**Abstract:** Bimetallic iron–ruthenium nanoparticles embedded in an acidic supported ionic liquid phase (FeRu@SILP + IL-SO₃H) act as multifunctional catalysts for the selective hydrodeoxygenation of carbonyl groups in aromatic substrates. The catalyst material is assembled systematically from molecular components to combine the acid and metal sites that allow hydrogenolysis of the C=O bonds without hydrogenation of the aromatic ring. The resulting materials possess high activity and stability for the catalytic hydrodeoxygenation of C=O groups to CH₂ units in a variety of substituted aromatic ketones and, hence, provide an effective and benign alternative to traditional Clemmensen and Wolff–Kishner reductions, which require stoichiometric reagents. The molecular design of the FeRu@SILP + IL-SO₃H materials opens a general approach to multifunctional catalytic systems (MM®@SILP + IL-func).

The catalytic hydrodeoxygenation of carbonyl groups to methylene units in the side chains of aromatic substrates has attracted considerable attention for the production of alkyl-substituted aromatic structures in commodity and fine chemicals. It is also considered an important enabler for the deoxygenation of building blocks from lignocellulosic biomass towards value-added chemicals and tailor-made fuels. However, the large-scale synthetic application of this transformation has been hindered by the lack of suitable catalysts that allow for selective catalytic hydrodeoxygenation of aromatic ketones without concomitant hydrogenation of the aromatic ring (Scheme 1). Stoichiometric methods such as the Clemmensen and Wolff–Kishner reductions often remain the methods of choice for the removal of carbonyl moieties from aromatic substrates, despite the fact that they rely on the use of toxic reagents and/or create large amounts of undesired and problematic waste. Current synthetic pathways involving the hydrodeoxygenation of aromatic substrates cannot fulfill the requirements of high yields, selectivity, stability, productivity, safety, and environmental compatibility. Consequently, recent efforts have been devoted to the development of selective hydrodeoxygenation catalysts, typically based on conventional materials for heterogeneous catalysis. While promising results have been obtained in some cases for individual substrates, most of the traditional solid catalysts show severe limitations such as low hydrogenation selectivity, restriction to only benzylic carbonyl groups, low stability, formation of side-products, or high catalyst loadings approaching almost stoichiometric amounts of the active metal component.

In the present paper, we describe the design, preparation, and application of novel bifunctional catalysts for the selective hydrodeoxygenation of aromatic substrates using a molecular approach to assemble the key components of the active materials.

The design of the catalyst was based on the analysis of the desired sequence of bond-breaking and bond-forming events to achieve the overall transformation, exemplified for benzylideneacetone (1) as a prototypical substrate in Scheme 2. The metal-catalyzed hydrogenation of the C=C and C=O bond leads to the corresponding alcohol 1b. Then, the C=O bond is broken through an acid-catalyzed E1- or E2-type mechanism, resulting in a carbocation or olefin intermediate (only the
latter is shown for clarity in Scheme 2). A second metal-catalyzed hydrogenation leads to butylenzene (1d) as the desired product. The catalytic hydrogenation of the aromatic ring must be strictly avoided at each stage. Thus, the challenge for catalyst design was to combine a highly selective metal component for hydrogenation with a sufficiently acidic functionality to facilitate the C=O bond cleavage.

A recently emerging approach to prepare multifunctional catalytic systems is based on well-defined metal nanoparticles (NPs) synthesized from organometallic precursors that are embedded in ionic liquid (IL) matrices.\[9b–e\] Herein, we present a version of such materials that combines covalently grafted non-functionalized IL-type structures with physisorbed functionalized ILs on silica as support (supported ionic liquid phases, SILPs). This approach allows the controlled formation of NPs on the non-functionalized SILP and provides a large degree of freedom for post-modification with the functionalized IL. The resulting materials are denoted as MM@SILP + IL-func, in which MM′ defines the metal(s), SILP the covalently grafted IL, and IL-func the physisorbed IL (e.g., IL-SO₃H for the acidic IL used in this study).\[10a–e\]

