

## Efficient Hydrogenation Catalysts of Ni or Pd on Nanoporous Carbon Workable in an Acidic Condition<sup>†</sup>

Donghwan Lee, Honggon Kim,<sup>‡</sup> Min Kang,<sup>§</sup> Ji Man Kim,<sup>§</sup> and Ik-Mo Lee\*

*Department of Chemistry, Inha University, Incheon 402-751, Korea. \*E-mail: imlee@inha.ac.kr*

*<sup>‡</sup>Korea Institute of Science and Technology, Reaction Media Research Center, Environment & Process Technology Division, Seoul 136-791, Korea*

*<sup>§</sup>Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea  
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Efficient catalytic systems, where Ni or Pd is introduced in a supporting material of nanoporous carbon, have been developed for a liquid-phase hydrogenation of carboxylic acids and ketones at room temperature. It has been found that the catalysts reliably show high activities and selectivities for the hydrogenation to alcohols even in acidic conditions, and the catalytic activities depend on the preparative method of catalysts, the hydrogen pressure, the agitation rate, and the catalytic species. The hydrogenation of carboxylic acids and ketones clearly shows that the reaction rate is affected by the electronic and the steric effects, and a plausible reaction mechanism using metal hydrides as catalytic species is proposed.

**Key Words :** Hydrogenation catalysts, Ni, Pd, Nanoporous carbon, Trifluoroacetic acid

### Introduction

In the economic production of various alcohols from carboxylic acids, the development of an efficient hydrogenation catalyst having high activity, selectivity and durability would play a key role. Despite of high activity and controllability, most homogeneous catalysts are limitedly used in the industrial process due to their low thermal stability and low efficiency in recycling. Hydrogenation of carboxylic acids in the liquid phase, therefore, requires supported catalysts for easy separation from the liquid products. In addition to the selection of active metallic species, such as Ni, Pd or Pt, in the supported catalysts, it is also necessary to develop supporting materials which can improve the catalytic properties and stability in an acidic condition because the reactants, carboxylic acids, usually make the reaction acidic, which may cause some limitations in the catalytic system. Carbon-based materials can be proposed as good acid-resistant supporting materials.

Even though supported catalysts with ultrawide pores have been sought for the hydrogenation of high molecular weight polymeric materials,<sup>1</sup> lots of interest has moved to the preparation of ordered mesoporous and macroporous materials composed of polymers, metal oxides, metals, or metal alloys.<sup>2,3</sup> Such metallic materials have been exploited well as active components in catalytic converters<sup>4</sup> and as recyclable heterogeneous catalysts for coupling reactions.<sup>5,6</sup> Furthermore, much attention has recently been paid to nanoporous and nanocrystalline materials for their potential application to catalysis. Both nanoporous and nanocrystalline materials possess tremendously high surface-to-volume ratios, which would offer a greatly increased number

of active sites for carrying out catalytic reactions.<sup>7</sup> In addition to the recent development and application of carbon nanotubes in various fields, much effort has been devoted to develop new nanostructured carbon materials. One representative example is the nanoporous carbon with hexagonally ordered mesostructure developed by Ryoo,<sup>8</sup> which can be an alternative to charcoal as a catalyst supporter. C-C coupling reactions have been successfully catalyzed by the nickel on this nanoporous carbon material.<sup>9</sup> In these papers, we demonstrated that these catalyst systems were far more active than the conventional one with active charcoal probably due to more homogeneous environment around the catalytically active species.

Among the hydrogenation reactions of carboxylic acids to alcohols, the hydrogenation of 2,2,2-trifluoroacetic acid (TFAA) to 2,2,2-trifluoroethanol (TFEA) may be an interesting reaction because TFEA is currently used as an important solvent in fluorine chemistry as well as an intermediate of fluorine-containing medicine, pesticides, and anesthetics. TFEA can also be adopted as a starting material for fluoroesters and fluoroethers, which are in turn utilized in preparing functional fluororesins containing oxygen useful for optical fibers. Moreover, it can be considered as an alternative to CFC cleaning agents because of its non-destructive nature to the ozone layer, lower global warming effect than HFC (hydrofluorocarbon) or HCFC (hydrochlorofluorocarbon) cleaning agents, high thermal stability, high cleaning power for organic compounds, and miscibility with water.

