

## Geochemistry

**Hydrogen Processing by Fe<sup>III</sup>-Exchanged Montmorillonite: A Unique Geochemical Protocol\*\***

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Hydrogen processing, such as the production of hydrogen by the reduction of protons and consumption of hydrogen by oxidation, is of renewed interest since hydrogen is regarded as a fuel for the future. Hydrogen has long been known as a biofuel—it can be produced by many microbes under anaerobic conditions and then consumed later on as a fuel<sup>[1]</sup>—and [Fe]-hydrogenase is known to produce hydrogen, whereas [NiFe]-hydrogenase consumes it.<sup>[1–4]</sup> During hydrogen production by [Fe]-hydrogenase, the electrons are relayed by hydride clusters. Hydrogenase model compounds, developed from complex and tedious synthetic protocols, are known to facilitate heterolytic H<sub>2</sub> activation and H/D exchange reactions or produce hydrogen catalytically in cyclic voltammetry.<sup>[5]</sup> Initial results from divergent approaches to the production of hydrogen by photoreduction of protons<sup>[6]</sup> or by water cleavage<sup>[7–9]</sup> are quite encouraging.

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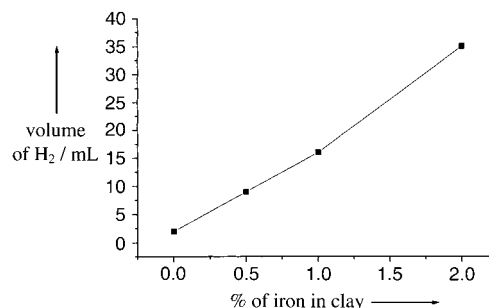
The Earth's crust has abundant reserves of hydrogen buried in it. Besides dehydrogenation of minerals, such as  $\text{Mg}(\text{OH})_2$  and silanols of silicates, the interaction of water with the reduced form of  $\text{Fe}^{\text{II}}$ , which is available in the subsurface of the Earth, is thought to contribute to the production and existence of such huge reserves of hydrogen.<sup>[10,11]</sup> However, the presence of only low quantities of this reduced form of  $\text{Fe}^{\text{II}}$ , which produces hydrogen stoichiometrically, brings into question the extent to which this process contributes to hydrogen production in the Earth's crust.<sup>[11]</sup> Another geochemically important reaction is the formation of dihydrogen and pyrite from  $\text{FeS}$  and  $\text{H}_2\text{S}$  under anaerobic conditions.<sup>[12]</sup>

Despite several attempts, the classical, stoichiometric production of hydrogen in situ by the reduction of protons with  $\text{Fe}^0$  powder and acids, which is currently used in industry for the reduction of nitroarenes to anilines and acetanilides,<sup>[13]</sup> has not yet been transformed into a catalytic reaction. We therefore conceived a nonbiological and nonphotochemical catalytic system for the production of hydrogen by a simple electron-transfer protocol with  $\text{I}^-$  as the electron source and metal-ion-exchanged montmorillonite clay as the catalyst. This clay is known to promote electron transfer and is abundant in the Earth's crust.<sup>[14]</sup> The standard Gibbs energy change of reaction for the formation of  $\text{H}_2$  and  $\text{I}_2$  from  $\text{H}^+$  and  $\text{I}^-$  at room temperature,  $\Delta G^\circ$ , is  $+25.79 \text{ kJ mol}^{-1}$ . Even though the free-energy change ( $\Delta G^\circ$ ) is positive, the above "uphill" reaction has been realized previously by choosing a suitable catalyst and reaction conditions.<sup>[15,16]</sup> We report herein a unique geochemical protocol for the effective, catalytic electron-transfer from  $\text{I}^-$  to  $\text{H}^+$  to generate  $\text{I}_2$  and  $\text{H}_2$ , two products of commercial importance. The reaction occurs at room temperature, employs carboxylic acids as proton source, iodide ions as electron source, and is catalyzed by recyclable  $\text{Fe}^{\text{III}}$ -exchanged montmorillonite ( $\text{Fe}^{\text{III}}$ -mont) [Eq. (1)].



The superiority of  $\text{Fe}^{\text{III}}$ -mont over the other catalysts in terms of turnover number in hydrogen production is clearly evidenced by the results summarized in Table 1 (see also Supporting Information). The activity is correlated to the higher number of acidic sites, which increase with the increased valence state of the cation.<sup>[17]</sup> Furthermore, the

production of hydrogen increases as the percentage of iron in the montmorillonite increases (Figure 1). This result unambiguously demonstrates that iron is the active ingredient in the clay support.



