Microwave effect on the surface composition of the Urushibara Ni hydrogenation catalyst and improved reduction of acetophenone†

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The Urushibara Ni (U-Ni) hydrogenation catalyst and some modified forms, and for comparison Raney-Ni, were subjected to conventional (oil bath) and MW heating, and subsequently characterized by electron dispersive X-ray analysis (EDX), by BET surface area, and by scanning electron microscopy (SEM); yields of the catalyzed hydrogenation of acetophenone to 1-phenylethanol in 2-propanol by one of the modified forms (U-Ni-B) were greatly improved (from 68% to 95%).

Several studies have reported on microwave-accelerated heterogeneous catalyzed reactions in organic syntheses[1] and on microwave assisted treatments of environmental contaminants.[2,3] Microwave radiation is an attractive dielectric heating source that leads to some remarkable improvements of reaction dynamics in various organic reactions. Microwave heating effects in such processes were delineated from conventional heating effects by considering that the catalyzed reaction may be influenced by temperature gradients (hot-spots) created within the catalyst beds.[2,4,5]

Although the reaction dynamics and selectivities of various solid catalysts are influenced by non-thermal effects when catalysts are subjected to microwave radiation fields (dielectric heating), such effects may arise from the impact of microwave fields on the nature of the catalyst. Dielectric heating can be used to some advantage in syntheses of catalysts during the drying, the calcination and reduction processes that can lead to favorable structural modification of the catalyst specimens.[6] Prompt reactions and high product yields have been reported in microwave assisted Ni-catalyzed hydrogenation of toluene,[6] in the cross-coupling of aryl Grignard reagents with aryl fluorides,[7] and in the reduction of acetophenones in aqueous media with a Ni/Al alloy catalyst yielding alkylbenzenes in good yields.[8] Larhed *et al.*[9] have summarized some of the significant advantages of microwave dielectric heating in enhancing various organic reactions catalyzed by transition metal compounds. Although reaction outcomes at different temperatures from comparisons of dielectric and conventional heating methods have often been reported, such reports have typically dealt only with the effects of different heat sources.

Herein, hydrogenation of acetophenone to phenylethanol is examined in 2-propanol as the hydrogen source with various nickel catalysts (Urushibara nickel: Ni/Zn[10] and Raney nickel: Ni/Al catalyst) to assess how microwave dielectric and conventional heating might affect the surface composition of these catalysts and the product yields. Preparations of the catalyst specimens were carried out as per the following procedures.

(i) Urushibara Ni catalyst (U-Ni): zinc powder (10 g; particle size, 15–90 μm by SEM) was added to 3 mL of boiling water in a round-bottomed flask with continued heating from a heat gun, after which a 4 mL aqueous solution of $NiCl_2\cdot 6H_2O$ (crystals, 4.04 g) was added to the flask with vigorous stirring; heating was continued for *ca.* 30 s. The resulting Ni/Zn powder was collected on a fritted glass filter (17G4) by suction in an O_2-free atmosphere (vacuum), followed by washing with boiling distilled water (200 mL). The catalyst was kept in 2-propanol solvent.

(ii) Modified Urushibara Ni catalysts A and B (U-Ni-A and U-Ni-B): a portion of the U-Ni specimen was treated either in an acid solution (160 mL of a 13% HCOOH solution: U-Ni-A) or in an alkali solution (100 mL of a 10% w/v NaOH solution: U-Ni-B). The black particles were collected as before, washed with water and then with 2-propanol.

(iii) Modified Urushibara Ni catalyst (U-Ni-N):[11] the U-Ni-N catalyst was prepared by refluxing a portion of the U-Ni specimen in 2-propanol (30 mL) for 1 h with stirring. The black particles produced were then treated as above.

(iv, v) Raney Ni catalysts W6 and W2 (R-W-6 and R-W-2): 2 g of the Raney alloy (Ni : Al ratio, 50 : 50) were slowly added to a 21% NaOH solution (100 mL) maintained at 10 °C. The solution was stirred for *ca.* 50 min while heating at 80 °C to give the R-W-6 specimen. Heating for 8 h at 50 °C gave the R-W-2 sample. The black particles were then collected and otherwise treated as above.

A Hitachi High-Technologies Co. S-4500 scanning electron microscope (SEM) with an embedded energy dispersive X-ray (EDX) analyzer for seamless observation and EDX analyses was used to determine the particle sizes of the catalysts and to analyze the nature and elemental composition of the catalyst specimens.