In this contribution, we report that Ni or Pd on nanoporous carbon (nano C) can be used as a highly active heterogeneous catalyst for hydrogenation of carboxylic acids, especially of TFAA, and that the activities of these catalysts can be controlled by modifying the synthetic procedure.

<sup>†</sup>This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

## Experimental Section

**General procedure for preparing Ni/nano C.** Synthesis of a mesoporous silica template, SBA-15 was performed following the procedures described in the literature.<sup>8</sup> Preparation of nanoporous carbon structure of CMK-3, and catalysts (ANi-1, ANi-2, ANi-3) was described elsewhere [9(a)].

**General procedure for preparing Pd/nano C.** The whole procedures were the same as those for Ni/nano C catalysts except that 0.83 g of PdCl<sub>2</sub> was used instead of 2.49 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. Three different types of catalysts were prepared and were denoted ANi-6-1, ANi-6-2 and ANi-6-3 according to the respective preparing procedures.

### Hydrogenation of carboxylic acids

**Hydrogenation of carboxylic acids and ketones:** The reactant (carboxylic acid or ketone, 0.1 mol) and catalysts (50 mg) were introduced in a glass-lined autoclave (100 mL), and 72 mL of THF was added. The solution was heated by a heating element with a temperature controller. After the temperature was reached to the preset point, hydrogen was introduced. The liquid-phase reaction product was sampled every 10 min and analyzed in GC.

**Hydrogenation of TFAA:** TFAA (8 mL) and catalysts (50 mg) were introduced in a flame-dried 3-neck flask (250 mL) or a glass-lined autoclave (100 mL), and 72 mL of THF was added. The solution was heated by an oil bath (ambient pressure) or a heating element with a temperature controller (high pressure). After the temperature reached to the preset point, hydrogen was introduced. The conversion of TFAA and the product distribution were monitored by the analysis of a liquid sample in GC every 10 min.

**Analysis of hydrogenation products.** Samples of the reaction products were analyzed by using a Young-In GC 680A gas chromatograph equipped with a FID and a packed column (HayeSep R, 80/100, 2 m). The flow rates of nitrogen, hydrogen, and air were 0.43, 0.77, and 7.0 cc/s while the injector and the detector temperatures were 200 and 250 °C, respectively. The column temperature was programmed from 100 °C (15min) to 200 °C (20 min) with a heating rate of 10 °C/min in the cases of TFAA, benzoic acid and acetic acid. In the cases of other carboxylic acids, the column temperature was programmed from 50 °C (15 min) to 200 °C (30 min) with a heating rate of 5 °C/min.

**Determination of metal contents by atomic absorption (AA) spectroscopy.** After weighing the sample to 0.1 mg, about 10 mg of sample was completely dissolved in 10 mL of aqua regia while stirring vigorously at 70 °C. Then the solution was used to determine the metal contents by AA spectroscopy (Spectr AA 220FS, Varian).

**Determination of the X-ray diffraction pattern and pore size of nanoporous materials.** The structure and order of mesoporous materials were determined by X-ray powder diffraction (XRD) analyses. The XRD patterns were obtained by using Cu-K $\alpha$  radiation with a Rigaku D/MAX-III instrument at room temperature. Nitrogen adsorption-desorption isotherms at liquid nitrogen temperature were

measured using an Autosorb-1 apparatus (Quantachrome), and pore size distributions were calculated by the BJH method. Before the measurements, samples were degassed for 12 h at 550 K.

## Results and Discussion

In the hydrogenation of unsaturated compounds, heterogeneous catalysts of Ni, Pd and Pt or homogeneous catalysts such as RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and RhCl(PPh<sub>3</sub>)<sub>3</sub> have been adopted and well studied. Metal hydrides such as LiAlH<sub>4</sub> and NaBH<sub>4</sub> have been also utilized. Recent new environmental legislation for strict limitation of the aromatic contents of fuels, oils and solvents drove the extensive studies on the hydrogenation of aromatic compounds.<sup>10</sup> Also the effect of stabilizers on the hydrogenation activity has been another issue in this area.<sup>11,12</sup> Recent issues on the hydrogenation by nano metal or metal alloy catalysis have been well reviewed.<sup>13</sup>

