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Hydrogenation of levulinic acid to γ-valerolactone over Fe-Re/TiO₂ catalysts

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ABSTRACT

Hydrogenation of levulinic acid to γ-valerolactone is a key reaction in the valorization of carbohydrates to renewable fuels and chemicals. State-of-the-art catalysts are based on supported noble metal nanoparticle catalysts. We report the utility of a bimetallic Fe-Re supported on TiO₂ for this reaction. A strong synergy was observed between Fe and Re for the hydrogenation of levulinic acid in water under mild conditions. Fe-Re/TiO₂ shows superior catalytic performance compared to monometallic Fe and Re catalysts at similar metal content. The hydrogenation activity of the bimetallic catalysts increased with Re content. H₂-TPR, XPS, XANES, EXAFS, Mössbauer spectroscopy, TEM, and low-temperature CO IR spectroscopy show that the bimetallic catalysts contain metallic Re nanoparticles covered by FeOₓ species and small amounts of a Fe-Re alloy. Under reaction conditions, the partially reduced surface FeOₓ species adsorb water and form Brønsted acidic OH groups, which are involved in dehydration of reaction intermediates. Under optimized conditions, nearly full conversion of levulinic acid with a 95 % yield of γ-valerolactone could be achieved at a temperature as low as 180 °C in water at a H₂ pressure of 40 bar.

1. Introduction

Due to dwindling reserves of easily accessible fossil resources and the increasing demand for fuels and chemicals, there is a growing need to develop efficient catalytic routes from renewable lignocellulosic biomass to fuels and chemicals. Cellulose, which is a renewable feedstock derivable, can be converted to platform chemicals such as 5-hydroxymethylfurfural (HMF) [1], levulinic acid (LvA) [2], and γ-valerolactone (GVL) [3]. In particular, GVL has attracted much attention in recent years, because it can be used in the chemical industry either directly or as an intermediate to food additives, nylon and green solvents [4]. GVL is also increasingly considered as a platform for the production of liquid biofuels [5].

GVL can be obtained by gas- or liquid-phase hydrogenation of LvA using a suitable metal-based catalyst and a hydrogen source. In the past few years, many different catalyst systems including noble [6–8] and non-noble metals [9–13] have been evaluated for the hydrogenation of LvA to GVL. In addition to the use of renewable feedstock, it is also of increasing importance to develop catalysts that are based on cheap and abundantly available metals. Many catalysts used in the chemical industry are currently based on expensive precious group metals. Accordingly, there is a strong incentive to replace them with non-noble metals.

The catalytic hydrogenation of LvA in the presence of molecular hydrogen using batch [14,15] and flow reactors [15–19] has been extensively studied in the last decade. The first example of catalytic hydrogenation of LvA was however already reported more than 50 years ago by Broadbent et al. [20] These researchers employed an unsupported Re black catalyst and were able to reach a 71 % yield of GVL after 18 h reaction at 106 °C at a H₂ pressure of 150 bar. The remaining products were mainly polymeric esters. Afterwards, a wide range of supported noble metal catalysts featuring mainly Ru [7,18,21], Ir [22], Rh [23], and Pt [17] as the key hydrogenation components were evaluated for their activity in LvA hydrogenation. Ruthenium-based
catalysts have emerged as promising candidates, because they typically combine high activity and selectivity. Non-noble copper-based catalysts such as Cu/ZrO₂ [24], Cu/SiO₂ [25], Cu-Cr [26], and Cu-Fe [27] have also been reported to be effective for producing GVL from LvA, although they typically require a higher reaction temperature and/or long reaction time for achieving high LvA conversion. Homogeneous catalysts have also been studied providing good results under relatively mild conditions. For instance, Yi and collaborators reported the hydrogenation of levulinic acid to GVL using a homogeneous Fe complex in aqueous solution, obtaining GVL yields as high as 97 % in 2 h at 100 °C and 50 bar [28].

There is growing evidence of the positive effect of bimetallic catalyst formulations for the hydrogenation of oxygenated substrates [29,30]. For instance, the group of Weckhuysen reported on the beneficial effect of Ru-Au nano-alloying for the catalytic conversion of LvA to GVL [31]. Bimetallic catalysts containing noble and non-noble metals (i.e., Ni-Ru, Ni-Pt, Ni-Au, and Ni-Pd) supported on supports such as zeolite, ZrO₂, γ-Al₂O₃, and SiO₂ have also been employed for the upgrading of biobased intermediates derived from lignin [32]. Supported Ni-Re [33] and Pt-Re [34] catalysts have been shown to be highly active for the selective hydrogenation of carbonylic acids. Higher conversion and selectivity of carbonylic acid hydrogenation were achieved with a Ni-Re catalyst compared to its single-metal and Pt-based counterparts [33]. Recently, Ni/Al₂O₃, Ni-Cu/Al₂O₃, Ni-Nb/TiO₂ and Ni/HZSM-5 were employed for the hydrogenation of LvA [15,19,35]. A high reaction temperature (220 – 275 °C) was however required to achieve reasonable performance. Shimizu and co-workers first reported a noble-metal-free Ni-MoO₃/C catalyst with a TON (turnover number) of 4950 [36], which is comparable to a state-of-the-art Ru catalyst for the hydrogenation of LvA to GVL at 250 °C [37]. Granwalld et al. reported a solvent-free method to obtain a 92 % GVL yield for LvA hydrogenation using Ni/Al₂O₃ [14]. However, reuse of the Ni catalyst resulted in a significantly lower activity. Shimizu’s group reported that Re/TiO₂ is a promising catalyst for the selective hydrogenation of aromatic and aliphatic carbonylic acids. In their study, 3-phenylpropanol was produced in 97 % yield from 3-phenylpropionionic acid under mild conditions (50 bar H₂ at 110 °C) [15].

