized using a variety of techniques including electron microscopy (TEM, SEM-EDX), wide-angle X-Ray scattering (WAXS), infrared spectroscopy (IR), and vibrating-sample magnetometry (VSM). In particular, studying the magnetic properties of $\text{Fe}_x\text{Pt}_{100-x}$ NPs by VSM proved to be a simple and powerful approach to collect information about the oxidation state of Fe. $\text{Fe}_x\text{Pt}_{100-x}@SILP$ materials were applied to the reduction of aromatic ketones, a transformation of great importance not only for the fine chemical and pharmaceutical industries, but also for the conversion of biomass feedstock to value-added chemicals.³⁸ The influence of the Fe:Pt metal ratio on activity and selectivity was explored in a systematic manner, evidencing strong synergistic effects.

RESULTS AND DISCUSSION

1 Synthesis of the $\text{Fe}_x\text{Pt}_{100-x}\text{@SILP}$ materials

An imidazolium-based SILP was used as a support for its proven ability to facilitate the formation and stabilization of mono- and bimetallic nanoparticles.^{22,23,39,40} The SILP support used in the present study was previously characterized by thermogravimetric analysis, and found thermally stable up to 350 °C.³⁹ It is chemically stable in most organic solvents, and can be used both under batch and continuous flow conditions. Preparation of the support was performed following a previously published procedure.³⁹ Briefly, the silane-functionalized IL [1-butyl-3-(3-triethoxysilylpropyl)imidazolium]NTf₂ (NTf₂ = bis(trifluoromethane)sulfonimide) was chemisorbed on dehydroxylated SiO₂ by silanization with a loading of 0.7 mmol.g⁻¹. The synthesis of bimetallic $\text{Fe}_x\text{Pt}_{100-x}$ NPs (with $x = 100, 80, 60, 50, 40, 20, 0$) was achieved by adapting an organometallic approach developed by our groups for bimetallic FeRu, CoRu, and CoRh@SILP.^{21–23} This approach involved the decomposition of the metal precursors {Fe[N(Si(CH₃)₃)₂]₂}₂ and [Pt₂(dba)₃] (dba = dibenzylideneacetone) *in situ* in the presence of the SILP material under H₂ (3 bar) at 150 °C for 18 h with a mixture of anisole and THF as a solvent, to ensure a good solubility of both precursors (total metal loading = 0.35 mmol.g⁻¹) (Figure 1). {Fe[N(Si(CH₃)₃)₂]₂}₂ and [Pt₂(dba)₃] were used since they possess similar decomposition rates. Using [Pt(nbe)₃] or [Pt(Me)₂(cod)] (nbe = norbornene, cod = 1,5-cyclooctadiene) resulted in large agglomerates (Figure S1). This synthetic approach provided access to a wide range of bimetallic $\text{Fe}_x\text{Pt}_{100-x}\text{@SILP}$ catalysts in which the Fe:Pt ratio was finely tuned by adjusting the relative amounts of precursors. To evaluate the influence of the SILP on the NP formation and catalytic properties, $\text{Fe}_x\text{Pt}_{100-x}$ NPs were also immobilized on unmodified silica ($\text{Fe}_x\text{Pt}_{100-x}\text{@SiO}_2$) following the same procedure to act as reference materials.

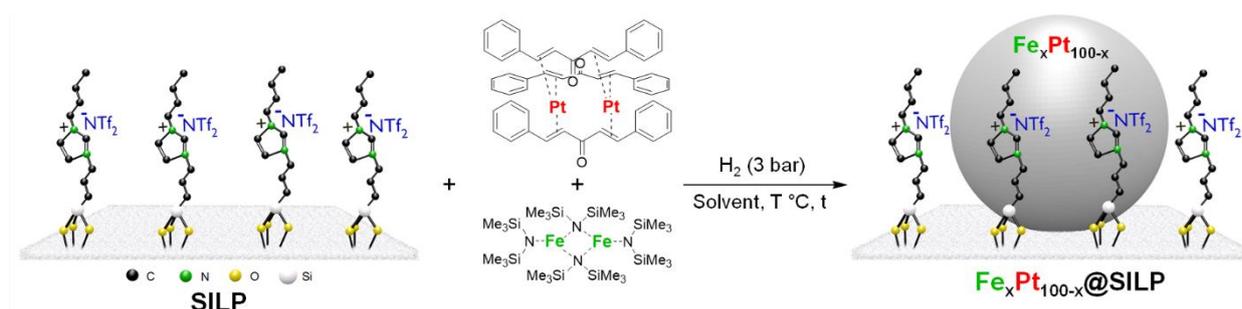


Figure 1. Illustration of our synthetic approach to $\text{Fe}_x\text{Pt}_{100-x}\text{@SILP}$ materials.

