**ABSTRACT:** The development of an efficient heterogeneous catalyst for storing H₂ into CO₂ and releasing it from the produced formic acid, when needed, is a crucial target for overcoming some intrinsic criticalities of green hydrogen exploitation, such as high flammability, low density, and handling. Herein, we report an efficient heterogeneous catalyst for both reactions prepared by immobilizing a molecular iridium organometallic catalyst onto a high-surface mesoporous silica, through a sol−gel methodology. The presence of tailored single-metal catalytic sites, derived by a suitable choice of ligands with desired steric and electronic characteristics, in combination with optimized support features, makes the immobilized catalyst highly active. Furthermore, the information derived from multinuclear DNP-enhanced NMR spectroscopy, elemental analysis, and Ir L₃-edge XAS indicates the formation of cationic iridium sites. It is quite remarkable to note that the immobilized catalyst shows essentially the same catalytic activity as its molecular analogue in the hydrogenation of CO₂. In the reverse reaction of HCOOH dehydrogenation, it is approximately twice less active but has no induction period.

**INTRODUCTION**

Energy transition from fossil to renewable fuels is the ultimate challenge of our society which might be successfully faced through the implementation of an efficient technology for producing “green” hydrogen, i.e., hydrogen derived from the photoelectrocatalytic splitting of water.¹⁻⁶ H₂ is surely a clean primary energy carrier having, nevertheless, with its high flammability, low density, and handling, some serious criticalities.⁷,⁸

An interesting alternative to using H₂ as such is to store it in the so-called liquid/solid hydrogen carriers and regenerate it when needed. One of the most promising H₂ carriers is formic acid (FA),⁹⁻¹² which can be generated by storing H₂ into CO₂, from which H₂ might be reformed by the reverse reaction.

\[ \text{H}_2 + \text{CO}_2 \rightleftharpoons \text{HCOOH} \]

Both forward and back reactions ask for suitable catalysts in order to be viable, and several efficient catalysts have been reported so far.⁹⁻¹² Supported nanoparticles of noble metals such as Pd and AuPd¹³⁻¹⁷ and, especially, organometallic complexes,¹⁸⁻³¹ mainly based on Fe,²¹⁻³¹ Ru,³²⁻⁴⁰ and Ir,⁴¹⁻⁴⁴ have shown promising catalytic performances in terms of both turnover numbers (TONs) and turnover frequencies (TOFs). Notably, Hazari and Bernskoetter reported a class of iron complexes (a and b in Scheme 1) capable of reaching very high values of TON (ca. 10⁶ in FA dehydrogenation and 6 × 10⁸ in...
CO₂ hydrogenation). Unfortunately, the conditions involve organic solvents and the presence of Lewis acids. Williams reported an Ir⁷-based complex (c in Scheme 1)⁴ with remarkable performance in FA dehydrogenation (TON value over 2 × 10⁴ with a maximum TOF of 3.7 s⁻¹) carried out in neat FA, whereas Nozaki developed an Ir⁸ pincer trihydride catalyst (complex d in Scheme 1)⁴⁵ very active in CO₂ hydrogenation (TON = 3.5 × 10⁶ and TOF = 1.5 × 10⁵ h⁻¹), operating in a basic aqueous solution, capable of catalyzing also FA dehydrogenation in 𝑃BuOH, in the presence of 𝑁Et₃.

Cp*Ir-based (Cp* = pentamethylcyclopentadienyl) complexes have been successfully exploited as efficient catalysts for both CO₂ hydrogenation and FA dehydrogenation in water, under mild conditions, without using any additive, except a base in the case of CO₂ hydrogenation.⁷⁶⁻⁷⁹