To address the present synthetic challenge, the combination of bimetallic iron–ruthenium nanoparticles (FeRu NPs) with an acidic support appeared very promising. Recently, FeₓRuᵧ NPs immobilized on a non-functionalized SILP (FeₓRuᵧ@SILP) were shown to exhibit high activity for the reduction of C=C, C=O, and C=N groups in substituted aromatic substrates, while preventing the reduction of aromatic moieties.\[11\] Another recent study also outlined a synergistic effect in bimetallic FeRu@SILP catalysts used for the hydrogenation of CO₂ to hydrocarbons.\[12\] However, attempts to synthesize FeₓRuᵧ NPs on supports in which the acid functions are covalently grafted prior to NP formation (SILP-SO₃H)\[7c–e\] proved unsuccessful owing to the unfavorable interaction of the Fe-precursor with the acid functionality. The hydridehydrogenation of 1 with the resulting materials only led to the hydrogenation intermediates 1a, 1b, 1e, and 1f without exhibiting any deoxygenation activity (see the Supporting Information, Tables S1 and S3 and Figure S1). Preparing FeₓRuᵧ NPs on a non-functionalized SILP and carrying out the transformation in the presence of p-toluenesulfonic acid (p-TsOH) as acidic additive yielded significant amounts of the desired product 1d, albeit with only low selectivity (1a:1b:1d = 36:31:32). Finally, excellent activity and selectivity were obtained using a sulfonic acid-functionalized imidazolium IL, [BSO₃H][NTf₂] (IL-SO₃H), as acid additive. 1d was detected by GC essentially as the sole product in the reaction mixture with greater than 99% yield at full conversion of 1 upon using 2.50 equivalents of IL-SO₃H with regard to the total metal loading (4 mol% relative to 1) within 16 h at 150°C under H₂ (50 bar at RT) (Table S4). Based on these promising results, the controlled preparation of the FeₓRuᵧ@SILP + IL-SO₃H material sketched in Figure 1 was targeted to ensure an intimate contact between the NPs and the acid moieties in

![Scheme 2](image18x803_to_58x825)

**Scheme 2.** The complex reaction network to be controlled for selective deoxygenation of aromatic substrates, exemplified for benzylideneacetone (1).
and metal concentration, with higher sulfur content (ca. 2-fold) in zones containing NPs as compared to zones without NPs. This observation indicates a preference of the NPs to accumulate in areas with large amounts of physisorbed IL-SO$_3$H. STEM/EDS elemental mapping and SEM/EDS demonstrated that, despite this noticeable redistribution, the NPs still contain both Fe and Ru (Figure 2) in an unaffected metal ratio (see the Supporting Information, Table S2 and Figures S2, S3, and S5, for complete characterization details).

These results indicate that the physisorption of the acidic ionic liquid onto Fe$_{25}$Ru$_{75}$@SILP did not affect the integrity of the Fe$_{25}$Ru$_{75}$ NPs (size, metal ratio). These data substantiate the conclusion that Fe$_{25}$Ru$_{75}$ NPs retain their oxidation state and alloy structure after physisorption of the acidic ionic liquid and consist of zerovalent Fe and Ru atoms organized in a homophilic bimetallic structure.

The reaction profile for the hydrodeoxygenation of benzylideneacetone (1) catalyzed by Fe$_{25}$Ru$_{75}$@SILP + IL-SO$_3$H is shown in Figure 3. A mixture of hydrogenation intermediates 1a and 1b (58%) and the deoxygenation product 1d (42%) was formed already after 1 h. As the reaction progressed, the hydrogenation intermediates, 1a and 1b, were gradually consumed and an almost quantitative yield of 1d was obtained after 12 h. During the entire reaction sequence, no species resulting from the hydrogenation of the aromatic moiety were observed.

The close vicinity of the IL-SO$_3$H with the bimetallic particles as evidenced by the STEM/EDS data appears to be crucial for efficient hydrogenolysis. In contrast to Fe$_{25}$Ru$_{75}$@SILP + IL-SO$_3$H, a physical mixture of non-functionalized Fe$_{25}$Ru$_{75}$@SILP and metal-free SILP-SO$_3$H resulted in only slow formation of 1d (7%) with 1a (70%) and 1b (18%) being the main products after 16 h under identical reaction conditions (see the Supporting Information, Table S4).