2 Characterization of the $\text{Fe}_x\text{Pt}_{100-x}\text{@SILP}$ materials

Characterization of the $\text{Fe}_x\text{Pt}_{100-x}\text{@SILP}$ materials by transmission electron microscopy (TEM) evidenced the formation of small NPs (1.5 – 2.5 nm) on the SILP for all the Fe:Pt ratios (Figure 2a, Figures S2 and S3). Pair distribution functions obtained by WAXS confirmed the face centered cubic structure for the NPs rich in platinum with correlation distances similar to the sizes obtained by TEM, thus proving the monocrystallinity of the nanoobjects (~2.5 nm for pure Pt and ~2.0 nm for $\text{Fe}_{40}\text{Pt}_{60}$ – Figure S4). On the contrary, for the $\text{Fe}_{80}\text{Pt}_{20}\text{@SILP}$ samples, rich in iron, only the Pt-Pt distance and its harmonics could be observed on correlation distances smaller than 1 nm. This finding indicates that the objects were significantly less crystallized, suggesting some amorphization due to a large amount of Fe. High resolution imaging using HAADF-STEM and elemental mapping using STEM-EDX confirmed the bimetallic nature of $\text{Fe}_x\text{Pt}_{100-x}$ NPs, as exemplified for $\text{Fe}_{40}\text{Pt}_{60}\text{@SILP}$ (Figure 2 and Figure S5; STEM = scanning transmission electron microscopy; HAADF = high angle annular dark field; EDX = energy-dispersive X-ray spectroscopy). Total metal loadings and ratios of metals were determined by SEM-EDX (SEM = scanning electron microscopy). The results are summarized in Table S1 and agree with theoretical values. TEM of $\text{Fe}_{40}\text{Pt}_{60}\text{@SiO}_2$ nanomaterials showed the formation of well-dispersed NPs

of 1.9 nm (Figure S3d). SEM-EDX evidenced only slight deviations from the theoretical loading and metal ratio, similar to the results obtained for $\text{Fe}_x\text{Pt}_{100-x}@\text{SILP}$ systems (Table S1).

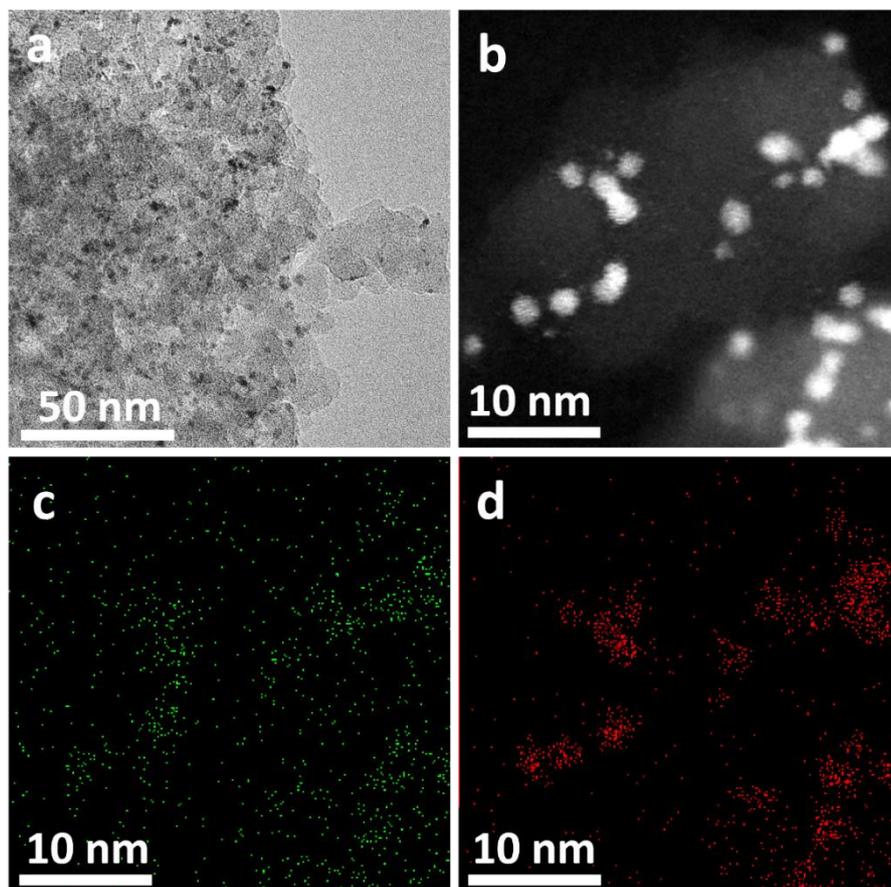


Figure 2. Characterization of $\text{Fe}_x\text{Pt}_{100-x}@\text{SILP}$ by electron microscopy, illustrated for $\text{Fe}_{40}\text{Pt}_{60}@\text{SILP}$. a) TEM ($d = 2.0 \pm 0.4$ nm); b) STEM-HAADF; c) STEM-HAADF-EDX elemental mapping of Fe-K; d) STEM-HAADF-EDX elemental mapping of Pt-L.