Remarkable results have been obtained by Himeda, Fujita, and co-workers using [Cp*Ir(R-pica)X] (pica = picolimamide) complexes (e and f in Scheme 1)⁵²,⁵³ in both FA dehydrogenation⁵⁵,⁵⁶,⁵⁷ and CO₂ hydrogenation.⁵³,⁵⁶⁻⁵⁸ Originally introduced by Watanabe and co-workers for the preparation of amine compounds,⁵⁹ [Cp*Ir(R-pica)X] complexes are a successful class of compounds that have been found to efficiently catalyze many other reactions including transfer hydrogenation in cell growth media,⁶⁰,⁶¹ reductive amination of ketones,⁶₂⁻⁶⁴ water oxidation,⁶⁵ NADH regeneration,⁵⁶,⁶⁶ hydroamination of halosilanes,⁶⁷ and hydrogen peroxide generation.⁶⁸ They also exhibited good performance as antimicrobial, antibacterial, and anticancer agents.⁶⁹⁻⁷²

Considering the versatility and success of [Cp*Ir(R-pica)X] complexes as catalysts, we decided to immobilize them into mesoporous silica, aiming at preparing a hybrid single-site organometallic heterogeneous catalyst, having the distinctive features of the analogous molecular catalysts, adding all the advantages of heterogeneous metal nanostructured catalysts in terms of recoverability and process intensification.⁷³⁻⁷⁶ Mesoporous silica was selected as support since it is inert and inexpensive, easily recoverable from the reaction mixtures, and characterized by a high surface area, thus facilitating the exposure of the catalytic species to the reactants and maximizing the exploitation of the noble metal.⁷⁷

Herein, we report the synthesis of a heterogeneous immobilized catalyst (Ir_PicaSi_SiO₂) and its successful application in CO₂ hydrogenation and FA dehydrogenation. The preparation of Ir_PicaSi_SiO₂ involved the initial synthesis of a modified version of the pica ligand (PicaSi), in which R is the (3-triethoxysilyl)propyl moiety, and the immobilization of PicaSi onto mesoporous silica (PicaSi⁻SiO₂) via a sol–gel process, which was recently reported as an effective strategy to provide homogeneously distributed ligands on high surface area materials.⁸⁰⁻⁸³ The catalytic iridium-single site was then implanted by the reaction of PicaSi⁻SiO₂ with [Cp*IrCl₃] (Ir_PicaSi_SiO₂) (Scheme 2).

To obtain a deeper molecular-level understanding of the surface, both materials were investigated via solid-state NMR spectroscopy and XAS. In order to increase the sensitivity of NMR toward surface sites, the dynamic nuclear polarization surface-enhanced NMR spectroscopy (DNP-SENS) approach was exploited. This technique allows the increase of NMR sensitivity by up to 2 orders of magnitude and thereby the recording of natural abundance ¹³C,¹⁵N, and ²⁹Si solid-state NMR spectra in a reasonable acquisition time.⁸¹⁻⁸⁵ Ir_PicaSi_SiO₂ exhibited remarkable catalytic performances in aqueous FA dehydrogenation and CO₂ hydrogenation that compare well with those of the analogous molecular catalysts. Extensive kinetic studies revealed that the reaction pathway for supported catalysts differs from the analogous molecular systems, because of the formation of cationic sites stabilized by the surface.

## RESULTS AND DISCUSSION

We will first discuss the preparation and comprehensive characterization of Ir_PicaSi_SiO₂ (Section 1) and then its application as a catalyst (Section 2). The first section provides evidence regarding the nature of the surface sites thanks to the use of state-of-the-art characterization, while the second section focuses on the performance of the catalyst and includes detailed catalytic and kinetic tests in both the CO₂ hydrogenation and the reverse reaction, FA dehydrogenation.

### 1. Preparation and Characterization of Ir_PicaSi⁻SiO₂

The hybrid material Ir_PicaSi⁻SiO₂ was prepared by a two-step procedure involving 1a) the synthesis and immobilization onto mesoporous SiO₂ of a pica-modified ligand (PicaSi⁻SiO₂) via a sol–gel process and 1b) a postfunctionalization to incorporate the iridium organometallic moiety (Ir_PicaSi⁻SiO₂), taking advantage of the coordination ability of PicaSi⁻SiO₂ (Scheme 2).
1a. Synthesis and Heterogenization of PicaSi onto SiO$_2$.

