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of the reaction mixture with Et_2O gave an oil: ^1H NMR δ 1.20 (3 H, t, J = 7 Hz), 2.26 (m), 2.94 (d, J = 8 Hz), 4.12 (2 H, q, J = 7 Hz), 7.07-7.4 (5 H, m). The deuterium incorporations at the α- and β-positions, determined in a similar way to that described above, were 44% (theoretical value 50%) and 12% (0%), respectively.

Acknowledgment. We are very grateful to Dr. H. Onoue for his helpful discussions.

Supplementary Material Available: Experimental details for the nonrepresentative reactions (3 pages). Ordering information is given on any current masthead page.

Hydrogenation and Deuteration with the System $Zn-NiCl_2$ in Aqueous Medium: Stirring and Ultrasonic Improvement Procedures

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The system $Zn-NiCl_2-H_2O$ is used for conjugate reduction of methyl cinnamate under stirring and ultrasonic irradiation. It appears that in both cases the three steps metallic nickel formation on the zinc surface, hydrogen gas formation by nickel-assisted zinc reduction of water, and catalytic olefin reduction with molecular hydrogen on the nickel-activated zinc surface constitute the main reaction pathways. Deuteration of the substrate is achieved by substitution of deuterium oxide for water, and better results are observed in the stirred reaction. Scanning electron micrographs of the catalyst show that ultrasonic irradiation has cleaned the surface of the particles.

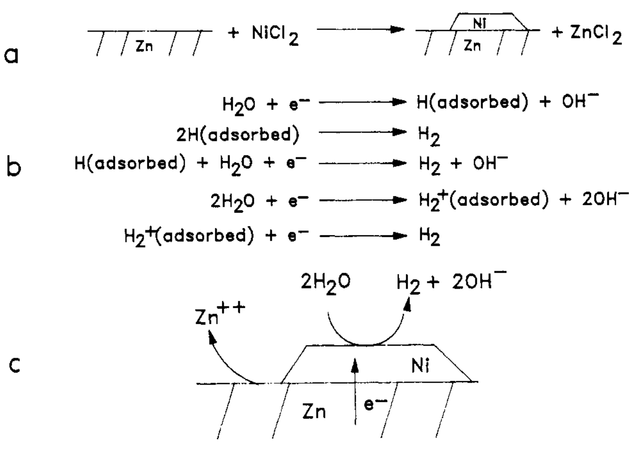
Introduction

Among the reactions improved by ultrasound,[1] hydrogenation has received some attention. Hydrogen transfer from formic acid or hydrazine with palladium on carbon has been successfully tested.[2,3] Reactions involving gaseous hydrogen in heterogeneous catalysis can also be promoted. It has been established that the catalyst surface is activated at 20 kHz by removal of the oxide shell.[4] Other results show optimum hydrogenation when the reaction is performed at higher frequencies, e.g., 500 kHz.[5]

Our investigations of ultrasonic reactions in aqueous media[6] have shown improvements of the reductive properties of the zinc-nickel chloride-water mixture, especially for the selective conjugate hydrogenation of α,β-unsaturated carbonyl compounds.[7] The method has several attractive features. It takes place in a neutral medium with simple reagents, and the reaction proceeds rapidly at a moderate temperature with excellent yields for the reduction of several functional groups.[8]

However the reduction mechanism has not been established. An interesting deuteration process would be expected if deuterium oxide replaces water, but a preliminary investigation gave inconsistent and erratic results when the reaction conditions were changed from sonication to stirring. A comparative study of hydrogenation and deuteration was carried out to provide some understanding of the reaction pathways and to study the modifications introduced in the catalytic process by sonication.

Scheme I[a]



[a] (a) Nickel chloride reduction on the zinc surface. (b) Electrochemical hydrogen formation.[17] (c) Proposed mechanism for the reduction of water on the nickel-coated zinc particle. Deuterium gas production follows the same pathways.