Here we report a novel TiO₂-supported Fe-Re bimetallic catalyst system, which is highly active in the hydrogenation of LvA to GVL under mild conditions. The catalysts were extensively characterized using H₂-TPR, XPS, XANES, EXAFS, Mössbauer spectroscopy, CO-IR spectroscopy and TEM. Strong interaction between Fe and Re was observed in terms of the formation of a Fe-Re-oxide phase, which upon reduction is partially converted into a metallic Fe-Re alloy covered by FeOx species. The interactions of Re and Fe with the titania support also play an important role in the formation of catalytically active nanoparticles. The strong synergy in levulinic acid hydrogenation is attributed to the interface between metallic Fe-Re particles and FeOx.

2.2. Catalyst characterization

Temperature-programmed reduction (TPR) experiments were performed in a Micromeritics AutoChem II 2920 instrument equipped with a fixed-bed reactor, a computer-controlled oven, and a thermal conductivity detector. Typically, samples (50 mg) were loaded in a tubular quartz reactor. Prior to reduction, samples were pretreated at 150 °C for 2 h. The sample was reduced in 4 vol% H₂ in N₂ at a flow rate of 8 mL/min, whilst heating from room temperature up to 900 °C at a heating rate of 10 °C/min. The H₂ consumption was monitored by a gas chromatography equipped with a thermal conductivity detector (TCD) and calibrated using a CuO/SiO₂ reference catalyst.

XPS measurements were performed using a Kratos AXIS Ultra spectrometer, equipped with a monochromatic X-ray source, and a delay-line detector (DLD). Spectra were obtained using an aluminum anode (Al Kα = 1486.6 eV) operating at 150 W. Survey scans were measured at a constant pass energy of 160 eV and region scans at 40 eV. The background pressure was kept at 2 × 10⁻⁹ mbar. Quasi-in situ XPS measurements for all of the catalysts were performed after reducing them in a tubular quartz reactor with 10 °C/min heating rate from room temperature to 500 °C in a flow of 10 vol% H₂ in He (total flow 100 mL/min). After cooling to room temperature, the lids at the inlet and outlet of the reactor were closed to prevent air exposure. The samples were prepared for XPS measurements in an Ar-flushed glove box and transferred in an air-tight transfer holder to the XPS apparatus. Data analysis was performed using CasaXPS software. The binding energy was corrected for surface charging by taking the C 1s peak of adventitious carbon as a reference at 284.6 eV.

X-ray absorption fine structure (XAFS) measurements were done at the Fe K-edge (ca. 7112 eV) and Re L-edge (ca. 15535 eV) in transmission mode on beamline BM26 at ESRF (DUBBLE, Grenoble). The photon flux of the incoming and outgoing X-ray beam was detected with two ionization chambers IO and I?, respectively. The obtained absorption data were background-subtracted, normalized and fitted as difference spectra using Athena software. EXAFS analysis was performed using VIPER on k³-weighted data. The amplitude reduction factor S₀² was determined by fitting the first Re-Co ordination to 12, of Re foil. In a typical experiment, ca. 15 mg catalyst sample (in tablet form) was placed in a stainless-steel XAS reactor equipped with two fire-rods and glassy carbon windows as described in ref [39]. Catalysts were reduced in this cell by heating at a rate of 3 °C/min from 40 °C to 500 °C followed by an isothermal dwell of 0.5 h in a flow of 20 vol% H₂ in He at a total flow rate of 50 mL/min. During reduction, the state of the samples was followed by XANES, while EXAFS spectra were recorded at 50 °C after the reduction.

Transmission ⁵⁷Fe Mössbauer spectra were collected at -153.2 °C with a sinusoidal velocity spectrometer using a ⁵⁷Co(Rh) source. Velocity calibration was carried out using an α-Fe foil at room temperature. The source and the absorbing samples were kept at the same temperature during the measurements. The Mössbauer spectra were fitted using the Mosswinv 4.0 program.

Low-temperature infrared spectra of CO adsorbed on the catalysts was recorded using a Bruker Vertex 70 FT-IR spectrometer. The IR spectra were acquired at a resolution of 2 cm⁻¹ and 32 scans were averaged for each spectrum. Typically, an amount of ca. 20 mg catalyst was pressed into a thin self-supporting wafer with a diameter of 13 mm, which was then placed inside a controlled-environment IR transmission cell capable of heating and cooling, gas dosing, and evacuation. Prior to CO adsorption, the catalyst wafer was reduced at 500 °C for 1 h in flowing 10 vol% H₂ in He, followed by cooling to 100 °C. The cell was then evacuated to ∼10⁻⁶ mbar and further cooled to liquid nitrogen temperature. The sample was then subjected to pulses of CO via a sample loop (10 μL) connected to a six-port sampling valve. CO was pulsed until saturation was reached as observed by saturation of the CO IR adsorption bands.

Transmission electron micrographs were acquired on a FEI cubed Cs...
corrected Titan at 300 kV. Typically, a small amount of the sample was ground and suspended in pure ethanol, sonicated and dispersed over a Cu grid with a holey carbon film. Samples were firstly reduced in 10 vol % H₂ in He (total flow 100 mL/min) at 500 °C for 2 h, followed by passivation in 1 vol% O₂ in He for 10 h. Bright field images (BF) were taken using a rather large objective aperture to enhance the contrast, specifically for lattice imaging. HAADF-STEM imaging was done to analyze the particle size. Elemental analysis was done with an Oxford Instruments EDX detector X-Max® 100TLE.