A modified version of the picolinamide ligand (PicaSi, Scheme 2) having a (3-triethoxysilyl)propyl group on the nitrogen atom of the amide moiety was prepared, following reported procedures (SI).$^{86,87}$ PicaSi was successively immobilized via a sol–gel procedure onto commercially available mesoporous silica beads (PicaSi-SiO$_2$), that are easy to handle and to recover due to a convenient particle diameter (from 60 to 200 μm). This support is also characterized by high surface area (738 m$^2$ g$^{-1}$), which is ideal for catalysis.$^{79,80}$

Specifically, TEOS (tetraethyl orthosilicate), PicaSi, and silica beads were contacted in an acidified solution in THF, at 343 K for 1 h. The collected solid was washed with water/THF, ethanol, and diethyl ether and dried at 408 K under high vacuum. The thus-obtained material (PicaSi-SiO$_2$) was characterized by means of IR spectroscopy, low-temperature N$_2$ adsorption (BET), elemental analysis (EA), and DNP-SENS. In order to assign the NMR resonances, DFT calculations were also conducted.

The Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectrum of PicaSi-SiO$_2$ (Figure S1, SI) displays all the characteristic bands of the picolinamide moiety, namely the C=O stretching (1670 cm$^{-1}$) of the amide and the C=C stretching (1545 cm$^{-1}$) of the aromatic carbons of the pyridine ring as well as the classic aromatic (3065 cm$^{-1}$) and aliphatic CH stretching (2964 and 2887 cm$^{-1}$). EA confirms the presence of nitrogen and carbon on the solid (SI). The incorporation of the ligand onto the surface caused a reduction of the surface area from 738 m$^2$ g$^{-1}$ (starting mesoporous silica) to 650 m$^2$ g$^{-1}$ (PicaSi-SiO$_2$).

In order to further understand the structure of the ligand on the surface, PicaSi-SiO$_2$ was characterized via DNP-SENS.

![Figure 1. DNP-enhanced MAS NMR spectra of PicaSi-SiO$_2$ and Ir_PicaSi-SiO$_2$ materials. a) $^{13}$C CPMAS NMR spectrum of PicaSi-SiO$_2$ (MAS 10 kHz, 100 K), b) $^{13}$C CPMAS NMR spectrum of Ir_PicaSi-SiO$_2$ (MAS 10 kHz, 100 K), c) $^1$H/$^{13}$C HETCOR NMR spectrum of Ir_PicaSi-SiO$_2$ (MAS 10 kHz, 100 K), d) $^{15}$N CPMAS NMR spectrum of PicaSi-SiO$_2$ (MAS 10 kHz, 100 K), e) $^{15}$N CPMAS NMR spectrum of Ir_PicaSi-SiO$_2$ (MAS 10 kHz, 100 K), and f) $^{29}$Si CPMAS NMR spectrum of PicaSi-SiO$_2$ (MAS 10 kHz, 100 K). Asterisks mark spinning sidebands.](https://doi.org/10.1021/acs.inorgchem.2c01640)
Using a typical sample formulation (PicaSi_SiO2 with an aqueous solution of AMUPol biradical to hyperpolarize the surface\textsuperscript{88,89} and DNP-SENS acquisition conditions (100 K, constant microwave (MW) irradiation and cross-polarization DNP cross effect),\textsuperscript{85} we recorded spectra with DNP solvent enhancement of the NMR sensitivity reaching 120. The DNP-enhanced \textsuperscript{13}C cross-polarization magic angle spinning (CPMAS) NMR spectrum exhibits (i) three different aliphatic resonances (at 43, 23, and 9 ppm) that can be assigned to the three CH2 of the propyl moiety that bonds the ligand onto the surface, (ii) five resonances in the aromatic region, and (iii) a resonance centered at 168 ppm consistent with the quaternary carbon of the amide moiety (Figure 1a). Interestingly, the pattern of resonances of the \textsuperscript{13}C NMR spectrum of PicaSi_SiO2 matches that of the PicaSi ligand in CD$_2$Cl$_2$ solution (Figure S3), indicating structural similarities between the immobilized and molecular organic moieties.