Results and Discussions

For reductions in protic media, zinc is generally activated and used under acidic or basic conditions.[9,10] Addition of a metallic salt to the suspension ($HgCl_2$, CuI, $NiCl_2$) is also known to provide a more reactive metal, but the effects of such treatments are not fully understood.[10,11] In

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the few cases in which nickel chloride and water are used, water has been shown to serve as the hydrogen donor.[7,8,12] Two mechanisms may be proposed: protons are added to an intermediate obtained after the transfer of electrons from the metal to the substrate,[10] or catalytic hydrogenation occurs on the metallic surface with hydrogen gas. In most of the cases involving a metal, the electron transfer followed by a proton addition from water is considered to be the reaction pathway. Hydrogen evolution is then considered as an undesirable side reaction that should be restricted.

In our preliminary communication hydrogen evolution from the reaction mixture was noted, and it appeared that catalytic hydrogenation may have been the reaction pathway.[7] To address this problem, our first experiments focused on the Zn–$NiCl_2$–H_2O (D_2O) system without any substrate.

The Reagent. Hydrogen gas evolution is observed when zinc and nickel chloride are added to the solvent mixture. With ultrasound the maximum level of gas evolution is reached more rapidly than with stirring. The same effect is observed for deuterium gas formation when deuterium oxide is substituted for water. Even during ultrasonic irradiation, the individual components (zinc, nickel chloride, nickel, or nickel and zinc chloride) are unable to produce hydrogen or deuterium.

Because of the low reductive potential of zinc, Ni^{2+} will be reduced on the metallic zinc surface, generating zinc particles that are coated with metallic nickel[13] (Scheme Ia). This bimetallic system is able to reduce water or deuterium oxide, until all zinc is consumed. Zinc is the primary reductive source for the molecular hydrogen or deuterium production, and the theoretical amount of gas, proportional to the remaining zinc after nickel reduction is obtained.

Zinc does not release hydrogen rapidly at neutral pH despite its low electronegative potential. Hydrogen formation catalyzed by the salt of a transitional metal from a highly reducing metal is known in the literature.[14] This phenomenon is similar to the electrochemical overpotential where, according to the nature of the electrode, the reduction of water occurs at a more negative potential than that expected from thermodynamics.[15,16] The deposition of a metal (Ni, Pd, Pt) with properties favoring hydrogen evolution decreases the overpotential, resulting in better hydrogen evolution.[16,17] In the same way, the microparticles of nickel that are deposited on zinc facilitate the H^+ reduction. As an electrochemical cell, electrons from zinc are discharged via the nickel surface with release of oxidized Zn^{2+} (Scheme Ib,c).

The Hydrogenation Procedure. Zinc consumption in the hydrogenation of methyl cinnamate is estimated by