2.3. Catalytic activity measurements

Aqueous-phase catalytic hydrogenation of LvA to GVL was performed in a 10 mL autoclave (HOKO Swagelok) at various temperatures (130–200 °C) and a (cold) H₂ pressure of 40 bar. In a typical reaction, 2 mmol LvA and 23 mg reduced catalyst were loaded into the autoclave in a nitrogen-flushed glove-box. The autoclave was sealed using a rubber plug before removing it from the glove-box. An amount of 4 mL degassed water was injected into the autoclave via the rubber plug using a syringe. The autoclave was then sealed and purged four times with H₂ before the pressure was increased to 40 bar. The reaction was started by heating the autoclave to the desired reaction temperature under continuous stirring (1000 rpm). At the end of the reaction, the autoclave was cooled rapidly to room temperature in an ice bath, after which the remaining H₂ was released. The catalyst was separated from the solution by filtration (0.45 μm filters). The reaction products were subjected to NMR analysis.

2.4. Product analysis

Quantitative analysis of the liquid products (LvA and GVL) was carried by ¹H-NMR using 1,4-dioxane as an internal standard. An amount of 100 μL 1,4-dioxane was added to the reaction mixture after the catalytic reaction. An aliquot of 300 μL of the reaction mixture was taken using a rather large objective aperture to enhance the contrast, specifically for lattice imaging. HAADF-STEM imaging was done to analyze the particle size. Elemental analysis was done with an Oxford Instruments EDX detector X-Max® 100TLE.

3. Results and discussion

A set of Fe-Re catalysts supported on TiO₂ with different atomic Fe/Re ratios were prepared by wetness impregnation. The Fe loading for all of the Fe and Fe-Re catalysts was kept at 2.0 wt%. The atomic Fe-to-Re ratio was varied between 5:1 and 1:2. The bimetallic catalysts are denoted as Fe-Re(x:y)/TiO₂ in which x:y stands for the atomic Fe/Re ratio. Monometallic Fe-2.0 wt%TiO₂ and Re-13 wt%TiO₂ (denoted as Fe (2.0)/TiO₂ and Re(13)/TiO₂, respectively) were prepared in the same way and served as reference catalysts.

We firstly screened these catalysts for their performance in the hydrogenation of LvA to GVL. For this purpose, the catalysts were reduced at 500 °C for 2 h and then tested in a batch reactor in water at 140 °C and 40 bar H₂ for 4 h. 0 Fig. 1 compares the performance of the reduced catalysts. Fe(2.0)/TiO₂ showed a very low GVL yield of less than 1%. The yield for Re(13)/TiO₂ was 3%. A much higher catalytic performance was achieved using Fe-Re bimetallic catalysts. With Fe-Re(1:1)/TiO₂ catalyst, a yield of 12 % GVL was obtained at the conversion of 14

% . The catalytic performance increased with increasing Re-to-Fe ratio. The best catalytic performance was obtained for Fe-Re(1:2)/TiO₂, which gave 17 % yield of GVL at the conversion of 18 %. These results evidence a significant synergy between Fe and Re. The addition of Re to Fe strongly improved LvA conversion.

TPR traces of the reduction of all catalysts are presented in Fig. 2. The Fe(2.0)/TiO₂ sample shows a very small reduction feature around 285 °C, which is due to the (partial) reduction of Fe³⁺ to Fe²⁺. A broad feature around 650 °C can be attributed to the reduction of Fe²⁺ to metallic Fe [40]. The active phase in Re(13)/TiO₂ sample is reduced at 350 °C. This suggests that it is easier to reduce Re than Fe on titania. For the Fe-Re samples, the main reduction peak becomes sharper and its position shifts to slightly higher temperatures compared with the Re-only and Fe-only samples. It is also noted that the first (partial) reduction peak at 285 °C, which is due to reduction of FeO₃ or Fe₂O₃ to FeO, is not present for the bimetallic Fe-Re catalysts and the second reduction peak at 650 °C shifts to higher temperature (cf. the dashed line in Fig. 2). A previous study showed that higher reduction temperature for bimetallic Fe-Re/SiO₂ catalysts compared to the monometallic ones can be attributed to a strong interaction between Fe and Re in the mixed oxide [40]. For the Fe-Re/TiO₂ samples, besides the small reduction feature of Fe²⁺ → Fe⁺, a single main reduction feature suggests that Fe and Re are present in a mixed-oxide phase.

Reduced Fe, Re, and Fe-Re samples were further characterized by XPS, which is a surface-sensitive technique. Fig. 3 shows the fitted Re 4f XPS spectra. Quantitative XPS data are collected in Table 1. A wide range of oxidation states of Re between +2 and +7 is observed for the reduced catalysts. At low Re content in Fe-Re(5:1)/TiO₂, the intensity of the Re signal was too low for reliable fitting. For Fe-Re(2:1)/TiO₂, the Re²⁺ : Re⁴⁺ : Re⁵⁺ : Re⁶⁺ : Re⁷⁺ ratio was 16 : 16 : 10 : 21 : 37. No metallic Re was observed for this sample. Samples with a higher Re content, Fe-Re(1:1)/TiO₂ and Fe-Re(1:2)/TiO₂, contained both metallic and oxidic Re. For reduced Fe-Re(1:1)/TiO₂, the metallic Re fraction was 53 % and the remainder was present as Re-oxide species with a large contribution of Re³⁺. The Re⁺ content increased to 70 % for Fe-Re (1:2)/TiO₂. It is important to mention that the metallic Re⁺ content in the Fe-Re(1:1)/TiO₂ and Fe-Re(1:2)/TiO₂ samples are higher in the Re (13)/TiO₂ sample (29 %). These results confirm that the presence of Fe resulted in a higher reducibility of the Re component in the reduced materials.