However, heterogenized supported catalysts have an advantage in the separation and recycle of the catalysts. Various supporters such as active charcoal, silica, zeolite, and MgO have been exploited in many catalytic reactions. In order to develop a new catalyst for the hydrogenation of carboxylic acids, two features should be considered; the formation of water and high acidity of the reaction condition. Carbon-based materials are proposed as possibly good acid-resistant supporters. Recent interests are focused on extending the surface area of carbon supporters. In this regard, a nanoporous carbon with hexagonally ordered mesostructure developed by Ryoo<sup>8</sup> can be a good alternative catalyst supporter. This material is known to have a high surface area, high chemical stability and a hydrophobic nature. Therefore, the introduction of Ni or Pd as an active species into this nanoporous carbon would be well fitted to the object of this system.

Three types of catalysts for each component of Ni or Pd were prepared by changing the order of introducing active species into the nanoporous carbon supporter; before, during and after carbonization. The catalysts are denoted as ANi-1, ANi-2, and ANi-3 for Ni catalysts or ANi 6-1, ANi 6-2, and ANi 6-3 for Pd catalysts, respectively. The structure and physical properties of each catalyst were examined by XRD and BET isotherm with N<sub>2</sub> adsorption. From Figure 1, catalysts show crystalline nature except ANi-3 and ANi 6-3. This character seems to be related with the heat treatment. Since these catalysts are just dried without heat treatment, they lost crystallinity during the drying process. As shown in Table 1, the surface areas of all catalysts were found tremendously large. But the surface areas and the pore volumes of the metallic catalysts were a little bit smaller than those of the pure CMK-3 without metallic species. The average pore size were measured around 3.7-4.3 nm according to the catalysts.

In an interesting example to produce TFEA by hydrogenation of TFAA in the liquid phase of THF, these catalysts were proven quite efficient and selective as expected from

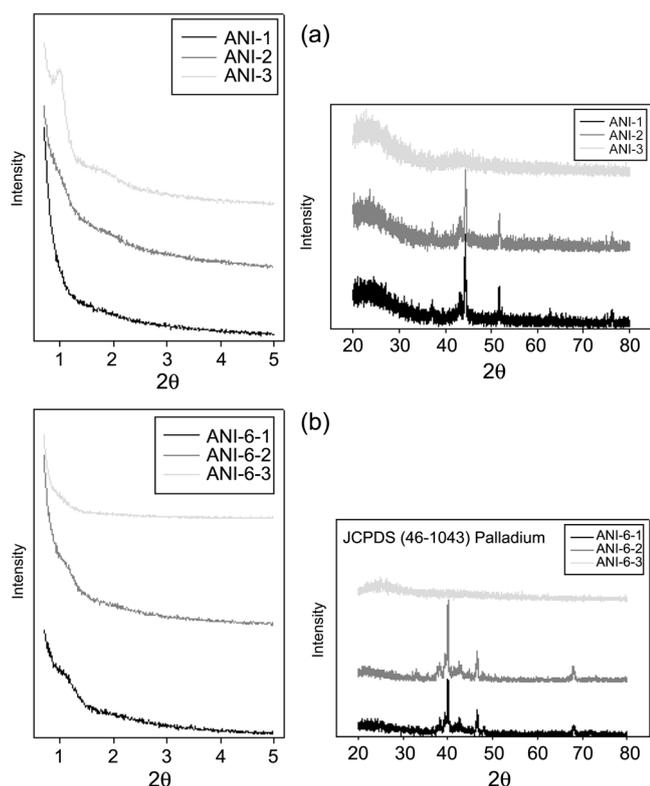


Figure 1. XRD results (a) Ni/nano C (b) Pd/nano C.

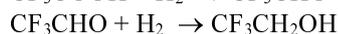
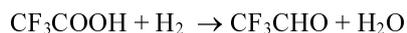
Table 1. Physical Properties of Ni and Pd on nanoporous carbon

Catalyst	Surface area $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Pore volume $V_{\text{P}}$ ( $\text{cc}/\text{g}$ )	Pore size $D_{\text{P}}$ (nm)
Ni	ANi-1	907	3.9
	ANi-2	890	4.4
	ANi-3	844	3.7
Pd	ANi 6-1	1105	4.0
	ANi 6-2	1017	3.7
	ANi 6-3	1088	3.9
Supporter CMK-3	1520	1.30	4.5

their high surface areas. Hydrogenation of TFAA can be represented by the following equation.