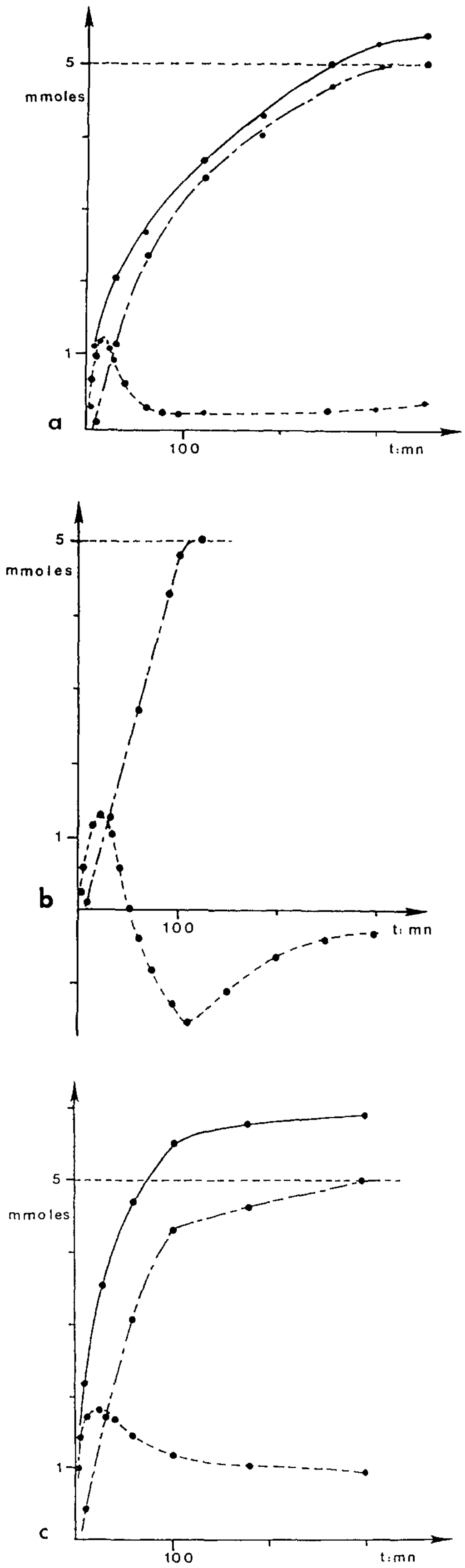

Figure 1. Typical methyl cinnamate hydrogenation with Zn–$NiCl_2$–H_2O versus time, at 313 K: methyl hydrocinnamate formation, – – –; hydrogen evolution, - - -; cumulate value of hydrogen and methyl hydrocinnamate, —. (a) Stirring experiment in argon atmosphere. (b) Stirring experiment in hydrogen atmosphere. (c) Ultrasonic experiment in argon atmosphere (identical result is observed in hydrogen atmosphere).

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summation of the molar amount of hydrogen and methyl dihydrocinnamate produced.

The reduction of the organic compound during ultrasonic irradiation or stirring proceeds by different reaction pathways. With stirring, hydrogen evolves rapidly, whereas the double-bond saturation begins after a small time lag (Figure 1a). The excess gas production ceases rapidly. Hydrogen is then taken up, and the level stabilizes at a low value limited by the partial pressure of hydrogen. The hydrogenation proceeds with a slower rate until the unsaturated ester disappears. The limiting effect of the hydrogen production is illustrated in Figure 1b. In this experiment, the buret was first partially filled with hydrogen (100 mL). The substrate was consumed faster than the rate of water reduction, as indicated by a decrease from the initial level of the gas buret. The complete reduction of substrate was indicated by increasing hydrogen gas volume in buret. The procedure using ultrasound shows rapid gas production and substrate reduction (Figure 1c). Further, hydrogen volume decreases as the reaction proceeds. After 100 min, the rate of hydrogenation decreases rapidly, and hydrogen uptake stops. The cumulative curve indicates that zinc is obviously the limiting reagent. Zinc is consumed and the reaction rate decreases sharply, even though hydrogen is present in the mixture. The experiment using a previously filled hydrogen buret exhibits a similar reaction rate. Therefore, the hydrogen partial pressure in the sonicated mixture is not involved in the reaction as was observed in the stirring experiment.

Reduction does not occur with zinc or with zinc/zinc chloride as described by Toda et al. for other system.[18] The metallic nickel deposited on zinc appears to be an essential catalytic element for the reduction of methyl cinnamate. Sonication accelerates both hydrogenation and water reduction. In both cases, ultrasonic or stirring, most of the reaction occurs by a catalytic addition of hydrogen gas to the substrate.

The Deuteration Procedure. When deuterium oxide is substituted for water under stirring conditions, the deuterium incorporation presents the same features as hydrogenation. The rate is slower and the reduction is limited by the production of molecular deuterium, similar to hydrogenation. The isolated yield of the product is excellent (98%), and the percentage of deuterium incorporation is good. From the ^{13}C NMR measurements: $-CHD_{\alpha}- = -CHD_{\beta}- = 88\%$. From mass spectrometric measurements corrected for background and ^{13}C natural abundance: $M = 5\%$, $M + 1 = 28\%$, $M + 2 = 58\%$, $M + 3 = 8\%$, $M + 4 = 1\%$. The nonquantitative deuterium content is comparable to that generally observed in the case of heterogeneous catalytic reactions. The undesired hydrogen addition is probably caused by some exchange reactions at the catalyst surface.[19]