**Figure 1.** A plot of volume of hydrogen liberated (mL) versus the amount of iron (%) in the clay.

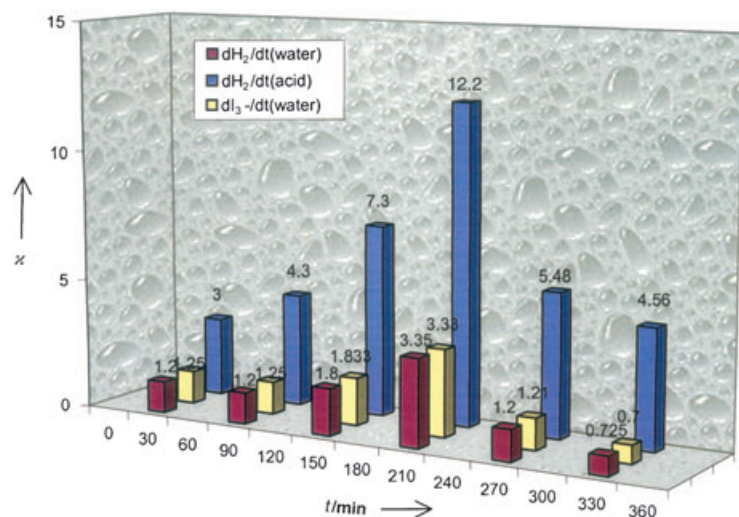
Hydrogen production is enhanced when higher homologues of organic acids or higher temperatures are used (Table 1). The maximum production of hydrogen was found to be 9.37 mmol per g of catalyst using hexanoic acid (Table 1, entry 5). When the production of hydrogen was attempted under identical conditions, but with water as the proton source, no reaction was observed. However, the reaction proceeded well after the addition of a small amount of  $\text{I}_2$  as initiator. This result indicates that  $\text{I}_2$  reacts initially with  $\text{I}^-$  to form  $\text{I}_3^-$  in situ, as determined spectrometrically;<sup>[18]</sup> it is known that  $\text{I}_3^-$  is a better electron source to induce proton reduction.<sup>[19]</sup> The formation of both  $\text{H}_2$  and  $\text{I}_3^-$  at identical rates in an aqueous medium, plotted in Figure 2 as a function of time, further reinforces the proposal that  $\text{I}_3^-$  is indeed the electron source here. These results are impressive when compared with other examples of electron transfer from  $\text{I}^-$  to  $\text{H}^+$ , which require temperatures of 300–400 °C and employ either expensive, noble-metal catalysts or an iodine–sulfur thermochemical process.<sup>[15,16]</sup> There was no oxygen evolution from the reaction, which further confirms that the electron transfer occurs from the iodide only. Moreover, deactivation of the catalyst was not noticed even after the fifth cycle in the production of hydrogen; the XRD pattern of the catalyst recovered after the fourth recycle remains unchanged (Table 1, entries 1, 5, 7).

In an effort to extend the scope of this reaction and to demonstrate the production and consumption of hydrogen in the reaction catalyzed by  $\text{Fe}^{\text{III}}$ -exchanged montmorillonite, the reductive N-acylation of azo-, cyano-, and nitroarenes was accomplished, in a one-pot reaction, under reflux conditions (Table 2). The selective reduction of azo-, cyano-, and nitroarenes in the presence of other susceptible functional groups, such as carbonyl and chloro groups, is a significant achievement. The catalyst, used for four cycles, shows a slight decrease in activity after each run (Table 2, entry 7). These catalytic reactions effected by the cheap and readily available  $\text{Fe}^{\text{III}}$ -mont are superior to the nonregenerable, stoichiometric hydride reagents or the expensive catalysts needed to reduce azo-<sup>[20,21]</sup> or cyanoarenes<sup>[22–24]</sup> under hydrogen pressure. Sim-

**Table 1:** Production of hydrogen gas catalyzed by  $\text{Fe}^{\text{III}}$ -mont at different temperatures using water/carboxylic acids as the proton source.

Entry	Proton Source	T [°C]	H <sub>2</sub> evolution (μmol)	Turnover number <sup>[a]</sup>
1	acetic acid	25	1562.5	8.0, 8.0 <sup>[b]</sup>
2	acetic acid	60	2700.0	13.8
3	acetic acid	150	3370.0	17.3, 17.2 <sup>[b]</sup>
4	propionic acid	150	5400.0	27.7
5	hexanoic acid	150	9370.0	48.0
6	water	25	446.0	2.3
7	water	60	713.8	3.7, 3.7 <sup>[c]</sup>

[a] The calculation is given in the Supporting Information. [b] HI was used in place of NaI. [c] Fourth recycle of the catalyst.



**Figure 2.** The activity profile diagram for the formation of both H<sub>2</sub> and I<sub>3</sub><sup>-</sup> at identical rates in aqueous medium at 60 °C as a function of time. A mixture of catalyst (1.0 g), sodium iodide (40 mmol), and carboxylic acid/water (50 mL) (when water is used as proton source 0.0250 g of iodine was added initially) was heated to 60 °C.  $x$  = formation rate of  $d/dt$  H<sub>2</sub> or I<sub>3</sub><sup>-</sup> [μmol min<sup>-1</sup> g cat<sup>-1</sup>].