To determine the binding mode of the ligand to the surface, the \textsuperscript{29}Si DNP-SENS NMR spectrum of PicaSi_SiO2 was also recorded. In addition to the classical resonances of the amorphous silica at ca. −90 to −110 ppm, two peaks centered at −55 and −63 ppm are observed (Figure 1f), showing that the ligand is bound to the surface of the material predominantly in T2 and T3 fashion.\textsuperscript{90} This result is in agreement with the findings of DFT computational studies conducted for various binding modes of the ligand to the SiO$_2$ surface (summarized in Table S2; detailed descriptions are in the SI).

To further understand the structure of the immobilized ligand, \textsuperscript{15}N NMR spectroscopy was also carried out. DNP-enhanced spectroscopy was used in order to enable such studies at \textsuperscript{15}N natural abundance. The spectrum (Figure 1d) shows a resonance at 122 ppm assigned to the amide nitrogen, while the resonance of the pyridinic nitrogen was not detected. The absence of the latter is likely due to the larger chemical shift anisotropy of the signal that decreases sensitivity.\textsuperscript{91}

Overall, all pieces of information confirm that PicaSi is present on the surface of the mesoporous SiO$_2$, and particularly, DFT calculations in combination with \textsuperscript{29}Si DNP-SENS allow establishing that the ligand is linked to the silica surface through the silane moiety predominantly in T2 and T3 fashion.

\textit{1b. Immobilization of an Iridium Organometallic Moiety.}

The immobilization of Ir was next carried out by reacting a solution of [Cp*IrCl$_2$]$_2$ with PicaSi_SiO$_2$ in anhydrous dichloromethane, under inert atmosphere, for 48 h at RT, in the presence of a base (NEt$_3$) (SI). The resulting material Ir_PicaSi_SiO$_2$ shows a small decrease of surface area from 650 m$^2$ g$^{-1}$ (PicaSi_SiO$_2$) to 595 m$^2$ g$^{-1}$ (Ir_PicaSi_SiO$_2$). The C:N:Ir:Cl experimental ratio in Ir_PicaSi_SiO$_2$ was also recorded with DNP solvent enhanced spectroscopy was used in order to enable such studies at \textsuperscript{15}N natural abundance. The spectrum (Figure 1d) shows a resonance at 122 ppm assigned to the amide nitrogen, while the resonance of the pyridinic nitrogen was not detected. The absence of the latter is likely due to the larger chemical shift anisotropy of the signal that decreases sensitivity.\textsuperscript{91}

Overall, all pieces of information confirm that PicaSi is present on the surface of the mesoporous SiO$_2$, and particularly, DFT calculations in combination with \textsuperscript{29}Si DNP-SENS allow establishing that the ligand is linked to the silica surface through the silane moiety predominantly in T2 and T3 fashion.

The DRIFT spectrum of Ir_PicaSi_SiO$_2$ (Figure S4, SI) shows all the expected bands of the organic moiety on the surface with appreciable shifts with respect to the spectrum of PicaSi_SiO$_2$ consistent with the binding of iridium on the immobilized ligand. In particular, C=O and C≡C stretchings shift from 1670 to 1625 cm$^{-1}$ and from 1545 to 1595 cm$^{-1}$, respectively.

The DNP-enhanced \textsuperscript{13}C NMR spectrum shows all resonances of the Cp* and pica moieties confirming the presence of the iridium complex onto the material (Figure 1b). Interestingly, the resonance belonging to the quaternary carbon of the amide moiety decreased from 122 to 117 ppm, indicating structural similarities between the immobilized and molecular organic moieties.
Table 1. Summary of the Performances of Ir_PicaSi_SiO2 in the FA Dehydrogenation Reaction