CO adsorption studies with FT-IR in transmission mode were performed for $\text{Fe}_x\text{Pt}_{100-x}@\text{SILP}$ materials (Figure S6), since this technique allows to investigate the alterations in electronic density on the surface of metal NPs. $\text{Fe}_x\text{Pt}_{100-x}@\text{SILP}$ powders were exposed to a CO atmosphere (3 bar) overnight, followed by CO gas removal under vacuum and analysis of the samples by FT-IR in a glovebox. For all samples, a vibration band of adsorbed CO was found in the $2018\text{--}2049\text{ cm}^{-1}$ range, which is characteristic of a linear adsorption mode of the CO molecule on Pt (Figure 3).^{41,42} The vibrations of bridged CO that are usually present at the region of $1800\text{--}1900\text{ cm}^{-1}$ are hindered by the overtone of Si-O in the framework of the silica support (Figure S6).⁴³ While the CO vibration band was observed at 2049 cm^{-1} on $\text{Pt}_{100}@\text{SILP}$, a red shift was systematically observed on bimetallic $\text{Fe}_x\text{Pt}_{100-x}@\text{SILP}$ materials ($\text{Fe}_{20}\text{Pt}_{80}$: 2037 cm^{-1} ; for $\text{Fe}_{40}\text{Pt}_{60}$: 2018 cm^{-1} ; $\text{Fe}_{60}\text{Pt}_{40}$: 2034 cm^{-1} , $\text{Fe}_{80}\text{Pt}_{20}$: 2043 cm^{-1}). These results suggest that Fe can donate electronic density to more electronegative Pt, in agreement with observations made by other groups.^{44,45} Interestingly, the red shift does not follow a linear trend as a function of the Fe content. This tendency may be explained by a change of the oxidation state of iron as a function of the Fe:Pt ratio. In a previous study on $\text{Fe}_x\text{Ru}_{100-x}@\text{SILP}$ materials, X-Ray absorption spectroscopy (XAS) evidenced the presence of metallic iron in the iron-poor alloys, but mainly oxidized iron in iron-rich alloys (Fe content > 50%).²¹ Since oxidized iron species are electrophilic and can withdraw electron density, an increase in the amount of oxidized iron may be a reason for the smaller red shift observed with $\text{Fe}_{60}\text{Pt}_{40}@\text{SILP}$ and $\text{Fe}_{80}\text{Pt}_{20}@\text{SILP}$ as compared to $\text{Fe}_{40}\text{Pt}_{60}@\text{SILP}$.

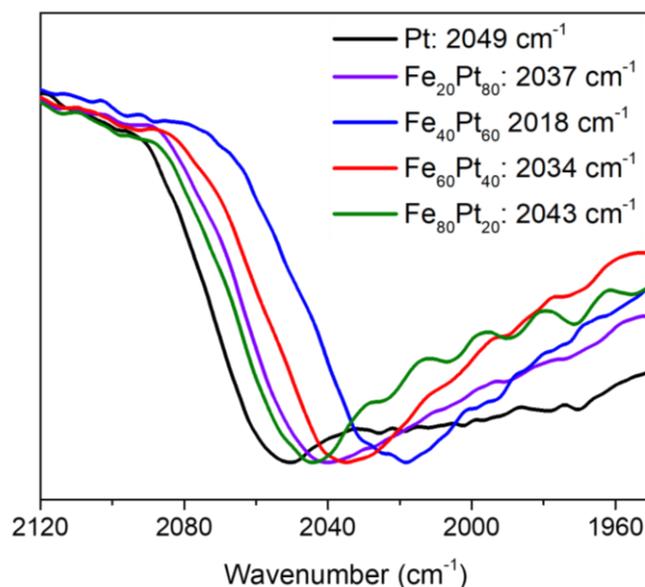


Figure 3. Transmission IR spectra of $\text{Fe}_x\text{Pt}_{100-x}@SILP$ after CO exposure – zoom on the terminal CO absorption band.