We also analyzed the oxidation state of Fe in these samples by XPS. The XPS spectra in the Fe 2p region and the results of their deconvolution are shown in Fig. 4 and Table 1, respectively. The reduced Fe (2.0)/TiO₂ sample contains a large amount of Fe²⁺ (78 %) with the remainder being Fe³⁺ (22 %). No metallic Fe was observed in this catalyst. This confirms that the first reduction peak in TPR is due to the
partial reduction of Fe$^{3+}$ to Fe$^{2+}$. It is seen that the amount of Fe$^{2+}$ is lower for the reduced Fe-Re(5:1)/TiO$_2$, Fe-Re(2:1)/TiO$_2$, and Fe-Re (1:1)/TiO$_2$ samples in comparison to Fe(2.0)/TiO$_2$. The finding that the Fe$^{3+}$/Fe$^{2+}$ ratios of these three catalysts are similar indicates that Re does not promote the reduction of Fe at a low Re content. Instead, its reducibility is decreased, which is likely due to the strong interaction of Fe in a mixed Fe-Re-oxide phase. On the other hand, at higher Re loading (Fe-Re(1:2)/TiO$_2$), the fraction of Fe$^{2+}$ in the reduced materials is already $\sim$85 %, suggesting that the presence of Re promotes the reduction of Fe. The well-known mechanism for this kind of reduction promotion is the spillover of H atoms from the first reduced metal phase to the other components \cite{41,42}. The difference is obviously due to the formation of metallic Re at higher Re content. Since the Fe content is constant in our samples, this may imply that a certain fraction of free Re-oxide is needed to obtain metallic Re.

We also investigated the reduction of Fe and Re in more detail by \textit{in situ} XANES, which is bulk sensitive in contrast to XPS. The XANES spectra of the selected Fe-, Re-, and Fe-Re samples were collected at reduction temperatures in the 50−500°C range under a 50 mL/min flow of a 10/40 v/v mixture of H$_2$ and He. Reference materials including the corresponding metals and metal oxides of varying oxidation states were also measured. The energy of the half-edge-step was used to compare the oxidation state of Fe and Re during the reduction process. Fig. 5a and c show the XANES spectra of Fe and Re reference samples,
respectively. Fig. 5b and d show the energy corresponding to the half-edge-step for Fe and Re, respectively, during reduction, which is employed here as a qualitative indicator of the oxidation state. Although the pre-edge feature of Fe XANES spectra can be analyzed to analyze the oxidation and coordination state of Fe, the data quality of the measured spectra was too low to extract useful information. Analysis of the energy of the half-edge-step shows a gradual reduction of Fe$^{3+}$ to Fe$^{2+}$ and Fe(0). The addition of Re increases the rate of Fe reduction. This is in line with the earlier finding that the addition of Re promotes the reduction of Fe$^{3+}$ to lower oxidation state. On the other hand, while the Re(13)/TiO$_2$ shows the highest reducibility, it is seen that the addition of Fe delays the reduction of Re to higher temperature. However, by comparing the energy at the half-edge-step of the Re-containing samples with the Re foil (Re°) reference, it can be concluded that all of the Re species can be reduced to their metallic state above 350°C. This seems to be inconsistent with the XPS results, where a larger amount of oxidized Re was observed. This difference is likely due to the in situ character of the XANES measurements, while XPS was carried out in a quasi in situ mode, including cooling to room temperature and sample transfer at ambient conditions via a glove-box. Although air exposure was avoided, traces of oxygen and water will likely oxidize reduced surface Re species. Obviously, the difference is substantial also because XPS is a surface-sensitive technique, while XANES probes the bulk as well. Notably, the Fe-Re bimetallic catalysts gave lower energies at the half-edge-step than the Re(13)/TiO$_2$ catalyst and the Re foil (Fig. 5d). This points to the formation of a Fe-Re alloy with a different electronic structure than reduced Re nanoparticles. The presence of this Fe-Re alloy can explain the higher reducibility of the Re component in reduced samples, revealed by XPS analysis.

In order to obtain more detailed structural information of the Fe-Re samples, extended X-ray absorption fine structure (EXAFS) data were collected both at the Fe K-edge and the Re L$_3$-edge after reduction at 500°C followed by cooling to 50°C. Due to the low Fe content in combination with the strong X-ray absorption by the titania support, the Fe K-edge EXAFS data quality was too low for reliable fitting. Fig. 6 depicts the experimental and fitted $k^3$-weighted R-space spectra for the Re foil and the Re(13)/TiO$_2$ and Fe-Re(1:2)/TiO$_2$ samples. The EXAFS fitted parameters are summarized in Table 2. The amplitude reduction factor was chosen such that the Re foil with its typical cubic closest packed structure has a Re-Re coordination number of 12. For the Re(13)/TiO$_2$ sample, the first Re-Re shell coordination number due to a metallic Re-Re bond is significantly lower (CN=7.2), implying the formation of nanoparticles. This sample also contains a first shell contribution from Re-O scattering at 2.072Å with a coordination number of 1.1, indicating that the Re phase was not fully reduced. This may be attributed to the strong interaction with the titania support. The difference in Debye-Waller factors between this sample and the reference also hints at such interactions. The fitting results for Fe-Re(1:2)/TiO$_2$ are very different. First of all, the Re-Re bond distance is reduced compared with the other two Re-only samples and a second shell is seen, which can be fitted with a Re-Fe scatterer. The theoretically determined Re-Fe and Re-Re bond length values in a stoichiometric Re-Fe

| Table 1 Deconvolution of XPS spectra of reduced Fe(2.0)/TiO$_2$, Fe-Re/TiO$_2$, and Re (13)/TiO$_2$ catalysts. |
| --- |
| Catalyst | Fe$^0$ | Fe$^{2+}$ | Fe$^{3+}$ | Re$^0$ | Re$^{2+}$ | Re$^{3+}$ | Re$^{4+}$ | Re$^{5+}$ | Re$^{6+}$ | Re$^{7+}$ |
| Fe(2.0) | 0 | 78 | 22 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Fe-Re(5:1) | 4 | 64 | 32 | 0 | n.a | n.a | n.a | n.a | n.a | n.a |
| Fe-Re(2:1) | 0 | 66 | 34 | 0 | 16 | 16 | 10 | 21 | 37 | 0 |
| Fe-Re(1:2) | 1 | 66 | 33 | 53 | 30 | 8 | 1 | 1 | 6 | 0 |
| Re(13) | 0 | 0 | 0 | 29 | 35 | 15 | 4 | 7 | 11 | 0 |