Even though this reaction appears to occur in a single step, it actually consists of two following sequential reactions.



Trifluoroacetic aldehyde is the intermediate. But the aldehyde might be quickly converted to TFEA with these catalysts, so that TFEA was the only product obtained in this catalytic system.

The conversion of TFAA to TFEA with the Ni and Pd catalysts used mostly followed S-shaped curves which consisted of three stages (Figure 2): the induction period where the TFAA conversion was very low in the initial

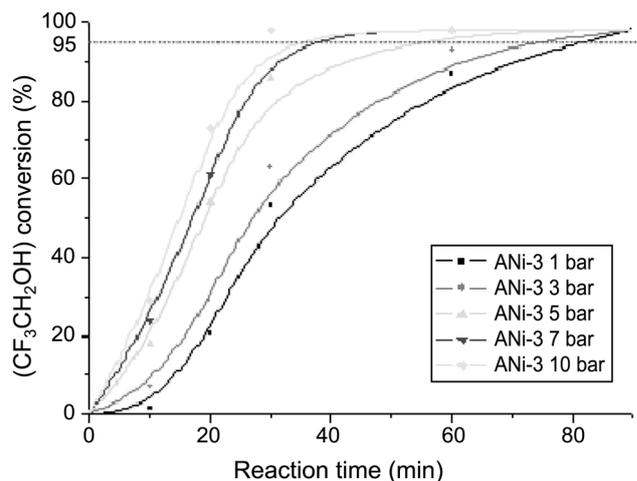


Figure 2. Typical reaction profiles in hydrogenation of TFAA.

Table 2. Hydrogenation of TFAA with Ni or Pd on nanoporous carbon

Metal	Catalyst	Reaction Condition		Reaction Time* (min)	AA-result (g/g %)
		Temp. ( $^{\circ}\text{C}$ )	$P_{\text{H}_2}$ (bar)		
Ni	ANi-1 (6.89 g/g %)	25	1	120	3.90
			10	60	2.87
	ANi-2 (5.17 g/g %)	25	1	240	3.88
			10	90	3.09
	ANi-3 (6.01 g/g %)	25	1	90	1.54
			3	90	
			5	60	2.21
			7	60	
			10	30	1.87
	Pd	ANi 6-1 (16.77 g/g %)	25	1	60
10				20	13.59
ANi 6-2 (18.17 g/g %)		25	1	90	17.45
			10	30	13.37
ANi 6-2'		25	1	120	12.56
			1	180	11.30
ANi 6-3 (4.80 g/g %)		25	1	60	4.32
			3	30	
			5	30	4.19
			7	20	3.93
	Ni'		Nickel nitrate	25 $^{\circ}\text{C}$ , 0.5 mg	10
		25 $^{\circ}\text{C}$ , 5 mg	10	60	

ANi 6-2' and ANi 6-2'' represent results obtained with the 1<sup>st</sup> and the 2<sup>nd</sup> recycled catalysts. \*Time required for 95% conversion of the initial substrate.

stage, the actively reacting period, and the equilibrium period where the reaction was almost completed. The conversion of TFAA in the actively reacting period was almost linear to the reaction time, so that the reaction was supposed to proceed following the 1<sup>st</sup> order reaction and the

reaction rate constant was determined from the average linear slope of the curve in that period. The relative hydrogenation activity of each catalyst was estimated by determining the time where the conversion of TFAA to TFEA reached at 95%. As shown in Table 2, it was found that ANi-3 or ANi 6-3 was the most efficient catalyst among each group (ANi-3 > ANi-1 > ANi-2; ANi 6-3 > ANi 6-1 > ANi 6-2), which was not consistent with the order of metallic contents in the catalysts. This could be explained by assuming that the order of the amount of active metallic species existing on the surface was different from that of the total amount of metallic species in the catalyst. In other words, the amount of active catalytic species was determined by the preparative methods of catalyst rather than simply by the amount of metallic species contained. The post impregnation of metallic species in the pre-made CMK-3 structure was proved to be the most efficient method of preparing catalysts. Pd catalysts were found to be commonly more active than Ni catalysts; for example, the 1<sup>st</sup> order rate constants were 0.88 min<sup>-1</sup> for ANi 6-2 of Pd and 0.69 min<sup>-1</sup> for ANi-2 of Ni at 25 °C and 1 bar of H<sub>2</sub>. The ratio of relative rates of ANi-3 to ANi-2 or ANi 6-3 to ANi 6-2 under the same condition was 2.5 or 2.7, respectively. Even though the hydrogenation reaction rates generally increased with the H<sub>2</sub> pressure, the activity of Ni catalyst was more sensitive to H<sub>2</sub> pressure than that of Pd catalyst; the ratio of relative rates of