The deuterium addition reaction under ultrasonic irradiation appears more complex (Figure 2). During the first 90 min, in the presence of the substrate, the process is largely dominated by deuterium gas formation. After 90 min of sonication the concentration of methyl dideuteriocinnamate increases sharply with consumption of deuterium. When all the zinc is consumed, the deuteration rate decreases rapidly, as does the deuterium uptake. It can be noted that the gas consumption starts when the amounts of zinc and nickel are equal. As was observed for hydrogenation, the presence of deuterium gas in the starting atmosphere does not change the course of the reaction. The deuterated compound exhibits the same spectroscopic characteristics as the sample from the stirring experiments, indicating no substantial difference in the stereoselectivities of both methods.

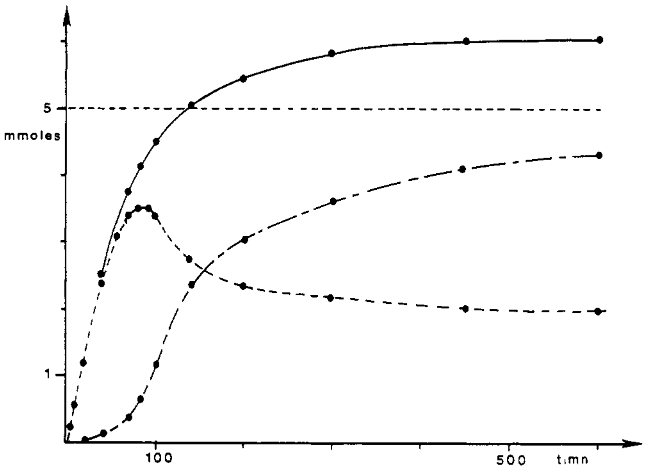

Figure 2. Typical methyl cinnamate deuteration withh Zn–$NiCl_2$–D_2O versus time in the ultrasonic experiment, at 313 K, in argon atmosphere (identical result is observed in deuterium atmosphere). Methyl deuteriocinnamate formation, – – –; deuterium evolution, - - -; cumulate value of deuterium and methyl deuteriocinnamate, —.

In the presence of excess zinc, deuterium is produced, but only a small amount of methyl cinnamate reduction is observed. If there is more nickel than zinc, reduction occurs. This difference does not appear when hydrogenation and deuteration are compared in the stirred experiments. Surface phenomena are obviously involved, and observations of the catalyst structure are directed toward elucidating the origin of this phenomenon.

The Catalyst Characteristics. The changes in catalyst morphology presented here are from the deuteration reactions which were slow enough to allow analysis at intermediate stages of the reaction. They are consistent with those performed in the absence of substrate and in the hydrogenation case.

Before the reaction, the zinc dust particles are spheres of different diameters, roughly 1.2–7.5 μm (Figure 3a). A study of the variations in their size with the course of the reaction was not undertaken.

Scanning electron micrographs of the catalyst obtained during the stirring and the sonication runs are displayed in Figure 3b,c. With stirring, hexagonal zinc deuteriooxide crystals gather around zinc metallic particles. The structures are the same throughout the course of the reaction, and the piles are larger at the end of the reaction. Ultrasonic irradiation gives smooth regular spheres and separated crystals. There is always a clear separation between the zinc oxide salt crystals and the spherical particles. Observation at increasing reaction times shows a general increase in the number of crystals, and dispersive X-ray surface analysis indicates a greater proportion of nickel at the surface of the spheres as the reaction progresses. Nickel is never coated onto the hexagonal crystals; it is found only on the dense metallic balls. These spherical particles are constituted only of nickel at the end of the reaction. When the catalyst is allowed to stand for 15 min at 313 K in the reaction mixture, after a 60 min of ultrasound reaction, the active catalyst spheres shows zinc deuteriooxide crystals on the surface.