Figure 3. Reaction profile for the hydrodeoxygenation of benzylideneacetone (1) using Fe$_{25}$Ru$_{75}$@SILP + IL-SO$_3$H. Reaction conditions: Fe$_{25}$Ru$_{75}$@SILP + IL-SO$_3$H (58 mg of catalyst containing 0.015 mmol total metal and 0.038 mmol (2.50 equiv.) IL-SO$_3$H), substrate (0.38 mmol), mesitylene (0.5 mL), H$_2$ (50 bar), 150°C. Conversion and product distribution were determined by GC using tetradecane as an internal standard.

These substrate scope for the selective hydrodeoxygenation using the bifunctional Fe$_{25}$Ru$_{75}$@SILP + IL-SO$_3$H catalyst was assessed with a range of carbonyl-substituted aromatic substrates (Table 1 and Table S7). Interestingly, while benzylideneacetone (1) was converted to the deoxygenation product 1d in quantitative yields at 150°C (Table 1, Entry 1), the efficient hydrodeoxygenation of 1-phenyl-1-
butanone (2) to give the same product 1d required a temperature of 175 °C (Table 1, Entry 2). The hydrodeoxygenation of the 1,3-diketone (3) at 175 °C also proceeded smoothly to give high yields of 1d (Table 1, Entry 3). Performing this reaction at 100 °C evidenced the presence of 2 (22%) and 4-phenyl-2-butanone (1a) (8%) as intermediates (see the Supporting Information, Table S9). 4-phenyl-2-butenone (1e) was also observed as an intermediate of the reaction at 100 °C (Table S9), which supports the reaction pathway discussed in Scheme 2. The greater amount of intermediate 2 as compared to 1a indicates that the deoxygenation of the non-benzylic ketone is favored over the benzylic ketone. This was confirmed by comparative rate studies for the hydrodeoxygenation of 2 and 1a, demonstrating a two-fold higher reaction rate for 1a (Figure 4 and Figure S8). This unique reactivity pattern is in sharp contrast to previously reported hydrodeoxygenation catalysts.

Table 1: Hydrodeoxygenation of carbonyl-substituted aromatic substrates using Fe<sub>25</sub>Ru<sub>75</sub>@SILP + IL-SO<sub>3</sub>H.[6]

| Entry | Substrate | Product [%]| |
|-------|-----------|------------|---|
| 1     | [1]       | >99<sup>[1]</sup> | |
| 2     | 2         | >99<sup>[1]</sup> | |
| 3     | 3         | 94         | |
| 4     | 4         | 82<sup>[1]</sup> | |
| 5     | 5         | 91         | |
| 6     | 6         | 92         | |
| 7     | 7         |  >99<sup>[1]</sup> | |
| 8     | 8         | >99<sup>[1]</sup> | |
| 9     | 9         | >99<sup>[1]</sup> | |

[a] Reaction conditions: Fe<sub>25</sub>Ru<sub>75</sub>@SILP + IL-SO<sub>3</sub>H (58 mg catalyst containing 0.015 mmol total metal and 0.038 mmol (2.50 equiv.) IL-SO<sub>3</sub>H), substrate (0.38 mmol, 25 equiv.), mesitylene (0.5 mL). [b] Yield determined by GC, conversion >99%. [c] 150 °C. Remainders of reaction mixtures were composed of dimeric by-products or [d] 4a (12%) and dimeric by-products (6%).

Figure 4. Comparative rate studies for the hydrodeoxygenation of 1-phenyl-1-butanone (2) and 4-phenyl-2-butanone (1a) using Fe<sub>25</sub>Ru<sub>75</sub>@SILP + IL-SO<sub>3</sub>H. Reaction conditions: Fe<sub>25</sub>Ru<sub>75</sub>@SILP + IL-SO<sub>3</sub>H (58 mg catalyst containing 0.015 mmol total metal and 0.038 mmol (2.50 equiv.) IL-SO<sub>3</sub>H), substrate (0.38 mmol), mesitylene (0.5 mL), H<sub>2</sub> (50 bar), 150 °C. Conversion was determined by GC using tetradecane as an internal standard.

\[ k = -0.47 \text{ h}^{-1} \]

\[ k = -1.08 \text{ h}^{-1} \]
The hydrodeoxygenation of Friedel–Craft acylation products such as 2 provides an interesting alternative to classical Friedel–Crafts acylation reactions, which are prone to over-alkylation and carbocation rearrangements. The Fe$_2$Ru$_2$@SILP + IL-SO$_2$H catalyst proved to be very versatile in this context. The hydrodeoxygenation of acetophenone (4) and its derivatives 5 and 6 gave the corresponding deoxygenation products in over 90% yield, irrespective of the presence of electron-donating (5) or electron-withdrawing (6) groups in the para-position. Acylated naphthalene (7) was converted to 2-ethynaphthalene (7a) in quantitative yields under standard reaction conditions. Notably, the conversion of diphenylketone (8) to diphenylmethane (8a) was also quantitative, indicating that the formation of an olefinic intermediate is not required in case sufficiently stable carbocations can be formed.