While catalysts are often studied by synchrotron-based XAS to determine their oxidation state, magnetometry, which is a fairly accessible technique, can be successfully used for magnetic materials such as Fe-, Co-, or Ni-containing systems. Indeed, the evolution of the magnetization M vs the applied magnetic field H , combined with the temperature dependence of the low field magnetization M vs T , allow distinguishing between a ferromagnetic state, expected for some of the purely metallic materials, and an antiferromagnetic/ferrimagnetic state, observed for oxidized materials. M vs H curves of $\text{Fe}_x\text{Pt}_{100-x}@SILP$ with $x = 40, 60, 80$ are presented and compared with pure $\text{Fe}@SILP$ on Figure 4a. For every catalyst, the 5 K magnetization curve does not saturate at high field but exhibit a linear contribution, typical for paramagnetic species. Such behavior is commonly observed for small nanoparticles⁴⁶ and arises from the large proportion of surface atoms which, depending on the nature of the ligands and their coordination mode, can exhibit paramagnetic properties. The paramagnetic contribution is fairly similar for all the catalysts, in agreement with the same mean diameter of the NPs determined by TEM. To further analyze the core properties, the paramagnetic contribution was subtracted as shown in Figure S7a and the resulting hysteresis loops were compared (Figure S8a). The spontaneous magnetization (M_{spont}) defined as the maximum magnetization after paramagnetic subtraction, was determined for each sample. Interestingly, the M_{spont} values were fairly similar for $\text{Fe}_{40}\text{Pt}_{60}@SILP$ and $\text{Fe}_{60}\text{Pt}_{40}@SILP$ but diminished significantly for larger Fe content, the lower value being obtained for pure Fe NPs (Table 1). Since Fe(0) atoms have a larger magnetic moment than Pt(0) atoms,⁴⁷ one would have expected an opposite trend for purely metallic nanoparticles. However, this trend is consistent with a partial oxidation of the iron-rich nanoparticles, which was further confirmed by the analysis of the coercive field. Positive and negative coercive fields (H_c^+ and H_c^-) correspond to the field at which the magnetization is null (Figure S7b). They are symmetrical for $\text{Fe}_x\text{Pt}_{100-x}@SILP$ NPs for $x = 40$ and 60 with slightly smaller values of H_c for $\text{Fe}_{60}\text{Pt}_{40}@SILP$ (Figure S8b and Table 1). However, the hysteresis cycle is shifted towards the negative value for $x = 80$ and 100 , as characterized by the exchange bias field $H_{ex} = \frac{H_c^+ + H_c^-}{2}$ (Table 1). The appearance of such a bias is characteristic of the presence of an oxide shell on the NPs.⁴⁶ To further confirm this conclusion, the $\text{Fe}_{40}\text{Pt}_{60}@SILP$ NPs were deliberately exposed to air for 7 days (Figure 4b). As expected, the spontaneous magnetization was reduced by 75%, the coercive field decreased by 40% and an exchange bias field appeared.

Additionally, the temperature evolution of the magnetization was investigated following the classical zero field cooling / field cooling experiments (ZFC/FC). At first, the samples were cooled down from 300 K to 5 K in the absence (resp. in presence) of external magnetic field. The so-called ZFC (resp. FC) magnetization was recorded during the warming up from 5 K to 300 K while applying a modest field of $\mu_0H = 10$ mT. ZFC/FC plots recorded for $\text{Fe}_x\text{Pt}_{100-x}@\text{SILP}$ samples display the usual signatures observed in magnetic nanoparticle systems (Figure S9). The curves overlap at high temperatures and exhibit a paramagnetic-like decay with increasing temperature, indicating the superparamagnetic behavior of the particles. The ZFC curve recorded for $\text{Fe}_{40}\text{Pt}_{60}@\text{SILP}$ and $\text{Fe}_{60}\text{Pt}_{40}@\text{SILP}$ follows a typical behavior of ferromagnetic NPs, namely a clear maximum on the ZFC curve, corresponding to the blocking temperature T_b , which indicates the temperature of the transition from the “frozen” ferromagnetic state to the superparamagnetic state. From 5 K to T_b the magnetization exhibits a monotonal increase. On the contrary, the ZFC curves recorded for $\text{Fe}_{80}\text{Pt}_{20}@\text{SILP}$, $\text{Fe}@\text{SILP}$ and oxidized $\text{Fe}_{40}\text{Pt}_{60}@\text{SILP}$ NPs showed a decrease at very low temperature, before increasing again up to T_b (Figure 4c). Such a behavior at low temperature is a signature of antiferromagnetic states due to the presence of oxides, thus again confirming that the particles are partially oxidized for an iron content higher than 60%.