Without ultrasound, zinc deuteriooxide crystals grow and mask the reactive surface, creating microstructures

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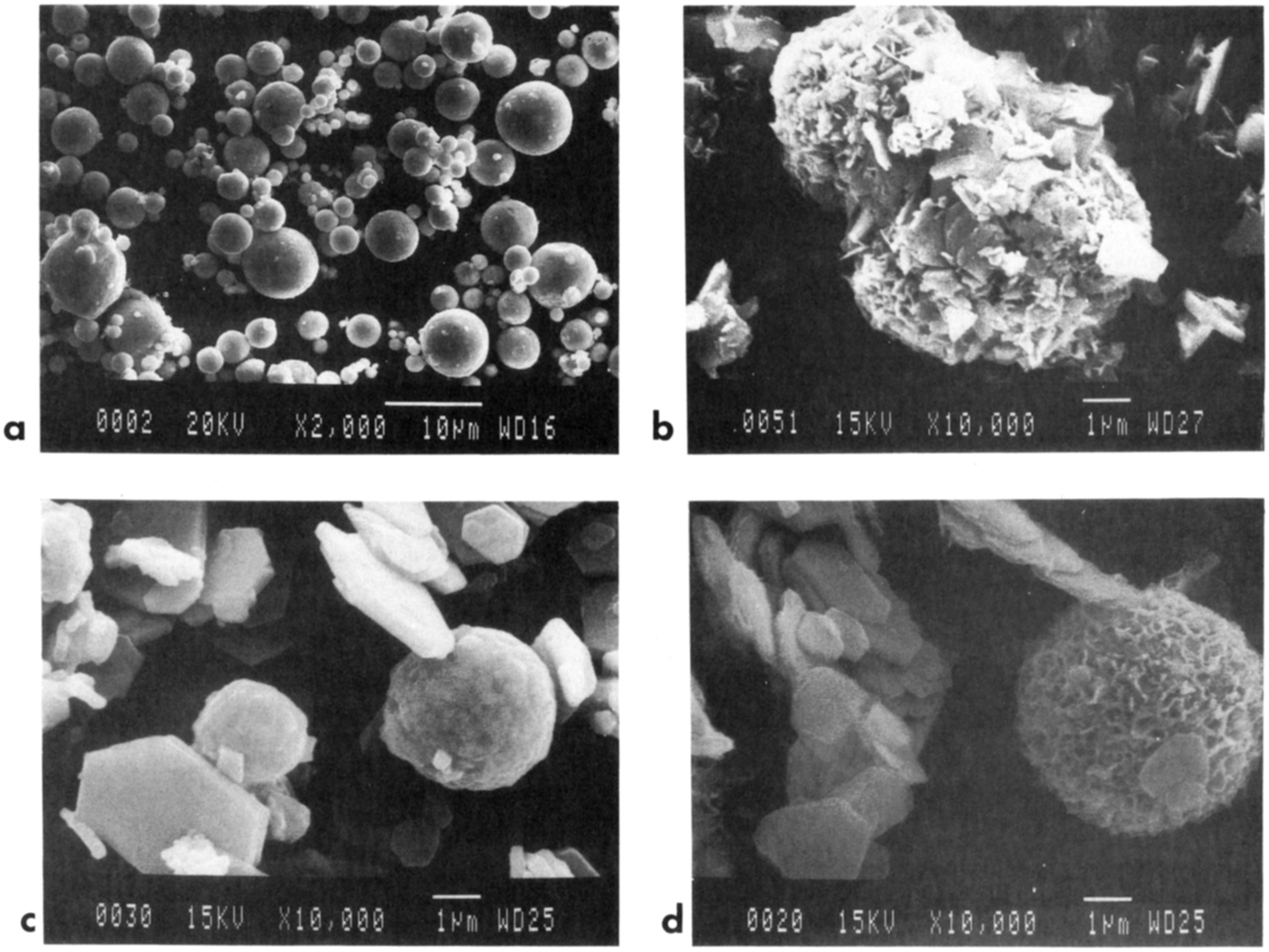

Figure 3. (a) Zinc powder before the reaction. Morphology of the catalyst during the deuteration of methyl cinnamate. (b) Stirred experiment. (c) Ultrasound experiment. (d) Morphology of a 60-min sonicated catalyst after standing 15 min at 313 K.

that modify the diffusion process.