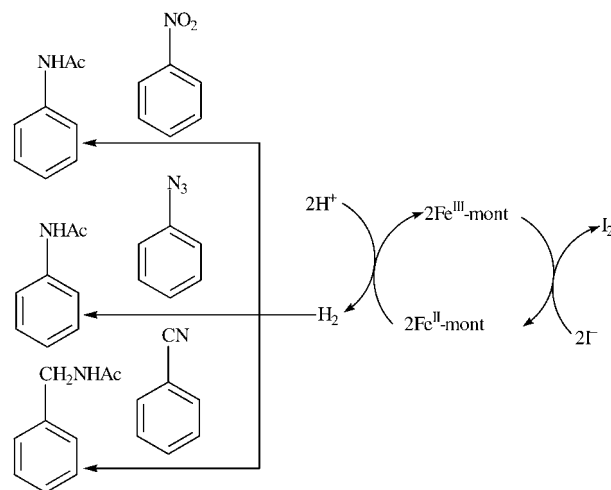
**Table 2:** Reductive N-acylation of azo-, cyano-, and nitroarenes catalyzed by Fe<sup>III</sup>-mont.<sup>[a]</sup>

Entry	Substrate	<i>t</i> [h]	Yield [%]
1	2-azidoanisoole	0.50	98, 92 <sup>[b]</sup>
2	4-azidonitrobenzene	0.50	98
3	4-azidochlorobenzene	0.50	100
4	2-azidobenzoic acid	0.50	92
5	benzonitrile	20.0	60
6	benzyl cyanide	20.0	80
7	nitrobenzene	12.0	82, 70, <sup>[c]</sup> 5 <sup>[d]</sup>
8	<i>p</i> -nitroanisoole	12.0	74
9	<i>p</i> -chloronitrobenzene	16.0	63
10	1-nitronaphthalene	12.0	70

[a] For azoarenes: NaI/acetic acid under reflux; for cyano- and nitroarenes: NaI/propionic acid under reflux. [b] HI/acetic acid under reflux. [c] Fourth recycle of the catalyst. [d] FeCl<sub>3</sub>/FeSO<sub>4</sub>.

ilarly, the reduction of nitroarenes<sup>[25–28]</sup> is usually performed by nonregenerable, stoichiometric carbonyl complexes or by expensive catalysts under hydrogen or CO pressure.

Fe<sup>III</sup>-mont was obtained by following a reported procedure.<sup>[29]</sup> The X-ray photoelectron spectrum (Fe 2p<sub>3/2</sub> band) of a catalyst sample generated by the treatment of freshly prepared Fe<sup>III</sup>-mont with NaI highlights the predominance of Fe<sup>II</sup> species. However, the heterogeneous catalyst obtained after reductive acylation of nitrobenzene shows larger amounts of Fe<sup>III</sup> in the montmorillonite (Figure 1 in the Supporting Information). These results provide strong evidence that, upon treatment with NaI, the Fe<sup>III</sup> centers in Fe<sup>III</sup>-mont are predominantly reduced to Fe<sup>II</sup>, which is, in turn, reoxidized to Fe<sup>III</sup> during the reductive acylation of nitrobenzene. The redox cycle Fe<sup>III</sup>/Fe<sup>II</sup>, involving the relay of two electrons from I<sub>3</sub><sup>-</sup> to H<sup>+</sup> to form hydrogen, is thus established in the present system (Scheme 1). Conversely, the reductive acylation of nitroarenes conducted in the presence of an



**Scheme 1.** Fe<sup>II</sup>/Fe<sup>III</sup> redox cycle in the production and consumption of hydrogen.

equimolar ratio of FeCl<sub>3</sub> or FeSO<sub>4</sub> instead of Fe<sup>III</sup>-mont, under otherwise identical conditions, afforded the desired products in less than 5% yield. These results reinforce our observation that the montmorillonite is an excellent support that facilitates the redox reaction.

In conclusion, the geochemical approach presented here, which provides unambiguous evidence for the production of hydrogen by reduction of protons with the iodide anion as an electron source, even at room temperature, opens up enormous opportunities in hydrogen chemistry. Production of hydrogen by geochemicals, as described here, provides evidence that the vast quantities of hydrogen found in the Earth's crust may be formed by a similar process. The cogeneratedation of H<sub>2</sub> and I<sub>2</sub> by simple electron transfer has great potential for the economical production of iodine and hydrogen. This methodology has also been used for the catalytic and selective reductive N-acylation of a variety of functional groups.

## Experimental Section

General procedure for the production and consumption of hydrogen in the reductive N-acylation of azo-, cyano-, and nitroarenes: A mixture of carboxylic acid (acetic acid for azoarenes and propionic acid for cyano- and nitroarenes; 40 mmol), sodium iodide (40 mmol), substrate (10 mmol), and Fe<sup>III</sup>-montmorillonite (1.0 g) was placed in a 100-mL, two-necked, round-bottomed flask, which was sealed with a rubber septum and fitted with a reflux condenser. The reaction mixture was then heated to reflux. After completion of the reaction (as monitored by GC), the reaction mixture was filtered. The filtrate was taken up in ethyl acetate (50 mL) and quenched with a 1% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (20 mL) to remove the iodine. It was then washed with a 5% sodium bicarbonate solution to remove the unreacted carboxylic acid. The resulting mixture was concentrated under vacuum and the crude product was purified by column chromatography using ethyl acetate/hexane (1:5) as eluent to yield the pure product.

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