| [Cat] (μM) | [HCOOH]+[HCOO−] (M) | [HCOOH] (M) | pH | T (K) | TOF (h−1) | TON | convn (%) |
|------------|---------------------|-------------|----|-------|----------|-----|----------|
| 1          | 250                 | 3           | 3  | 1.4   | 298      | 254 | 12000    | >99   |
| 2          | 250                 | 3           | 2.8| 2.4   | 298      | 480 | 11200    | >99   |
| 3          | 250                 | 3           | 1.5| 3.7   | 298      | 636 | 5640     | 94    |
| 4          | 250                 | 3           | 0.8| 4.2   | 298      | 505 | 3370     | >99   |
| 5          | 250                 | 3           | 0  | 8.2   | 298      | 2   | 120      |       |
| 6          | 25                 | 1           | 0.5| 3.7   | 298      | 425 | 17600    | 88    |
| 7          | 50                  | 1           | 0.5| 3.7   | 298      | 448 | 9200     | 92    |
| 8          | 100                 | 1           | 0.5| 3.7   | 298      | 354 | 5100     | >99   |
| 9          | 250                 | 1           | 0.5| 3.7   | 298      | 469 | 2160     | >99   |
| 10         | 350                 | 1           | 0.5| 3.7   | 298      | 450 | 1490     | >99   |
| 11         | 500                 | 1           | 0.5| 3.7   | 298      | 359 | 1020     | >99   |
| 12         | 250                 | 0.5         | 0.25| 3.7  | 298      | 212 | 1000     | >99   |
| 13         | 250                 | 0.75        | 0.375| 3.7 | 298      | 235 | 1410     | 94    |
| 14         | 250                 | 5           | 2.5| 3.7   | 298      | 890 | 10400    | >99   |
| 15         | 50                  | 1           | 0.5| 3.7   | 288      | 105 | 5600     | 56    |
| 16         | 50                  | 1           | 0.5| 3.7   | 313      | 1070 | 7200    | 72    |
| 17         | 50                  | 1           | 0.5| 3.7   | 333      | 5400 | 7400    | 74    |
| 18         | 50                  | 1           | 0.5| 3.7   | 353      | 11200 | 5800    | 58    |

Cl path, the degeneracy of which was found to be \((N = 1.2 \pm 0.4, R = 2.34 \pm 0.02 \text{ Å})\) from the fit obtained. The presence of an Ir−Cl path is consistent with the data from elemental analysis, which suggests that some chloride is retained after synthesis.

For Ir_PicaSi_SiO2, the combination of elemental analysis and the assignment made on the basis of the obtained EXAFS fits suggests that there are two distinct Ir species present in the material, both of which contain both Cp* and picolinamide moieties bound to Ir, as well as an additional ligand which can be either a chloride anion or a water molecule.

In order to address this issue further, reaction of Ir_PicaSi_SiO2 with \(^{15}\text{N}\)-pyridine (Py) was carried out, and the recovered material was studied by means of DNP-enhanced \(^{15}\text{N}\) CPMAS NMR (Figure S13, SI). Two resonances were observed at 219 and 287 ppm corresponding to the interaction of Py with iridium and silanol groups, respectively. Whereas the latter one is commonly observed in silica-supported materials, the presence of the former interaction indeed further suggests that iridium sites in Ir_PicaSi_SiO2 have a cationic character.

The general picture emerging from such an in-depth characterization indicates that Ir_PicaSi_SiO2 is a hybrid material in which rather dispersed cationic iridium sites are coordinated at PicaSi moieties anchored onto the silica surface.

2. Catalytic Applications of Ir_PicaSi_SiO2. 2a. FA Dehydrogenation. Ir_PicaSi_SiO2 was tested as a catalyst in the FA dehydrogenation to CO\(_2\) and H\(_2\) at different pH values (1.4–8.2 range, entries 1–5, Table 1), catalyst concentrations (25–500 μM range, entries 6–11, Table 1), [HCOOH]+[HCOO−] concentrations (0.5–5 M range, entries 3, 9, and 12–14, Table 1), and temperatures (288–353 K range, entries 7 and 15–18, Table 1). The progress of the reactions was followed by means of differential manometry and solution NMR spectroscopy. The experiments were conducted by adding formic acid to a suspension of Ir_PicaSi_SiO2 in a HCOO− solution. Conversion was evaluated by measuring the amount of residual formic acid/formate via \(^1\text{H}\) NMR spectroscopy. The complex [Cp*Ir(N-Me-pica)Cl] (3) was
used as a literature benchmark. All the results are summarized in Table 1.