ANi-3 at 10 bars to at 1 bar was 2.6 while that of ANi 6-3 at 10 bars to at 1 bar was 2.1.

The catalysts were collected after the reaction, and the metal content of each catalyst was analyzed by the atomic absorption (AA) spectroscopy. In the case of Ni in nanoporous carbon, it was found that more Ni was leached out from ANi-3 than from other nickel catalysts, and it was suspected that the possible homogeneous catalysis was also involved during the reaction. When the hydrogenation rate was tested with Ni(NO<sub>3</sub>)<sub>2</sub> of the same amount of Ni as in the original catalyst of ANi-3, the activity was far lower than that of the supported catalyst, ANi-3. This indicated that the contribution of supported catalysts to the activity of metallic species could not be ignored even though both heterogeneous and homogeneous catalysis have occurred simultaneously in this system. It is also interesting that more metallic species were leached out under higher hydrogen pressure. Differently from the Ni catalysts, ANi 6-3 and ANi 6-2 of Pd are the catalysts from which the fewest Pd and the most Pd were leached out after the reaction, respectively. The activities of recycled catalysts gradually decreased according to the number of recycle even though lots of metallic species were found remaining in the catalyst. This again proved that most of the active species were the metals on the catalyst surface, which could be exposed to the reacting substrate.

**Table 3.** Hydrogenation of Carboxylic Acids with Ni catalysts

Entry	Substrate	Catalyst	Reaction Conditions		Reaction Time* (min)	AA-result (g/g %)
			Temp. (°C)	P <sub>H2</sub> (bar)		
1	CF <sub>3</sub> COOH	ANi-3 (6.01 g/g %)	25	1	120	1.54
				5	60	2.21
				10	30	1.87
2	PhCOOH	ANi-3	25	10	60	
3	PhCH(CH <sub>3</sub> )COOH	ANi-3	25	10	150	
4	Ph <sub>2</sub> CHCOOH	ANi-3	25	10	120	
5	CH <sub>3</sub> COOH	ANi-3	25	10	60	
6	Me <sub>2</sub> CHCOOH	ANi-3	25	10	150	
7	Me <sub>3</sub> CCOOH	ANi-3	25	10	180	

\*Time required for 95% conversion of the initial substrate.

**Table 4.** Hydrogenation of Carboxylic Acids with Pd catalysts

Entry	Substrate	Catalyst	Reaction Conditions		Reaction Time*(min)	AA-result (g/g %)
			Temp. (°C)	P <sub>H2</sub> (bar)		
1	CF <sub>3</sub> COOH	ANi 6-3 (4.80 g/g %)	25	1	60	4.32
				5	30	4.19
				10	20	3.93
2	PhCOOH	ANi 6-3	25	10	60	
3	PhCH(Me)COOH	ANi 6-3	25	10	120	
4	Ph <sub>2</sub> CHCOOH	ANi 6-3	25	10	90	
5	CH <sub>3</sub> COOH	ANi 6-3	25	10	60	
6	Me <sub>2</sub> CHCOOH	ANi 6-3	25	10	120	
7	Me <sub>3</sub> CCOOH	ANi 6-3	25	10	150	
8	PhCHO	ANi 6-3	25	10	30	

\*Time required for 95% conversion of the initial substrate.