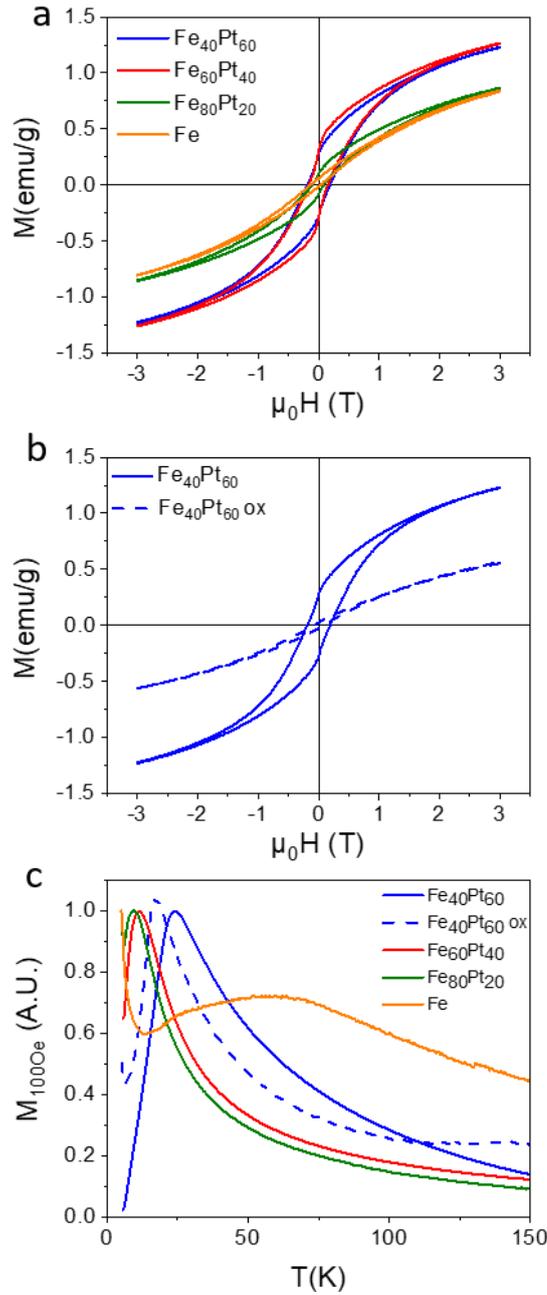


Figure 4. a) Hysteresis cycle (M vs H curve) recorded between ± 3 T at 5 K for the different catalyst $\text{Fe}_x\text{Pt}_{100-x}@SILP$; b) 3 T hysteresis cycle recorded at 5 K for $\text{Fe}_{40}\text{Pt}_{60}@SILP$ catalyst as prepared (blue line) and after 7 days of air exposure (dash line); c) M vs T curve recorded at $\mu_0H = 10$ mT after zero-field cooling procedure.

Table 1. Coercive field, exchange bias field, and saturation magnetization values for different $\text{Fe}_x\text{Pt}_{100-x}@SILP$ materials.

Sample	μ_0H_c , mT	μ_0H_{ex} , mT	M_{spont} , emu/g
$\text{Fe}_{40}\text{Pt}_{60}@SILP$	220	-	0.77
$\text{Fe}_{40}\text{Pt}_{60}@SILP$ (oxidized)	130	-5	0.20
$\text{Fe}_{60}\text{Pt}_{40}@SILP$	180	-	0.82
$\text{Fe}_{80}\text{Pt}_{20}@SILP$	115	-15	0.44
Fe	125	-75	0.36

H_c : coercive field, H_{ex} : exchange bias field; M_{spont} corresponds to the spontaneous magnetization, calculated after the removal of the paramagnetic contribution.

3 Catalysis

The catalytic performance of the $\text{Fe}_x\text{Pt}_{100-x}@\text{SILP}$ materials was studied using the hydrogenation of acetophenone (**1**) as a model reaction (Figure 5a). Selective reduction of aromatic ketones is a synthetically important transformation since the formed secondary alcohols are used as versatile building blocks and as target compounds in fragrances and flavors.^{48,49} In a more general context, reduction of ketones is an important transformation for biomass valorization.^{16,50,51} Substrate **1** possesses an aromatic ring and a benzylic ketone, giving the opportunity to probe the reactivity of $\text{Fe}_x\text{Pt}_{100-x}@\text{SILP}$ catalysts for different prototypical functional groups. The hydrogenation of **1** can proceed through two different pathways, with either 1-phenylethanol (**1a**) or 1-cyclohexylethan-1-one (**1b**) as intermediates before reaching the fully saturated product 1-cyclohexylethanol (**1c**). Eventually, HDO of **1a** and **1c** can also be observed, typically using multifunctional catalytic systems possessing acidic functionalities.^{50,52,53} Figure 5b shows conversions and product yields as a function of the Pt content in $\text{Fe}_x\text{Pt}_{100-x}$ NPs, where all the reactions were performed under identical conditions ($T = 175^\circ\text{C}$, $p(\text{H}_2) = 50$ bar, $t = 16$ h, solvent - heptane). Monometallic $\text{Fe}@\text{SILP}$ did not show any activity under these conditions, consistent with previous observations.²² Increasing the Pt content in $\text{Fe}_{80}\text{Pt}_{20}@\text{SILP}$ resulted in 34% conversion with **1a** (30%) as a major product. Full conversion was reached using $\text{Fe}_{60}\text{Pt}_{40}@\text{SILP}$, still with **1a** (56%) as a main product. Interestingly, a large amount of ethylbenzene (**1d**, 44%) was observed as well, indicating a promising hydrodeoxygenation activity of $\text{Fe}_x\text{Pt}_{100-x}@\text{SILP}$ catalysts. The yield of **1d** was substantially higher using $\text{Fe}_{40}\text{Pt}_{60}@\text{SILP}$, reaching 83% with only traces of aromatic ring hydrogenation. Remarkably, such hydrodeoxygenation activity of unsubstituted acetophenone was not observed with other bimetallic NPs immobilized on the same SILP.^{21–23} Further increasing the Pt content led to a switch in the product distribution, with the formation of **1c** as the major product with $\text{Fe}_{20}\text{Pt}_{80}@\text{SILP}$ and $\text{Pt}_{100}@\text{SILP}$ (53% and 97%, respectively). Strikingly, only traces of hydrodeoxygenated product with saturated ring (ethylcyclohexane **1e**) could be observed when using $\text{Pt}_{100}@\text{SILP}$. Based on this result we assume that 80% of Pt led to the formation of Pt atom ensembles that were big enough to enable planar adsorption and hydrogenation of the aromatic ring.⁵⁴ The same catalytic test was also performed with the reference $\text{Fe}_{40}\text{Pt}_{60}@\text{SiO}_2$. In this case, together with 43% of the product **1d**, a large amount of products with saturated ring **1c** (14%) and **1e** (43%) was formed. Since Pt ensembles are responsible for ring hydrogenation as it was observed for $\text{Fe}_{20}\text{Pt}_{80}@\text{SILP}$ and $\text{Pt}_{100}@\text{SILP}$, this result indicated that it might be difficult to achieve a controlled formation of bimetallic $\text{Fe}_{40}\text{Pt}_{60}$ NPs on unmodified silica support, in agreement with previous observations.^{22,23,40}