The purity of acetophenone and 1-phenylethanol were ascertained by 500 MHz ^{1}H-NMR spectroscopy (JEOL Model LA500; $CDCl_3$ solutions; TMS as the reference) and by GC-MS techniques (Shimadzu Model QP5000 apparatus using an Ultra Alloy column (dimethylpolysiloxane 100%; Frontier Laboratory Ltd); helium was the carrier gas).

A 30 mL 2-propanol solution of acetophenone (3.02 mL) was hydrogenated under an Ar atmosphere in the presence of a Ni catalyst (100 mg) under reflux in a three-necked flask (Fig. 1S†) by continuous microwave dielectric heating (power, 100 W) in an IDX Inc. green-motif I microwave-type apparatus (mono-mode;

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† Electronic supplementary information (ESI) available: Proton NMR data and mass spectral results of acetophenone and the product 1-phenylethanol, as well as the reactor setup (Fig. 1S), temperature profiles (Fig. 2S), SEM images (Fig. 3S), TEM images (Fig. 4S) and XPS analyses for the U-Ni-B catalyst (Table 1S). See DOI: 10.1039/b808188c

maximal power, 300 W; frequency, 2.45 GHz) for organic chemical reactions or by conventional heating (oil bath).

The % yield of the 1-phenylethanol product was estimated using a Shimadzu GC14A gas chromatograph and an RTX-5 capillary column (GL Sciences Inc.).

The rates of increase of temperature of 2-propanol (bp 82.4 °C) under microwave dielectric or conventional heating were examined since microwaves can affect the Ni-catalyzed reaction, and/or the nature of the catalysts surfaces. The initial temperature was 25 °C increasing to *ca.* 82 °C within 3 min under dielectric and conventional heating (Fig. 2S†). In the former, the rate of temperature increase was nearly linear; with conventional heating the temperature increased linearly to *ca.* 55 °C followed by a slower linear increase to the boiling point of 2-propanol, also reached in *ca.* 3 min. Note that hydrogenation of acetophenone by conventional heating was carried out in a pre-heated oil bath (100 °C).

Prior to the hydrogenation reaction, the particle shapes of each catalyst specimen were observed by electron microscopy (JEOL scanning electron microscope; SEM images at magnification factor 5000 are illustrated in Fig. 3S,† except for the R-W-6 specimen for which magnification was 3000). The figure also displays images of the catalyst specimens after 150 min into the hydrogenation reaction with microwave dielectric heating (MW) and with conventional heating (CH), albeit at different magnifications. No changes in particle shape were observed under these heating conditions after 150 min, and no collapse of the particles occurred on microwave heating.

Particles of the U-Ni, U-Ni-A, U-Ni-B and U-Ni-N specimens tended to be spherical, whereas the Raney-Ni catalyst particles tended to be geometrically ill-defined, consisting of aggregated platelets. SEM images of U-Ni-B show particles to be somewhat porous relative to U-Ni, U-Ni-A and U-Ni-N specimens. Surface area measurements confirm this assertion for the U-Ni-B specimen (Table 1). The Raney-Ni catalysts R-W-6 and R-W-2 also consisted of aggregated platelets. No changes in shape of the catalysts were observed after the hydrogenation reaction.

Table 1 Elemental surface compositions and BET surface areas of various nickel catalysts after 150 min of microwave and conventional heating, and corresponding % yields of the hydrogenated product 1-phenylethanol

		% Content			Surface area/ $m^2 g^{-1}$	Yield[a] (%)
		Ni	Zn	Al		
U-Ni	0 min	10.9	89.1	—	10.8	—
	MW	7.8	92.2	—	9.2	52
	Oil bath	9.9	90.1	—	8.9	49
U-Ni-A	0 min	81.4	18.6	—	6.0	—
	MW	82.8	17.2	—	5.8	11
	Oil bath	78.1	21.9	—	5.5	12
U-Ni-B	0 min	22.7	77.3	—	20.2	—
	MW	17.7	82.3	—	20.0	95
	Oil bath	12.4	87.6	—	17.8	68
U-Ni-N	0 min	1.1	98.9	—	6.7	—
	MW	0.2	99.8	—	5.7	42
	Oil bath	1.1	98.9	—	5.2	37
R-W-6	0 min	88.3	—	11.7	13.5	—
	MW	79.5	—	20.5	10.2	93
	Oil bath	80.3	—	19.7	7.4	95
R-W-2	0 min	87.9	—	12.1	11.0	—
	MW	91.2	—	8.8	8.1	81[b]
	Oil bath	93.3	—	6.7	9.8	80[b]