In a liquid, ultrasonic irradiation creates an intense turbulent flow induced by shock waves formed by collapse of transient cavitational bubbles and by variation of the acoustical pressure.[20,21] In such a system small particles are swept to high speed. The resulting microstreaming and interparticle collisions are able to remove the passivating oxide shell of a metal.[4,21] This surface cleaning is an ultrasonic activation process generally observed in many reactions. With zinc and nickel chloride in aqueous media, the system can be thought of as a surface producing zinc hydroxide or deuteriooxide that is constantly being striped.

The Reaction. In the first step the nickel chloride is reduced and coats the zinc surface. Surface nickel promotes the H_2 or D_2 evolution (Scheme I). Taking into account the different experimental data, hydrogenation and deuteration of methyl cinnamate appear to be consistent with the classical heterogeneous catalytic reduction mechanism.[22] In the stirring experiments the hydrogenation rate is directly related to the gas concentration so the mechanism must involve heterogeneous catalytic hydrogenation. With the ultrasound, there is no doubt that this process is occurring for the deuteration case, since the gas uptake and the methyl dideuteriocinnamate production start and stop at the same time. For hydrogenation, the data are not conclusive. The observation that hydrogen gas is also consumed is consistent with the mechanism, and it is unlikely than another mechanism occurs only in this case.

The reaction produces a large amount of zinc salts that shield the active surface and then limit mass transfer. Sonication has the double effect of cleaning the surface and degassing the solution.[23] As a consequence, the amount of hydrogen or deuterium adsorbed on the surface is lowered, and the gas production is increased. These two effects do not inhibit hydrogenation but have a dramatic influence on deuteration. Most of the deuterium gas escapes the reaction mixture rather than adding to the substrate.

No definite conclusions about the precise catalytic properties of nickel plated onto zinc can be drawn. One hypothesis is that the olefin reduction and the gas production occur on the same surface, which should lead to a high reaction rate. The properties of the nickel on zinc catalyst are continuously changing in connection with the zinc–nickel ratio. This phenomenon is emphasized in the sonication experiments. In this case mass transfer around

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the catalyst particles is not hindered by the zinc salts, and the partial pressure of the gas is kept constant. In the deuteration case especially there is a maximum in the catalytic activity when there is more nickel than zinc, but the absence of zinc slows down the reaction. The exact composition of the surface is of course not well established, but a similar enhancement for hydrogenation by Raney nickel was observed when a metallic promoter (Co, Fe, Cu, Mo, Cr) was added in the starting alloy.[24]

Conclusion

The heterogeneous reagent made of zinc and nickel chloride in deuterium oxide is able to effect the conjugate addition of deuterium on methyl cinnamate.

This reaction is identical, with respect to the isotope effect, with that previously described for the same reagent in water. The reaction is most consistent with a catalytic deuterium or hydrogen gas addition to the substrate with the gas coming from deuterium oxide or water. The zinc–nickel mixture is essential in the two steps of the process, formation of gas and reduction of the organic compound.

Compared with the stirring experiments, ultrasound introduces an important perturbation on the catalyst surface and on the course of the reaction. The deuteration is better done with stirring than with ultrasonic irradiation. The interactions between zinc and nickel are the key in this efficient reductive process.

Experimental Section

Infrared spectra were obtained on a Perkin Elmer Model 297 spectrometer. The electron impact mode was used in the mass spectrum recorded on a AEI Model MS 30 instrument. NMR data were recorded on a Bruker AM 300 spectrometer in $CDCl_3$ solution with tetramethylsilane as an internal standard. The differences between the chemical shifts of nondeuterated and deuterated carbon permitted the deuterium evaluation in a quantitative DEPT 90° experiment with a ±5% accuracy.[25,26] Scanning electron micrographs and the dispersive X-rays analysis were obtained with a JEOL J.S.M.-840 microscope and a micro system Tracor TN 5500.

Zinc dust and nickel chloride hexahydrate were obtained from Prolabo. Anhydrous nickel chloride obtained by heating the hexahydrate under vacuum at 323 K was stored under argon. Deuterium oxide (99.8%) and methyl cinnamate were purchased from Aldrich. 1,4-Dioxane was distilled over sodium benzophenone ketyl.