HDO of acetophenones typically requires the presence of an acid additive,^{52,53,55–59} activating substituents,^{40,60} or high temperatures.⁶¹ For example, using similar reaction conditions (50 bar H_2 , 175°C , 16 h), an acidic $\text{Fe}_{25}\text{Ru}_{75}@\text{SILP}-\text{SO}_3\text{H}$ catalyst was required to produce 91% of **1d** from **1**.⁵³ Meanwhile, the use of $\text{Fe}_{25}\text{Ru}_{75}@\text{SILP}$ without acidic sites resulted only in 21% of **1d**.⁶⁰ In FePt bimetallics, Fe species are known to possess a Lewis acidic character, allowing them to act as adsorption sites and activate CO or NO_2 groups for example.^{62,63} Therefore, we attribute the observed HDO activity to the presence of oxophilic iron sites in the $\text{Fe}_x\text{Pt}_{100-x}$ serving as weak Lewis acids and assisting selective activation and cleavage of aromatic C=O. This hypothesis is supported by several studies showing that incorporation of oxophilic 3d metals (in particular Fe or Co) in Pt or Pd NPs facilitates C-O adsorption and cleavage promoting the HDO of furfural derivatives.^{17,18,37,64} For example, Luo and co-workers reported the selective hydrodeoxygenation of 5-hydroxymethylfurfural to dimethylfuran using Pt_3Co_2 NPs composed of a Pt-rich core and a Co_2O_3 surface.¹⁷ The authors showed through DFT studies the importance of this cobalt oxide surface to promote HDO activity.

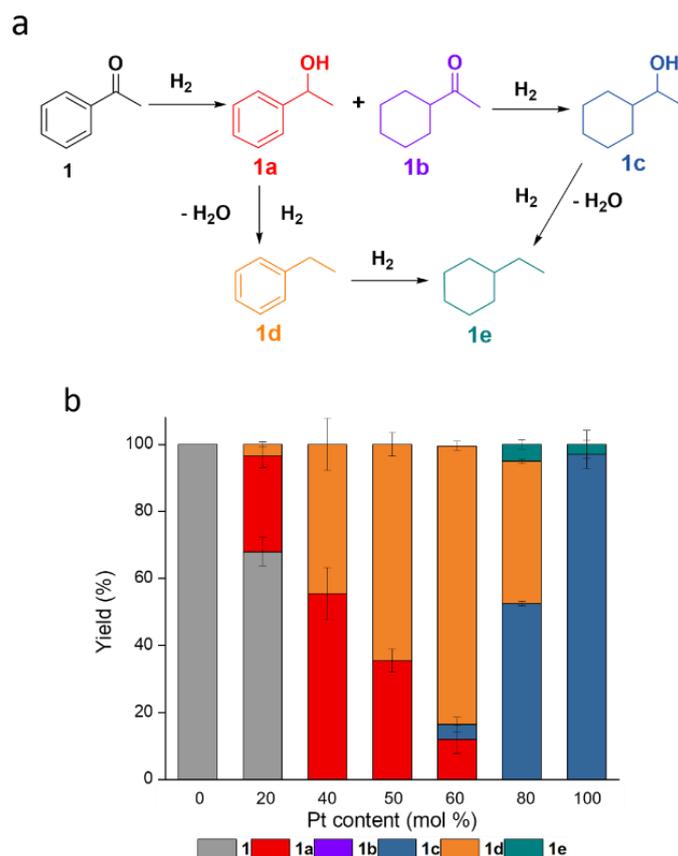


Figure 5. a) Reaction pathways for the reduction of acetophenone; b) reduction of acetophenone using a series of $\text{Fe}_x\text{Pt}_{100-x}$ @SILP catalysts with different Fe:Pt ratios. Reaction conditions: Catalyst (0.005 mmol metal), **1** (0.125 mmol, 25 eq.), heptane (0.5 mL), H_2 (50 bar), 175 °C, 16 h. Yields were determined by GC-FID using tetradecane as an internal standard. Data points are average values of a minimum of two experiments and error bars represent standard deviations.