Fig. 4. XPS spectra of Fe 2p region for the reduced Fe(2.0)/TiO$_2$ and Fe-Re/TiO$_2$ catalysts.
alloy are 2.587 Å and 2.689 Å, respectively. Both are shorter than the Re-Re bond length (2.75 Å) in Re(13)/TiO2 and the Re foil. The shorter Fe-Re bond length is due to the smaller size of the Fe atom with respect to the Re atom. The Re-Re bond length is 2.653 Å with a coordination number of 7.6, implying a similar coordination number as for the Re-

Table 2

| Sample      | Shell | R     | \(\sigma^2\) [Å²] | CN (±) | ΔE(ev) (±) |
|-------------|-------|-------|-------------------|-------|-------------|
| Re-foil     | Re-Re | 2.750 | 0.00275           | 12    | 5.07 (0.1)  |
| Re(13)      | O     | 2.072 | 0.00716           | 1.1 (0.1) | 6.87 (0.1)  |
| Re-Re       | 2.749 | 0.00776 | 7.2 (0.1)          |       |
| Fe-Re(1:2)  | O     | N/A   | N/A               | 0     | -7.92 (0.7) |
|             | Re-Re | 2.453 | 0.0130            | 2.2 (0.1) | 7.6 (0.3)  |

Error margins reported in brackets, CN is the number of neighboring atoms, R the distance from the central atom to the neighboring scatterers, and \(\sigma^2\) the Debye-Waller factor.

only sample. The occurrence of a Fe-Re coordination of 1.2 at 2.453 Å indicates that a Re-Fe alloy is formed with a high Re/Fe ratio. The inclusion of a Re-O contribution did not significantly improve the fitting results for the Fe-Re(1:2)/TiO2 catalysts.

Given the poor quality of the Fe K-edge XAS data, we used Mössbauer spectroscopy to characterize the Fe phase in our samples. The Mössbauer absorption spectra were recorded at -153.2 °C after reduction at 500 °C. The obtained spectra are presented in Fig. 7, while the Mössbauer fit parameters are summarized in Table 3. The Fe(2.0)/TiO2 sample can only be reduced to metallic Fe to a small extent (6%). The remaining Fe is present as Fe\(^{3+}\) (bulky hematite, FeO\(_x\) 15 %), super-paramagnetic Fe\(^{3+}\) (small hematite particles, FeO\(_x\) 52 %), and Fe\(^{2+}\) (wüstite-like structures, FeO, 27 %). The hyperfine sextet with a hyperfine field of 51.9 T is characteristic for large bulky hematite particles, indicating that a part of the Fe phase sintered during the reduction. The sample containing Re had a higher Fe reduction degree, evidenced by the increase of the relative intensity of the Fe\(^{3+}\) singlet. The hyperfine sextet is no longer visible in the Re-

![Fig. 5. Fe K-edge and Re L3-edge XANES spectra of (a) Fe and (c) Re reference samples, and energy at the half-edge-step of the (b) Fe- and (d) Re-containing samples during temperature-programmed reduction under a H\(_2\)/He flow.](image)

![Fig. 6. Fourier-transforms of the \(k^3\)-weighted EXAFS data (not phase-corrected) at the Re L3-edge for Re(13)/TiO2 and Fe-Re(1:2)/TiO2 samples. Corresponding data of a metallic Re foil is included as a reference. The open circles represent the data points, the solid lines the fit results.](image)
containing samples, indicating that the sintering of Fe-oxide did not occur. This is very likely due to the interaction between Fe and Re. For the FeRe(1:2)/TiO₂, the intermediate Fe²⁺ phase is not visible, which we take as an indication that only part of the Fe atoms can be promoted by Re and reduced at the applied temperature. The (remaining) non-reducible Fe³⁺ species are likely experiencing a strong interaction with the TiO₂ support. The Fe reduction degree in this sample is close to 40%. Given that the reduction degree probed by XPS was much lower, we speculate that the reduced Fe species might be part of a Fe-Re alloy. We cannot exclude however that part of the difference in Fe reduction degree can be due to the sensitivity of reduced Fe species to oxygen during the transfer from the XPS pre-chamber to the high-vacuum chamber.

The reduced and passivated samples were analyzed on a Cs-corrected TEM. In all samples, nanoparticles were found on micron-sized agglomerates of titania particles. Although the bright-field images showed the presence of 1–2 nm nanoparticles, the active phase could not be clearly observed in this way. Accordingly, HAADF-STEM images were recorded as well from which the particle size distribution was determined. EDX maps and particle size distributions are shown in Figs. 8–11. The average particle size for Fe-Re(2:1)/TiO₂, Fe-Re(1:1)/TiO₂, and Fe-Re(1:2)/TiO₂ are roughly similar at 1.0 ± 0.4 nm. Re(13)/TiO₂ contains slightly larger nanoparticles with an average diameter of 1.3 ± 0.8 nm. All samples contain few nanoparticles larger than 2 nm. Notably, the Re-only sample contains a fraction of significantly larger nanoparticles (cf. Fig. 11). By comparing Fe-Re(1:2)/TiO₂ and Re(13)/TiO₂ with the same Re content, it can be stated that the presence of Fe in the bimetallic catalyst results in a better Re dispersion.