TOF vs pH exhibits a volcano-shaped trend (entries 1−5, Table 1, Figure 3a). The highest TOF value (636 h⁻¹) was observed around pH = 3.7, corresponding to the pKₐ of the formic acid, as already reported for other Ir-based catalysts. This can be explained considering the simplified reaction mechanism illustrated in Scheme 3 involving two steps. The first step is the activation of the C−H bond of FA, leading to a L₅Ir=H intermediate, generating CO₂ and H₃O⁺; in the second step, the protonation of the L₅Ir=H species liberates H₂. Indeed, low pH makes the deprotonation of HCOOH and the consequent formation of Ir=H complicated, whereas at higher pH, the protonation of Ir=H and the consequent evolution of H₂ become slightly probable.

TOF values were found to be slightly dependent on the concentration of Ir_PicaSi_SiO₂ (354−469 h⁻¹, entries 6−11, Table 1, Figure 3b), indicating a first-order dependence on catalyst concentration. On the other hand, the trend of TOF vs [HCOOH]+[HCOO⁻] (entries 3, 9, and 12−14, Table 1, Figure 3c) suggests a noninteger reaction order (0.6) on FA concentrations. In all cases, quantitative consumption of HCOOH was achieved.

Catalytic tests at different temperatures (288−353 K, entries 7 and 15−18, Table 1) show an increase of TOF from 105 h⁻¹ at 288 K to 11200 h⁻¹ at 353 K. The apparent activation energy (Eₐ = 14 ± 1 kcal mol⁻¹), evaluated from the Arrhenius plot (Figure 3d), is considerably lower than that of the previously determined value for 3 (Eₐ = 20 kcal mol⁻¹). This can be explained considering an active role of the Si−OH functionalities, which might facilitate the deprotonation of FA and/or the protonation of Ir=H, under the assumption that the thermodynamics of HCOOH adsorption on the surface is not affecting the apparent activation energy.

The activity and stability of the heterogenized catalyst Ir_PicaSi_SiO₂ were compared to that of 3 by performing catalytic experiments under the same conditions ([Ir] = 25 μM, [HCOOH]+[HCOO⁻] = 1 M, pH = 3.7, 298 K, TON_expected = 20000). Gas evolution was monitored by differential manometry for 7 h (Figure 4a). TON vs time trends were interpolated using a composite mathematical function developed by Peters and Baskin. The first derivative of these "smooth" trends allows obtaining the evolution of TOF versus time (Figure 4b).

Interestingly, albeit TOF_max of Ir_PicaSi_SiO₂ (303 h⁻¹) is ca. two times slower than that of 3 (620 h⁻¹), at t = 0, the former exhibits a higher TOF (303 h⁻¹) with respect to 3 (248 h⁻¹) (Figure 4b). The trend of TOF versus time of 3 clearly shows an induction period of ca. 30 min, which is absent in

**Scheme 3. Simplified Reaction Mechanism of FA Dehydrogenation Mediated by Ir-Based Catalysts**

$L =$ ancillary ligand.
that of Ir_PicaSi_SiO2 (Figure 4b). This induction period might be due to the possible formation of poorly active (or inactive), out-of-cycle, dinuclear species.101 As discussed above, most of the Ir sites in Ir_PicaSi_SiO2 are well separated (≥1 Ir every 10 nm2), making the associative process unlikely. After 6 h, the activity of Ir_PicaSi_SiO2 decreased to 231 h⁻¹, whereas that of 3 decreased down to 418 h⁻¹. This decrease of activity is more accentuated than that expected based on the 0.4 and 0.6 dependence of the reaction rate on the concentration of formic acid in homogeneous and heterogeneous catalysis, respectively, and of similar entities, suggesting that catalyst transformation/deactivation processes occur for both catalysts. The main degradative pathway of complex 3 is the reductive deoxygenation of the C=O moiety of the ligand to form the corresponding amino species;35 the same degradation mechanism might also take place in the case of Ir_PicaSi_SiO2. Nevertheless, after 7 days, both Ir_PicaSi_SiO2 and 3 reached a TON of 17600, over the 20000 expected cycles based on thermodynamics, corresponding to 88% of conversion.