To gain additional insight into the reactivity of the catalysts, time profiles of product formation were recorded using $\text{Fe}_{40}\text{Pt}_{60}$ @SILP and $\text{Fe}_{20}\text{Pt}_{80}$ @SILP (Figure 6). With $\text{Fe}_{40}\text{Pt}_{60}$ @SILP, full conversion was observed after 1 h, with a product mixture composed of **1a** (55%), **1d** (43%, initial rate = 18 $\text{mmol}\cdot\text{L}^{-1}\cdot\text{mmol}_{\text{Pt}}^{-1}$), and traces of **1c** (2%). With increasing reaction time, **1a** was progressively converted into **1d**, giving the hydrodeoxygenated aromatic product **1d** in excellent yield and selectivity (95%) after 24 h. In this case, the hydrogenation clearly proceeded through the hydrogenation of the carbonyl moiety, while aromatic ring hydrogenation was shut down. Using $\text{Fe}_{20}\text{Pt}_{80}$ @SILP, a mixture of **1a** (22%), **1c** (50%), and **1d** (28%, initial rate = 8.5 $\text{mmol}\cdot\text{L}^{-1}\cdot\text{mmol}_{\text{Pt}}^{-1}$) was observed after 1 h, indicating that the reaction also proceeded through the intermediate **1a**, and that this catalyst is active for aromatic ring hydrogenation. Interestingly, extending the reaction time to 4 h led to a mixture of **1c** (52%) and **1d** (40%) that was not significantly further converted even after 16 h (52% and 42%, respectively). While the very slow hydrodeoxygenation of **1c** to **1e** can be related to the difficulty to form a stable carbocation intermediate from **1c**, the fact that **1d** was barely further hydrogenated to **1e** (4%) is more surprising, as $\text{Fe}_{20}\text{Pt}_{80}$ @SILP clearly possesses aromatic ring hydrogenation activity. Thus, the hydrogenation of ethylbenzene (**1d**) was investigated with this catalyst under standard reaction conditions. Strikingly, only 2% conversion to ethylcyclohexane (**1e**) was observed with $\text{Fe}_{20}\text{Pt}_{80}$ @SILP after 16 h (Table S2), supporting the results of the time profile. In contrast, full conversion was achieved with the monometallic catalyst Pt@SILP, and with $\text{Fe}_{40}\text{Pt}_{60}$ @ SiO_2 . To identify the reaction intermediates formed when using the monometallic Pt@SILP catalyst, 2 h reactions were conducted with a larger substrate: catalyst ratio (1500 eq. of **1** with respect to Pt – Table S3). At 79% of conversion, both the unsaturated alcohol **1a** (52%) and the saturated ketone **1b** (13%) were observed, indicating

that both hydrogenation pathways occur simultaneously with Pt@SILP. However, **1a** being the major intermediate suggests that C=O hydrogenation proceeds faster than aromatic ring hydrogenation. Interestingly, for bimetallic $\text{Fe}_x\text{Pt}_{100-x}\text{@SILP}$ catalysts, the formation of intermediate **1b** was never observed, indicating a decrease in the rate of the aromatic ring hydrogenation upon addition of Fe. A similar behavior was previously observed with other bimetallic catalysts (*e.g.* FeRu, CoRu, CoRh),²¹⁻²³ and can be attributed to the absence of ensembles of 3-4 adjacent noble metal atoms required to hydrogenate 6-membered aromatic rings.^{22,23}

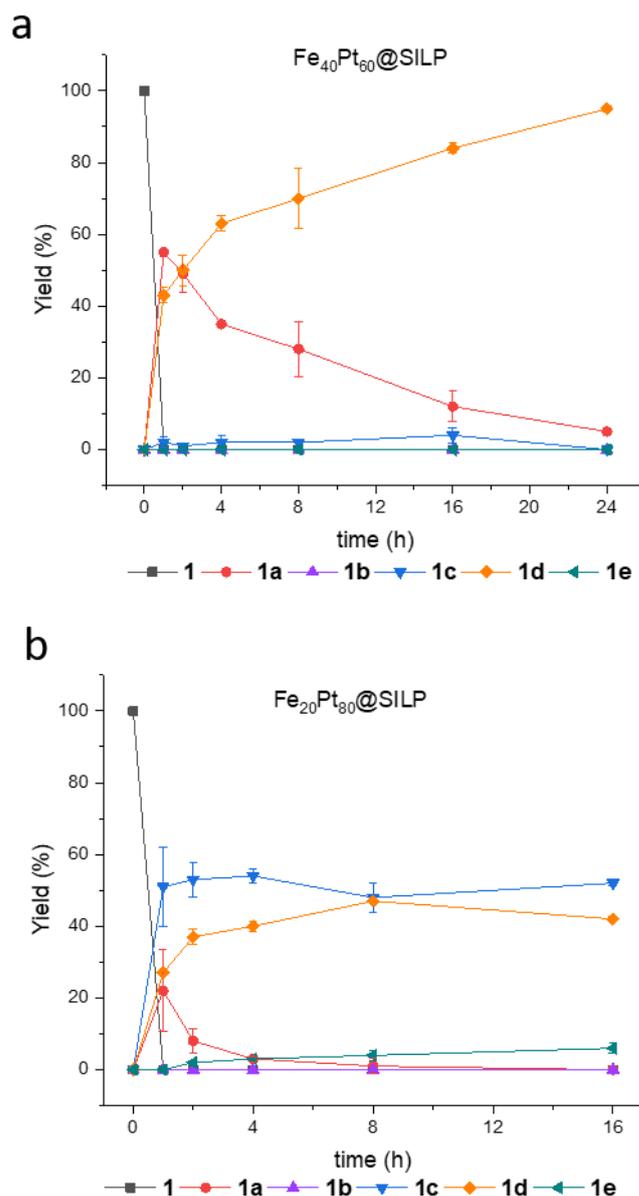
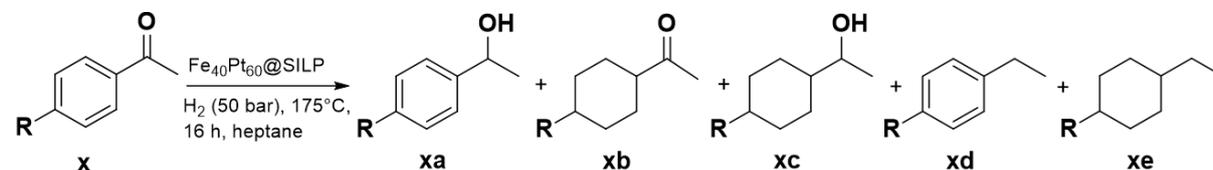