EDX mapping in STEM mode showed the presence of Fe and Re over the surface of the titania support. The reported quantitative Fe signals (determined by wide electron probe EDX) were corrected for signals due to secondary electrons using the Co signal. In general, the Fe/Re ratio in areas where no clear nanoparticles are visible is higher than in areas where Re nanoparticles can be observed (Table 4). For instance, the Fe/Re ratio on the titania surface for Fe-Re(2:1)/TiO₂ is higher (~2.0) than the Fe/Re ratio on the nanoparticle displayed in Fig. 8. The EDX maps of the nanoparticle shown in Fig. 8d–f also suggest a core-shell structure in which the shell contains more Fe than the core. The presence of Fe and Re across the titania surface is in agreement with recent aberration-corrected TEM images of a Ni-Re catalyst, which showed that Re is dispersed on the surface in the form of atoms, clusters, and nanoparticles [33]. In the present study, STEM can only image the nanoparticles. Accordingly, we can conclude that the titania-supported Fe-Re samples contain Re nanoparticles in close contact with Fe and very highly dispersed Fe and Re species homogeneously distributed over the titania surface.

IR spectroscopy of adsorbed CO was used to investigate the active phase of the reduced catalysts. As XPS showed that the samples contain oxidic Re and Fe, we recorded the CO IR spectra at liquid N₂ temperature. We also included the bare TiO₂ support for comparison. Fig. 12 shows the IR spectra of CO adsorbed on the samples as a function of the CO partial pressure in the cell (0.02–1 mbar CO range). The IR spectra in the CO stretching region contain bands at 2178 cm⁻¹, 2157 cm⁻¹, and 2042 cm⁻¹. According to the literature [45,46], CO stretching bands between 2200–2100 cm⁻¹ can be assigned to CO adsorption on Lewis-acidic metal cations and OH groups, while metals in a lower oxidation state usually give rise to lower CO stretch.

### Table 3

| Sample                  | IS (mm s⁻¹) | QS (mm s⁻¹) | Hyperfine field (T) | Γ (mm s⁻¹) | Phase | Spectral contribution (%) |
|-------------------------|-------------|-------------|---------------------|------------|-------|----------------------------|
| Fe(2.0)/TiO₂            | 0.03        | –           | –                   | 0.33       | Fe⁰   | 6                          |
|                         | 0.29        | 0.85        | –                   | 0.61       | Fe³⁺  | 52                         |
|                         | 1.10        | 1.37        | –                   | 0.98       | Fe²⁺  | 27                         |
|                         | 0.33        | –          | 0.21                | 0.80       | Fe⁰   | 15                         |
| Fe-Re(2:1)/TiO₂         | 0.05        | –           | –                   | 0.58       | Fe³⁺  | 60                         |
|                         | 0.28        | 0.89        | –                   | 1.18       | Fe²⁺  | 31                         |
|                         | 1.10        | 1.38        | –                   | 0.39       | Fe⁰   | 19                         |
| Fe-Re(1:1)/TiO₂         | 0.04        | –           | –                   | 0.99       | Fe³⁺  | 54                         |
|                         | 0.28        | 0.98        | –                   | 1.20       | Fe²⁺  | 27                         |
|                         | 1.06        | 1.41        | –                   | 0.56       | Fe⁰   | 41                         |
| Fe-Re(1:2)/TiO₂         | 0.04        | –           | –                   | 0.57       | Fe³⁺  | 59                         |
|                         | 0.29        | 1.04        | –                   | –          | –     | –                          |

Experimental uncertainties: Isomer shift: I.S. ± 0.02 mm s⁻¹; Quadrupole splitting: Q.S. ± 0.02 mm s⁻¹; Line width: Γ ± 0.03 mm s⁻¹; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%.

Fig. 7. Mössbauer spectra obtained for the Fe(Re)/TiO₂ samples recorded at -153.2 °C. The spectra were deconvoluted into contributions of Fe⁰, Fe²⁺, magnetic (MAG) Fe³⁺, and supermagnetic (SPM) Fe³⁺.
Fig. 8. Transmission electron microscopy characterization of Fe-Re(2:1)/TiO$_2$: representative (a) TEM and (b) HAADF-STEM images, (c) particle size distribution histogram derived from various STEM images, and (d-f) nanoscale elemental EDX maps. The latter three panels show a particle with a Fe/Re ratio of 1.3 in which the area covered by Fe is larger than that covered by Re, suggesting a core-shell structure.

Fig. 9. Transmission electron microscopy characterization of Fe-Re(1:1)/TiO$_2$: representative (a) TEM and (b) HAADF-STEM images, (c) particle size distribution histogram derived from various STEM images, and (d-f) nanoscale elemental EDX maps, showing a rather homogeneous distribution of Fe over the surface including regions where a Re particle is localized.
frequencies. In particular, bands between 1900 and 2100 cm$^{-1}$ can be assigned to linearly adsorbed CO on the surface of metals. For the bare TiO$_2$ support, a sharp band at 2181 cm$^{-1}$ increased with CO pressure concomitant with a red shift to 2178 cm$^{-1}$. This feature is due to CO adsorbed on Lewis acidic Ti$^{4+}$ sites. Another weaker band at 2156 cm$^{-1}$ can be assigned to weaker Ti–OH···CO complexes [47]. The presence of surface OH groups is also evident from the OH stretching region. Similar IR spectra were obtained for Fe(2.0)/TiO$_2$ (Fig. 12b). The presence of Fe on TiO$_2$ (Fe(2.0)/TiO$_2$) resulted in a lower intensity of the OH stretching bands in the 3500–3800 cm$^{-1}$ region, suggesting
that during the preparation Fe$^{3+}$ has reacted with titania OH groups forming Fe-O-Ti species. It is seen that the more acidic OH groups are preferentially consumed. There are no indications of the presence of metallic Fe, consistent with the other characterization data (Fig. 4, Table 2). The spectra did not contain other bands than those observed for bare TiO$_2$, which suggests that Fe is present as a dispersed Fe-oxide phase, which does not adsorb CO. Based on the reported OH density of this type of titania (4.5 OH/nm$^2$), we can estimate that a Fe content of 2 wt% corresponds to about 80 % of the monolayer capacity.