Using Fe$_2$Ru$_2$@SILP + IL-SO$_2$H, the hydrogenation of aromatic moieties was not observed for any of the substrates, even at prolonged reaction time. In sharp contrast, the use of monometallic Ru$_{80}$@SILP + IL-SO$_2$H catalysts under similar reaction conditions led to deep hydrogenation of all substrates, yielding completely saturated deoxygenation products or product mixtures (for detailed results, see the Supporting Information, Table S8). Monometallic Fe$_{10}$@SILP catalysts were previously tested and found inactive for the reduction of C=O bonds.[11] This emphasizes how the bimetallic FeRu@-SILP + IL-SO$_2$H catalyst provides a highly selective route towards the synthesis of a wide range of aromatic deoxygenation products that are not accessible using standard catalytic systems.

As a general conclusion, the combination of ionic liquid (IL)-modified surfaces and nanoparticle (NP) synthesis from organometallic precursors provides a highly flexible and versatile molecular approach to control the metal as well as the acid component of multifunctional catalytic systems. Covalent grafting and physisorption of the ILs allows separation of the functionalization from the stabilization effect of the SILP. This largely extends the range of possible metal precursor complexes as demonstrated in this study for the acid sensitive iron sources, opening a huge parameter space for multi-metallic NPs to be assembled on the SILP surface. The post-synthesis modification through the physisorption of functionalized ILs ensures an intimate contact between the desired functionality and the metal components. The potential of this approach for designing and generating multifunctional catalytic systems with tailor-made reactivity for challenging catalytic transformations is exemplified with the Fe$_2$Ru$_2$@SILP + IL-SO$_2$H material for the selective hydrodeoxygenation of aromatic ketones. Thus, the presented multifunctional catalytic system constitutes an interesting alternative to Clemmensen and Wolff–Kishner reductions, opening a greener approach to alkylated aromatic compounds.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: bimetallic nanoparticles · hydrodeoxygenation · iron · ruthenium · supported ionic liquid phases

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[1] R. O. Hutchins, M. K. Hutchins in Comprehensive Organic Synthesis, Vol. 8 (Ed.: I. Fleming), Elsevier, Oxford, 1991, pp. 327–362.
[2] a) A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411–2502; b) A. M. Ruppert, K. Weinberg, R. Palkovits, Angew. Chem. Int. Ed. 2012, 51, 2564–2601; Angew. Chem. 2012, 124, 2614–2654; c) M. Besson, P. Gallezot, C. Pinel, Chem. Rev. 2014, 114, 1827–1870; d) T. vom Stein, J. Klankermayer, W. Leitner in Catalysis for the Conversion of Biomass and Its Derivatives (Eds: M. Behrens, A. K. Dayte), epubli, Berlin, 2013, pp. 411–434; e) K. L. Luksa, P. Migowski, W. Leitner, Green Chem. 2015, 17, 3195–3206; f) W. Leitner, J. Klankermayer, S. Pischinger, H. Pitsch, K. Kohse-Höinghaus, Angew. Chem. Int. Ed. 2017, 56, 5412–5452; Angew. Chem. 2017, 129, 5500–5544.
[3] J. Magano, J. R. Dunetz, Org. Process Res. Dev. 2012, 16, 1156–1184.
[4] E. Vodejs, Org. React. 1975, 22, 401–422.
[5] D. Todd, Org. React. 1948, 4, 378–422.
[6] K. Hattori, H. Sajiki, K. Hirota, Tetrahedron 2001, 57, 4817–4824.
[7] a) C. Van Doorslaer, J. Wahlen, P. G. N. Mertens, B. Thijss, P. Nockemann, K. Binnewies, D. E. de Vos, ChemSusChem 2008, 1, 997–1005; b) X. J. Kong, L. G. Chen, Catal. Commun. 2014, 57, 45–49; c) L. Petitjean, R. Gigante, E. S. Beach, D. Xiao, P. T. Anastas, Green Chem. 2016, 18, 150–156; d) M. Li, J. Deng, Y. Lan, Y. Wang, Chem.StorySelect 2017, 2, 8486–8492; e) C. Gonzalez, P. Marin, F. V. Diez, S. Ordóñez, Ind. Eng. Chem. Res. 2016, 55, 2319–2327; f) V. Kagan, Z. Aizenshtat, R. Neumann, Angew. Chem. Int. Ed. 1999, 38, 3331–3334; Angew. Chem. 1999, 111, 3551–3554; g) F. Zacerchia, N. Ravasio, M. Ercoli, P. Allegrini, Tetrahedron Lett. 2005, 46, 7743–7745; h) M. Bejblová, P. Zázmostný, L. Červený, J. Čejka, Appl. Catal. A 2005, 296, 169–175; i) D. Procházková, P. Zázmostný, M. Bejblová, L. Červený, J. Čejka, Appl. Catal. A 2007, 332, 56–64; j) J. Ma, S. Liu, X. Kong, X. Fan, X. Yan, L. Chen, Res. Chem. Intermed. 2012, 38, 1341–1349.
[8] a) P. N. Rylander in Hydrogenation Methods, Academic Press, New York, 1985, pp. 66–77; b) S. Nishimura in Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis,
Wiley-VCH, New York, 2001, pp. 170–225; c) A. Stanislaus, B. H. Cooper, Catal. Rev. Sci. Eng. 1994, 36, 75–123.