Figure 6. Time profiles of acetophenone hydrogenation recorded using a) $\text{Fe}_{40}\text{Pt}_{60}\text{@SILP}$, b) $\text{Fe}_{20}\text{Pt}_{80}\text{@SILP}$. Reaction conditions: Catalyst (0.005 mmol metal), **1** (0.125 mmol, 25 eq.), heptane (0.5 mL), H_2 (50 bar), 175°C. Yields were determined by GC-FID using tetradecane as an internal standard. Data points are average values of a minimum of two experiments and error bars represent standard deviations.

To explore the versatility of the $\text{Fe}_{40}\text{Pt}_{60}\text{@SILP}$ catalyst in hydrodeoxygenation reactions, para-substituted acetophenone derivatives were selected for a reaction scope and tested under standard conditions (50 bar of H_2 , 175°C, 16 h). The results are summarized in Table 2. High yields (70% - 99%) of the aromatic alkane products were obtained in all cases, without any aromatic ring hydrogenation.

Hydrodeoxygenation appeared to be facilitated by the presence of electron-donating substituents on the aromatic ring, while electron-withdrawing group such as CF₃ slowed down the reaction, in agreement with previous observations.⁶¹

Table 2. Selective hydrogenation of acetophenone derivatives using Fe₄₀Pt₆₀@SILP.



x	R	X (%)	Y xa (%)	Y xb (%)	Y xc (%)	Y xd (%)	Y xe (%)
1	H	>99	12	0	4	84	0
2	OCH ₃	>99	0	0	0	>99	0
3	CH ₃	>99	0	0	0	>99	0
4 ^a	Cl	>99	0	0	0	96	0
5 ^a	F	>99	1	0	0	97	0
6	CF ₃	>99	30	0	0	70	0

Reaction conditions: Catalyst (13.6 mg, 0.005 mmol metal), substrate (0.125 mmol, 25 eq.), heptane (0.5 mL), H₂ (50 bar), 175°C, 16 h. Conversion and yield were determined by GC-FID using tetradecane as internal standard. Data points are average value of minimum two experiments. X = conversion, Y = yield. ^a side product is **1d**.

CONCLUSIONS

In conclusion, new Fe_xPt_{100-x}@SILP materials with tunable ratios of Fe:Pt were synthesized and fully characterized with a combination of electron microscopy techniques, structural analysis by WAXS, FTIR spectroscopy, and magnetometry. Magnetometry is an uncommon tool to characterize catalytic materials, nevertheless it proved to be highly efficient in characterizing the oxidation degree of our magnetic catalyst, and act as a widely accessible alternative to XAS in synchrotron facilities. Catalytic performances of Fe_xPt_{100-x}@SILP materials were probed for the hydrogenation and hydrodeoxygenation of acetophenone derivatives. Both activity and selectivity were found to be highly sensitive to the Fe:Pt ratio. Monometallic Pt@SILP gave saturated alcohols, whereas having 40% Fe in the catalyst resulted in HDO of the ketone, while preserving aromaticity of the ring. The scope of substrates includes para-substituted acetophenones for which selective HDO was observed with a beneficial effect of electron-donating substituents. Importantly, HDO activity was not observed with FeRu@SILP, CoRu@SILP, or CoRh@SILP bimetallic catalysts previously reported by our groups. Thus, the remarkably high HDO activity of Fe₄₀Pt₆₀@SILP, without acid addition, is presumably originating from synergetic interactions between Pt and Fe. These results show that a careful control of the Fe:Pt ratio in Fe_xPt_{100-x}@SILP materials allows the preparation of multifunctional catalytic systems with tailor-made reactivity toward challenging transformations involving H₂ activation and transfer.

SUPPORTING INFORMATION

Experimental details, materials and methods, and supplementary characterization data.

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