The recoverability of Ir_PicaSi_SiO2 was evaluated by performing successive tests in which the catalyst was separated and reused in the dehydrogenation of fresh FA aqueous solutions ([HCOOH]+[HCOO⁻] = 1 M, pH = 3.7) (see the SI for experimental details). After each catalytic run, Ir leaching from the solid was determined by means of Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) analysis, and the activity of the separated supernatant solution was tested. The activities of Ir_PicaSi_SiO2 and those of the respective supernatant solutions along with Ir content and leaching for each run are reported in Table S6.

Table 2. Summary of the Performances of Ir_PicaSi_SiO2 and 1 in the CO₂ Hydrogenation Reaction

| cat. | Ir content (μmol) | n_{Formate} (mmol) | [Formate] (M) | base | t (h) | TON |
|------|------------------|--------------------|---------------|------|-------|-----|
| 1    | Ir_PicaSi_SiO2    | 0.057              | 0.67          | 0.080 | DABCO | 24  | 6983 |
| 2    | Ir_PicaSi_SiO2    | 0.115              | 0.67          | 0.134 | DABCO | 24  | 5836 |
| 3    | Ir_PicaSi_SiO2    | 0.230              | 0.88          | 0.176 | DABCO | 24  | 3829 |
| 4    | Ir_PicaSi_SiO2    | 0.230              | 0.88          | 0.215 | DABCO | 24  | 2327 |
| 5    | Ir_PicaSi_SiO2    | 0.693              | 1.19          | 0.238 | DABCO | 24  | 1720 |
| 6    | Ir_PicaSi_SiO2    | 0.925              | 1.16          | 0.232 | DABCO | 24  | 1253 |
| 7    | Ir_PicaSi_SiO2    | 1.16               | 1.36          | 0.273 | DABCO | 24  | 1178 |
| 8    | I                | 0.120              | 0.63          | 0.126 | DABCO | 24  | 5235 |

Figure 4. Kinetic trends of the performances of Ir_PicaSi_SiO2 and 3 in the FA dehydrogenation reaction. a) TON vs t (h) ([HCOOH]+[HCOO⁻] = 1 M, pH = 3.7, [Cat] = 25 μM, T = 298 K) for 3 and Ir_PicaSi_SiO2. b) TOF (h⁻¹) vs t (h) ([HCOOH]+[HCOO⁻] = 1 M, pH = 3.7, [Cat] = 25 μM, T = 298 K) for 3 and Ir_PicaSi_SiO2.

Overall, the supported catalyst Ir_PicaSi_SiO2 showed remarkable performance in FA dehydrogenation comparable to those of its homogeneous analogue 3 and of the best heterogenized iridium catalysts reported so far. Particularly, Ir_PicaSi_SiO2 reached a TOF value up to 11200 h⁻¹ ([HCOOH]+[HCOO⁻] = 1 M, pH = 3.7, [Ir_PicaSi_SiO2] = 250 μM, T = 353 K) and a TON value up to 17600 ([HCOOH]+[HCOO⁻] = 1 M, pH = 3.7, [Ir_PicaSi_SiO2] = 25 μM, T = 298 K) in aqueous solution and in the absence of any additives. The catalyst was reused four times, and ICP-AES analysis of the supernatant solutions showed a low Ir leaching for each run. However, from the kinetic data, it is possible to observe a decrease of activity over time consistent with the presence of active catalyst transformation/deactivation processes.