For the Re-containing samples, the intensity of the broad band at 2157 cm$^{-1}$ is much higher than for TiO$_2$ and Fe(2.0)/TiO$_2$. Moreover, these bands already appear at a much lower CO coverage and, importantly, before the band at 2178 cm$^{-1}$ appears. This completely different behavior suggests that a different and stronger CO adsorption complex gives rise to the 2157 cm$^{-1}$ band in these samples. This is further underpinned by the strong erosion of the band due to OH groups in the 3500−3800 cm$^{-1}$ range when Re is present. It is interesting to note that the OH stretch intensity becomes weaker with increasing Re content. On the other hand, the reduced Re(13)/TiO$_2$ only contains a very weak band at 2158 cm$^{-1}$ band, which must be due to the consumption of most of the weakly acidic Ti−OH groups. This is consistent with the 13 wt% Re loading corresponding to 1.8 monolayer coverage of the titania surface hydroxyl groups. All of the IR spectra of the Re-

| Samples     | Fe/Re ratio | Particles size (nm) |
|-------------|-------------|---------------------|
|             | Expected    | Region | Nanoparticle | Average | SD $^*$ |
| Fe-Re(2:1)  | 2           | 2.0    | 1.0          | 0.9     | 0.3     |
| Fe-Re(1:1)  | 1           | 1.0    | 0.5          | 1.1     | 0.5     |
| Fe-Re(1:2)  | 0.5         | 1.1    | 0.6          | 1.1     | 0.4     |
| Re(13)      | 0           | 0      | 0            | 1.3     | 0.8     |

$^*$ SD is the standard deviation.

![Fig. 12. CO IR spectra recorded at liquid N$_2$ temperature for reduced (a) TiO$_2$, (b) Fe(2.0)/TiO$_2$, (c) Fe-Re(2:1)/TiO$_2$, (d) Fe-Re(1:2)/TiO$_2$, and (e) Re(13)/TiO$_2$ after adsorption of CO; (f) OH stretching regions before CO adsorption.](image-url)
show that the oxides of Fe and Re strongly bind to the titania surface in line with previous literature [20]. Our characterization data demonstrating that reduced Re is the active phase for LvA hydrogenation. The Re reduction degree is much higher for the bimetallic catalyst, and/or the formation of a bimetallic Fe-Re alloy.

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containing samples contain a broad band in the 2030-2048 cm⁻¹ regime, which can be associated with Re⁺. The intensity of this band for the Fe-Re(1:2)/TiO₂ sample is much weaker than for the Re(13)/TiO₂ one. We also notice a red shift of the Re⁺ feature with increasing Re content, which could be due to the close proximity of CO adsorbed on Re to FeOx and/or the formation of a bimetallic Fe-Re alloy.

The CO IR spectra show that the Fe-Re(1:1)/TiO₂ and Fe-Re(1:2)/TiO₂ samples contain a lower amount of reduced Re⁺ surface sites than Re(13)/TiO₂. On the other hand, while TEM shows that the nanoparticles in these catalysts are approximate ~1 nm, XPS and TPR point to a substantially higher reduction degree of Re in the bimetallic catalysts. Together with the Fe/Re ratios on the nanoparticles derived by STEM-EDX maps, we can conclude that the metallic Re particles are covered by small Fe-oxide clusters that partially block the reduced Re sites. A similar conclusion has been drawn in studies of related Fe-Re/ SiO₂ [40] and Pd-FeOx/SiO₂ [48] catalysts.

The CO IR spectra of the bimetallic Fe-Re catalysts contain a feature at 2157 cm⁻¹, which shows a maximum at intermediate Fe/Re ratio. It is not likely that this feature is related to the highly dispersed Fe-oxide and Re-oxide species on the titania support, because the signal is absent for the monometallic catalysts. Therefore, we speculate that the 2157 cm⁻¹ is due to Lewis acid cations, likely Fe cations, at the interface between metallic Re nanoparticles and a partially reduced Fe-oxide (Scheme 1).