[9] a) N. Yan, Y. Yuan, R. Dykeman, Y. Kou, P. J. Dyson, Angew. Chem. Int. Ed. 2010, 49, 5549–5553; Angew. Chem. 2010, 122, 5681–5685; b) Y. Zhu, Z. N. Kong, L. P. Stubbs, H. Lin, S. Shen, E. V. Anslyn, J. A. Maguire, ChemSusChem 2010, 3, 67–70; c) S. Winterle, M. A. Liauw, Chem. Ing. Tech. 2010, 82, 1211–1214; d) J. Julis, W. Leitner, Angew. Chem. Int. Ed. 2012, 51, 8615–8619; Angew. Chem. 2012, 124, 8743–8747; e) K. L. Luska, J. Julis, E. Stavitski, D. N. Zakharov, A. Adams, W. Leitner, Chem. Sci. 2014, 5, 4895–4905; f) K. L. Luska, P. Migowski, S. El Sayed, W. Leitner, Angew. Chem. Int. Ed. 2015, 54, 15750–15755; Angew. Chem. 2015, 127, 15976–15981; g) K. L. Luska, P. Migowski, S. El Sayed, W. Leitner, ACS Sustainable Chem. Eng. 2016, 4, 6186–6192.

[10] a) R. Fehrmann, A. Riisager, M. Haumann in Supported Ionic Liquids: Fundamentals and Applications, Wiley-VCH, Weinheim, 2014; b) A. Riisager, P. Wasserscheid, R. van Hal, R. Fehrmann, J. Catal. 2003, 219, 452–455; c) M. H. Valkenberg, C. deCastro, W. F. Holderich, Green Chem. 2002, 4, 88–93; d) C. P. Mehnert, R. A. Cook, N. C. Dispenziere, M. Ateworki, J. Am. Chem. Soc. 2002, 124, 12932–12933; e) U. Kernchen, B. Etzold, W. Korth, A. Jess, Chem. Eng. Technol. 2007, 30, 985–994.

[11] K. L. Luska, A. Bordet, S. Tricard, I. Sinev, W. Grünert, B. Chaudret, W. Leitner, ACS Catal. 2016, 6, 3719–3726.

[12] M. I. Qadir, A. Weilhard, J. A. Fernandes, I. de Pedro, B. J. C. Vieira, J. C. Waerenborgh, J. Dupont, ACS Catal. 2018, 8, 1621–1627.

[13] a) P. Migowski, K. L. Luska, W. Leitner, Nanocatalysis in Ionic Liquids, Wiley-VCH, Weinheim, 2017, pp. 249–273; b) P. Zhang, T. Wu, B. Han, Adv. Mater. 2014, 26, 6810–6827.