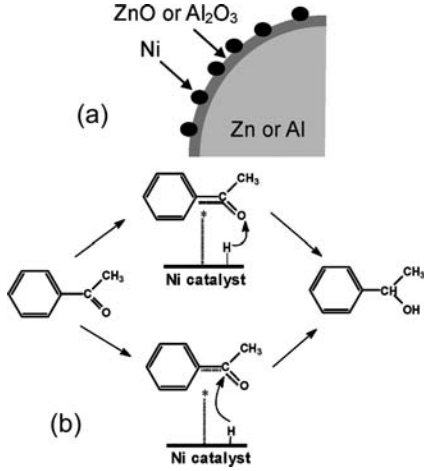
[a] After 150 min. [b] After 60 min.

The initial elemental compositions of the catalysts and subsequent to microwave and conventional heating for 150 min are given in Table 1. Catalysts containing the greater quantity of Ni in the Ni/Zn systems vary in the order U-Ni-A > U-Ni-B > U-Ni > U-Ni-N, in accord with earlier observations.[10,11] No significant correlation appears between the microwave effect and the Ni content ratio. Also reported are the BET surface areas before and after the hydrogenation reaction, since the surface area of a solid catalyst is an important factor that can impact on the hydrogenation reaction as evidenced by the greater microwave effect(s) for the U-Ni-B specimen which displayed the greater surface area: U-Ni-B ≫ U-Ni > U-Ni-N ≈ U-Ni-A and R-W-6 > R-W-2.

Adsorption and desorption processes at the interface of the catalyst surface are enhanced by microwave radiation in a manner that recalls the effects of microwave radiation fields on the surface characteristics of the TiO_2 catalyst.[12] Along similar lines, Kamitani and co-workers[13] observed that adsorption of trimethylamine on zeolite under conventional heating reached saturation after 60 min, whereas the saturation level failed to be reached even after 90 min of microwave irradiation. Nonetheless, yields improved under microwave radiation because the reaction also took place within the pores of the mesoporous zeolite.

Initially the elemental composition of the R-W-2 and R-W-6 catalysts differed little. Under dielectric and conventional heating, however, the level of Ni of the W-R-6 specimen dropped by nearly 8%, whereas for W-R-2 it increased, albeit by only *ca.* 3–5% after 150 min. By contrast, for Ni/Zn catalysts, the change in elemental composition after dielectric and conventional heating was less significant for the U-Ni-N specimen, whereas for U-Ni-B the decrease in Ni was 5% under dielectric heating and *ca.* 10% under conventional heating. TEM microscopic and XPS analyses (Fig. 4S, Table 1S†) confirmed the greater loss of Ni for U-Ni-B under the latter conditions. For U-Ni-A, dielectric heating had little effect, whereas conventional heating decreased the level of Ni by *ca.* 3%. Regardless, most noteworthy are the changes in the composition brought about when the U-Ni sample was acid-treated and alkali-treated to produce the U-Ni-A and U-Ni-B specimens, respectively. Acid treatment removed a relatively large fraction of Zn from the Ni/Zn particles and significantly less under alkali treatment conditions. Acid/alkali treatments of the U-Ni specimen also brought about considerable changes in the shapes of the catalyst particles (see Fig. 3S†) and not-insignificant changes in surface area from *ca.* 11 $m^2 g^{-1}$ for the U-Ni sample to 20 $m^2 g^{-1}$ for U-Ni-B and 6 $m^2 g^{-1}$ for U-Ni-A. Refluxing the U-Ni specimen in 2-propanol caused no changes in particle shape but did decrease the surface area of the particles somewhat (U-Ni-N; Table 1). No clear correlations are evident between surface area and product yields.