2b. CO₂ Hydrogenation. Ir_PicaSi_SiO2 was also tested as a catalyst for the selective CO₂ hydrogenation to formate under batch conditions. Typically, the reaction was carried out for 24 h at 423 K and 50 atm (CO₂:H₂ = 1:1) in the aqueous solution, in the presence of an organic base. The amount of produced formate was quantified by ¹H NMR spectroscopy using 3-trimethylsilylpropanesulfonate sodium salt as the standard; in all the experiments, no other product was observed. Complex 1 was used as the molecular benchmark of the reaction. In the absence of the catalysts, no appreciable formation of formate was observed. The catalytic performances of Ir_PicaSi_SiO2 were evaluated at different catalyst loadings (0.057–1.16 μmol range, entries 1–7, Table 2) and in the presence of different bases (entry 2, Table 2, and entries S1 and S2, Table S7).
An increase of formate production was observed up to ca. 4.5 mol of Ir content (Figure 5); after that, a plateau is reached indicative of an equilibrium between reactants and products, which precluded the possibility of determining a kinetic order on catalyst (Figure 5). However, the TON observed with the lowest Ir loading (TON = 7 × 10^3, entry 1, Table 2) is comparable to that of other already reported supported Ir complexes under similar experimental conditions.48,49,79,80

In summary, Ir_PicaSi_SiO2 is an active catalyst for the selective hydrogenation of CO2 to formate with catalytic performance comparable to those of the molecular complex 1 and to those of the best heterogenized iridium catalysts reported so far.

**CONCLUSIONS**

A hybrid catalyst consisting of the [Cp*Ir(R-pica)X] complex immobilized onto mesoporous silica (Ir_PicaSi_SiO2) was prepared by means of a sol−gel procedure and characterized by a battery of instrumental techniques. The latter allowed the understanding that Ir_PicaSi_SiO2 maintains a very high surface area (595 m² g⁻¹) and has a rather dispersed single-site Ir(III) center (∼1Ir every 10 nm²), still bearing Cp*- and pica-ligands but with a coordination vacancy, generated by the substitution of a chloride ligand by a water molecule or a Si−OH moiety. These features are essential in determining the remarkable catalytic performance of Ir_PicaSi_SiO2 in both CO2 hydrogenation and FA dehydrogenation. CO2 is hydrogenated to formate with comparable performance to its molecular counterpart, under the same conditions (Table 2). Interestingly, a strict comparison of the catalytic performance of Ir_PicaSi_SiO2 and its molecular analogue in FA dehydrogenation shows that, whereas the former has a TOF about 2 times lower, the latter does not exhibit any induction time. This might be due to having Ir species in its cationic form or, most likely, by the inhibition of any associative deactivation process in Ir_PicaSi_SiO2.

Kinetic studies (effect of pH, catalyst and FA concentration, temperature) further reveal a strict analogy between Ir_PicaSi_SiO2 and its molecular counterpart also in terms of the reaction mechanism, strongly suggesting that the species involved in the catalytic cycle are the same. The parallelism appears to be also applicable to the degradation of the catalytic center that occurs through the reductive deoxygenation of the C=O moiety of the ligand to form the corresponding amino species in Ir_PicaSi_SiO2, as previously observed for analogous molecular catalysts.55 Having observed that such a degradation pathway is active also in the immobilized catalyst allowed the understanding that it occurs intramolecularly, indicating that only an inhibition of the amide moiety rotation might avoid it.49 Minimizing catalyst degradation might pave the way to the development of catalysts with TON large enough to be really applied in storing green hydrogen into CO2 and releasing it from FA when needed.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01640.

Details on materials and methods; synthesis and characterization of PicaSi_SiO2, Ir_PicaSi_SiO2, (N-propyl)picolinamide, and Ir; additional NMR spectra; XAS details; and additional catalytic data (PDF)

**Accession Codes**

CCDC 2164448 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01640.

Details on materials and methods; synthesis and characterization of PicaSi_SiO2, Ir_PicaSi_SiO2, (N-propyl)picolinamide, and Ir; additional NMR spectra; XAS details; and additional catalytic data (PDF)

**Accession Codes**

CCDC 2164448 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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