Stirred reactions were performed in a 15-mL two-necked, screw-head, round-bottom flask immersed in a thermostated oil bath. Ultrasonic irradiations were performed in a homemade reactor equipped with a thermostated jacket. The ultrasonic generator (Ultrasons Annemasse, 150 W, 30 kHz) was coupled to a lead titanate transducer. The shape of the titanium horn ensured a good airtight seat up to 10 atm. For each reactor, one arm was closed with two rubber disks, and the other connected through nylon tubing to a gas buret filled with diethyl phthalate. Thus the gas volume was read to ±2 mL of accuracy over a 20-h period.[27] The system was flushed with argon, and the dead volume adjusted to 25 mL before beginning the experiment. The internal temperature was monitored with a chromel–alumel thermocouple.

The reactions were performed in dioxane (8 mL) with water or deuterium oxide (2 mL), a ratio that ensured complete solubility of the starting and final organic products. Methyl cinnamate was chosen because under these conditions the ethylenic bond is selectively and quantitatively reduced. The temperature, 313 K, avoids the erratic induction times observed in the stirred experiments. In a typical run, zinc dust (7.64 mmol), nickel chloride (1.93 mmol), and (if present) methyl cinnamate (5 mmol) were mixed with the solvent in the tightly closed reactor. The reaction progress was followed by periodic withdrawals (10 μL). After dilution with diethyl ether and drying, the sample was analyzed by VPC on a Erba Science chromatograph equipped with a 10% Carbowax 20 M column (2.5 m × 2 mm). The measurements were done with a 5% accuracy on a Shimatsu integrator. At least three runs of each reaction were analyzed, and typical data are presented.

Samples for surface characterization were prepared by centrifugation of the reaction mixture after dilution with dioxane (20 mL). The aqueous solution was then discarded. The solid was washed in dioxane (30 μL) and then centrifuged. The powder was dried under vacuum. Storage and handling of the samples were done under argon.

Analytical samples were prepared by diluting the final mixture with ethyl acetate, filtering on Celite, and drying with sodium sulfate. The solvent is evaporated under reduced pressure, and the product purified by chromatography on a silica gel column (Merck, 70-230) using a pentane/ethyl acetate mixture (9/1) as eluent.

Methyl 2,3-Dideuteriocinnamate (colorless oil): IR (neat) 3040, 2950, 2150, 1600, 1490, 1430, 1260, 1200, 740, 706 cm^{-1}; MS, *m/e* 168 (0.8%), 167 (7.7%), 166 (31%), 165 (14%), 164 (2.6%), 106 (100%), 92 (48.5%), 78 (13.5%), 66 (0.5%); ^1H NMR (300 MHz) δ 3.66 (s, 3 H, $\mathrm{OC}\mathit{H}_3$), 2.61 (m, $\mathrm{C}\mathit{H}\mathrm{DCO_2CH_3}$), 2.94 (m, $\mathrm{C_6H_5C}\mathit{HD}$), 7.29 (m, 5 H, $\mathrm{C_6}\mathit{H}_5$); ^{13}C NMR (75.47 MHz) δ 173.07 ($\mathit{C}\mathrm{O_2CH_3}$), 52.35 ($\mathrm{CO_2}\mathit{C}\mathrm{H_3}$), 30.67 ($\mathit{C}\mathrm{H_2CO_2CH_3}$), 30.35 ($\mathit{C}\mathrm{HDCO_2CH_3}$), 35.40 ($\mathrm{C_6H_5}\mathit{C}\mathrm{H_2}$), 35.11 ($\mathrm{C_6H_5}\mathit{C}\mathrm{HD}$), 140.27, 128.30, 128.06, 126.06 ($\mathit{C}_6\mathrm{H_5}$).

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Supplementary Material Available: ^1H NMR and mass spectra, hydrogen production and deuterium uptake vs time, catalyst morphology, and diagram of ultrasonic cell (6 pages). Ordering information is given on any current masthead page.

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