Results from the EDX analysis (Table 1) indicate that the Ni catalyst did not completely coat the surface of the Zn and Al powder. Rather, the nickel exists as small deposits on the Zn and Al supports, as ascertained by XPS analysis for the U-Ni-B catalyst, although there is evidence that the surfaces of the Zn and Al supports consist of ZnO and Al_2O_3, respectively,[14] (Scheme 1a). Comparison of the Ni content for U-Ni-N and U-Ni shows loss of such deposits on refluxing the U-Ni



Scheme 1 (a) Proposed surface of the Urushibara and Raney Ni catalysts and (b) proposed mechanism for the hydrogenation of acetophenone to 1-phenylethanol.

specimen in 2-propanol. Moreover, the data also indicate that treatment of U-Ni in acid media to give the modified U-Ni-A leads to significant loss of Ni from the surface through dissolution of the amphoteric ZnO surface and as a consequence to a not-insignificant loss of catalytic features of the Urushibara catalyst. By contrast, the alkali treatment of U-Ni specimen showed considerable improvement of the catalytic characteristics of the U-Ni-B specimen (see below), and no doubt the high absorption of the microwaves by the ZnO and Al_2O_3 surfaces improves further the catalyst surfaces.[15] However, any such improvement of the catalyst surfaces by microwave dielectric heating is tempered by the high dielectric loss solvent used, 2-propanol, which absorbs the microwaves and thus attenuates absorption of the microwaves by the ZnO and Al_2O_3 surfaces. The microwave effect also impacts on the adsorption/desorption processes occurring on heterogeneous catalysts.[12,16] Nonetheless, the synthesis of 1-phenylethanol by hydrogenation of acetophenone takes place on the Ni surface (Scheme 1b). Yet, it is not the Ni content that dictates the yield of product; compare the U-Ni-A catalyst with the Raney-Ni specimens R-W-6 and R-W-2, for which, although they have a similar Ni content on their surfaces, the yields are significantly lower for the U-Ni-A catalyst. Evidently, the support also plays a role.

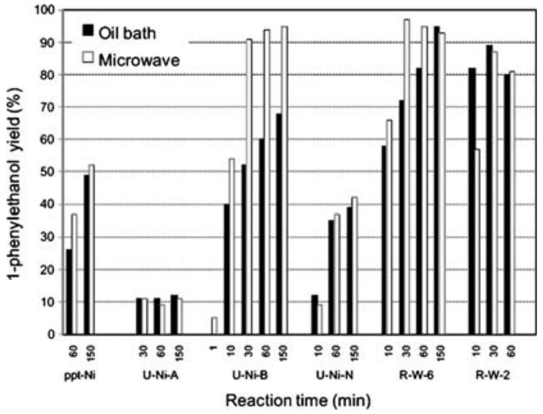


Fig. 1 Synthesis yields of 1-phenylethanol in the presence of U-Ni, U-Ni-A, U-Ni-B, U-Ni-N, R-W-6 and R-W-2 hydrogenation catalysts from microwave and conventional heating.

The quantities (% yield) of 1-phenylethanol produced with each of the catalyst specimens are reported in the histograms of Fig. 1 at various time intervals up to 150 min. Under otherwise identical temperature conditions, the microwave effect was clearly evident for the U-Ni-B catalyst and to some extent for the R-W-6 specimen, as shown by the large difference in yields between conventional heating and microwave dielectric heating. Compare for instance the ~52% yield by conventional heating with the ~92% yield of phenylethanol after only 30 min using U-Ni-B, which represents a nearly 70% increase in yield with the microwaves. At 150 min into the reaction, the yield was *ca.* 95% with microwave heating relative to *ca.* 68% under conventional heating. The worst performing catalyst was the acid-washed Urushibara Ni specimen U-Ni-A regardless of heating methods, whereas the best performing catalysts were the alkali-washed U-Ni-B sample and the Raney Ni specimen R-W-6, followed by the R-W-2, U-Ni and U-Ni-N specimens.

Reaction dynamics of the catalyzed reactions are no doubt governed by the heating factor. However, not all Ni catalyst specimens showed superior microwave irradiation effects *vis-à-vis* conventional heating, as exemplified by the data for the R-W-2 specimen, which show that conventional heating yields a greater quantity of the product for the same time interval (Fig. 1).

In summary, we have demonstrated a significant microwave effect on the surface catalytic properties for the alkali-treated Urushibara hydrogenation U-Ni-B specimen. The root cause(s) of the specific microwave effect has remained thus far elusive, although some suggestions have been proposed. In this regard, Takashima and co-workers[17] have suggested that the major advantages of microwave radiation in Ni- and Pt-catalyzed cleavage of a C–Cl bond on α-Al_2O_3 were the direct, selective and rapid heating of the catalyst, as well as the thermal conductivity of the support.

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