3.1. Mechanistic proposal

In attempting to explain the Fe-Re synergy, we compare the highly active Fe-Re(1:2)/TiO₂ catalyst with the nearly inactive Re(13)/TiO₂ one. The Re reduction degree is much higher for the bimetallic catalyst, demonstrating that reduced Re is the active phase for LvA hydrogenation in line with previous literature [20]. Our characterization data show that the oxides of Fe and Re strongly bind to the titania surface via reaction with the OH groups. When the total Fe + Re content is higher than the monolayer capacity of TiO₂ as for Fe-Re(1:2)/TiO₂, hardly any OH groups are observed in the IR spectrum. Therefore, the higher Re reduction degree in the bimetallic catalyst can be related to a fraction of Re-oxide species that are not bound to the titania surface. When the Re loading is too low, a significant fraction of Re remains strongly bound to the titania surface and cannot be reduced, leading to a low hydrogenation activity. Thus, we can conclude that a role of Fe is to compete for surface OH groups of the titania support and decrease the interaction of Re with the support, thereby resulting in a higher reducibility of Re. This is supported by the Mössbauer data, which shows that only 41 % of Fe can be reduced to the metallic state with the remainder being Fe³⁺ (Fig. 7, Table 2). Despite the higher Re reduction degree in bimetallic catalysts, the Re surface area probed by CO IR spectroscopy is small, which is due to the coverage of part of the Re nanoparticles with Fe-oxides (Scheme 1). It is less likely that a very small amount of reduced Fe forming an alloy can cause this, since the combined XPS and Mössbauer data suggest that most of the reduced Fe species are in the core of a bimetallic Re-Fe alloy phase. We speculate that a second role of partially reduced Fe oxides (FeO) is to dissociate water and provide slightly acidic OH groups, which can catalyze the dehydration step of 4-hydroxypentanoic acid intermediate to γ-valerolactone in the mechanism of LvA hydrogenation (Scheme 1) [49,50]. This kind of promoting effect has been discussed for earlier dehydration relevant to aqueous phase reforming by bimetallic Ir-Re, Pt-Re, and Rh-Re catalysts [51–53]. A similar mechanism involving acid-catalyzed dehydration followed by Pt-catalyzed hydrogenation for selective glycerol hydrogenolysis was also proposed by Davis and co-workers [54]. The promotion of metal catalysts with partially oxidized oxophilic MOx species, such as ReOₓ-promoted Rh has also been suggested by a DFT study [55]. In those cases, the oxophilic nature of Re facilitated the activation of water, while we speculate that for the Fe-Re bimetallic catalysts partially reduced Fe-oxide species play this role. The close proximity of metallic Re, Fe-Re alloys and their oxides including titanate can also improve the hydrogenation activity via fast heterolytic activation of H₂ at their interface. Such metal-support interfaces are known to facilitate heterolytic H₂ activation [56].

Encouraged by these findings, we further optimized the reaction conditions by varying the reaction temperature. Fe-Re(1:2)/TiO₂ was selected for this optimization study as it was the most active catalyst in the screening stage. Fig. 13 shows that this catalyst is active for LvA hydrogenation at a temperature as low as 130 °C. Increasing the reaction temperature resulted in a remarkable increase of the catalytic performance. Nearly full conversion was achieved after reaction at 180 °C for 4 h, yielding 95 % GVL. The results at 200 °C were similar and demonstrate that the catalyst is very active and selective for LvA hydrogenation to GVL in water. The sigmoidal activation with respect to temperature might be due to the higher water coverage on the reduced Re surface at too low temperature, which may also lead to partial re-oxidation. Further operando spectroscopy would be required to investigate the catalytic surface during aqueous phase LvA hydrogenation.

![Scheme 1. Proposed mechanism for LvA hydrogenation reaction catalyzed by Fe-Re/TiO₂ catalysts.](image-url)
We performed additional LvA hydrogenation reactions by varying the reaction time from 30 min to 6 h at a temperature of 180 °C. The performance of Fe/TiO₂, Re/TiO₂, and Fe-Re(1:2)/TiO₂ are compared in Fig. 14. It is clear that the bimetallic catalyst is much more active in LvA hydrogenation. About 50 % yield of GVL at 50 % LvA conversion was achieved after 2 h reaction for Fe-Re(1:2)/TiO₂, whereas Re(13)/TiO₂ and Fe(2.0)/TiO₂ were nearly inactive. Notably, the two monometallic catalysts became slightly active after prolonged reaction but afforded only GVL yields of 40 % and 5%, for Re(13)/TiO₂ and Fe(2.0)/TiO₂ after 6 h. For Fe-Re(1:2)/TiO₂, the maximum yield of GVL ~ 95 % was already reached after 4 h.

4. Conclusions

Hydrogenation of levulinic acid towards γ-valerolactone is one of the most promising reactions in the fields of biomass valorization to fine chemicals and liquid transportation fuels. A series of Fe-Re supported on TiO₂ (P25) catalysts were tested for hydrogenation of levulinic acid in water. Remarkable improvements in catalytic performance were observed for the Fe-Re bimetallic catalysts, in comparison with their monometallic counterparts, suggesting a synergistic effect. H₂-TPR results show that the reduction peak of Fe-Re samples shifts to higher temperature regime due to the close interaction between Fe and Re species. XANES shows that the presence of Re promotes the reduction of Fe and there is an interaction between Fe and Re. EXAFS analysis further reveals the presence of Fe-Re alloy. XPS and low-temperature CO-FTIR results evidenced large fractions of FeOx and ReOx are present and part of the metallic Re is covered by FeO₆. The Mössbauer study shows that only part of Fe can be reduced to metallic Fe, due to the strong interaction between Fe and TiO₂ support. The coverage of TiO₂ surface hydroxyl by Fe species was believed to be the reason for the improved reducibility of Re. The Fe-Re alloy, improved Re reducibility and Fe-ReOx species are likely present in the bimetallic samples and believed to be the main reason for the enhanced catalytic activity. The presence of FeOₓ and ReOₓ are highly oxophilic and might introduce Re-OH acidic groups via hydration during the reaction, facilitating the dehydrogenation, a key intermediate step for levulinic acid hydrogenation. Under optimized conditions, nearly full conversion of levulinic acid could be achieved after reaction at 180 °C for 4 h, obtaining 95 % yield of GVL.

CRediT authorship contribution statement

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Nikolay A. Kosinov: Methodology, Investigation, Formal analysis
Evgeny A. Pidko: Conceptualization, Supervision
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Declaration of Competing Interest

There are no conflicts to declare.

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