There was a distinct induction period for the hydrogenation under a low H<sub>2</sub> pressure but any clear induction period was not observed under a high H<sub>2</sub> pressure. The hydrogenation with the catalysts which were reduced with H<sub>2</sub> prior to the reaction did not appreciably decrease the induction period, so that the reduction of M(II) to M(0) (M = Ni or Pd) did not seem the major reason. Instead, the adsorption of hydrogen (or activation of hydrogen) or desorption and recoordination of aldehydes, the intermediates, might be a main reason for the induction period. It is generally recognized that the adsorption of H<sub>2</sub> occurs more easily on Pd than on Ni and that the standard reduction potential for M<sup>2+</sup>/M couple in Pd (0.987 V) is much higher than that in Ni (-0.246 V), which allows easier reduction of Pd<sup>2+</sup> than Ni<sup>2+</sup>. Therefore, the induction periods in hydrogenation with Pd catalysts were commonly shorter than with Ni catalysts. In addition to the high H<sub>2</sub> pressure, high agitation rates improved the hydrogenation rate, which indicated that the diffusion rate of H<sub>2</sub> to the active site also importantly affects the reaction rate.

The activities and selectivities of the catalysts of Ni and Pd impregnated in CMK-3 (ANi-3, ANi 6-3) were investigated for the hydrogenation of various carboxylic acids. The reaction times when the conversions of the reactants reached at 95% are summarized in Table 3 (Ni) and Table 4 (Pd). In comparing the entries of 1, 2, and 5 in both tables, it was found that a strong electron-withdrawing substituent such as -CF<sub>3</sub> adjacent to the -COOH group allowed H to easily attach to the carbon in -COOH so that the hydrogenation rate was accelerated. In comparing the entries of 5, 6, and 7, sterically bulky substituents prevented H from coming to the adjacent carbon so that the hydrogenation rate was reduced. Sterically bulky substituent seemed to prevent the reactant from coordinating to the metal, and the transfer of the metal hydride to the carbonyl carbon seemed retarded. Substitution of proton with a phenyl group in the acetic acid (entry 2) might show the electronic and the steric effects simultaneously. In comparing the entry 3 to the entry 5 in each table, the hydrogenation rate decreased due to the bulkiness of phenyl group. But, further introduction of another phenyl group (entry 4 vs. 3) showed an increase of the hydro-

genation rate, which might be due to the electron-withdrawing nature of phenyl group dominating its steric bulkiness.

In order to design a reaction mechanism, the pure electronic effect was investigated by using several para-substituted benzoic acids (Table 5). Hammett plots<sup>14</sup> with both Ni and Pd catalysts, ANi-3 and ANi 6-3, clearly showed the cationic character of the active intermediate. The hydrogenation rate of benzoic acid with an electron-withdrawing substituent is faster than that with an electron-donating group (Figure 3). Hydride transfer to the carbonyl carbon with cationic character would be the rate-determining step, and a plausible reaction mechanism with an intermediate containing molecular hydrogen ligands is proposed to explain the observed experimental results. The scheme 1 represents the reaction mechanism proposed for the hydrogenation of carboxylic acids with Ni or Pd on nanoporous carbon. The presence of molecular hydrogen ligands can avoid the unstable oxidation state of metal, M(IV), the oxidation state after activation of two moles of H<sub>2</sub>, is less stable than M(II) proposed in this mechanism. Another advantage of introducing molecular hydrogen intermediates in the mechanism is as follows; the molecular hydrogen is

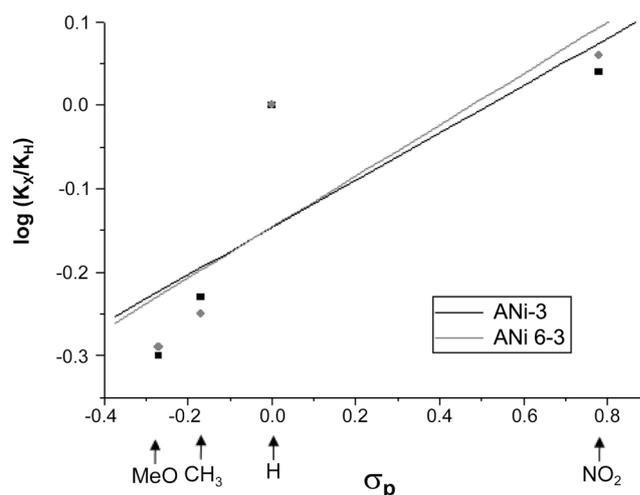
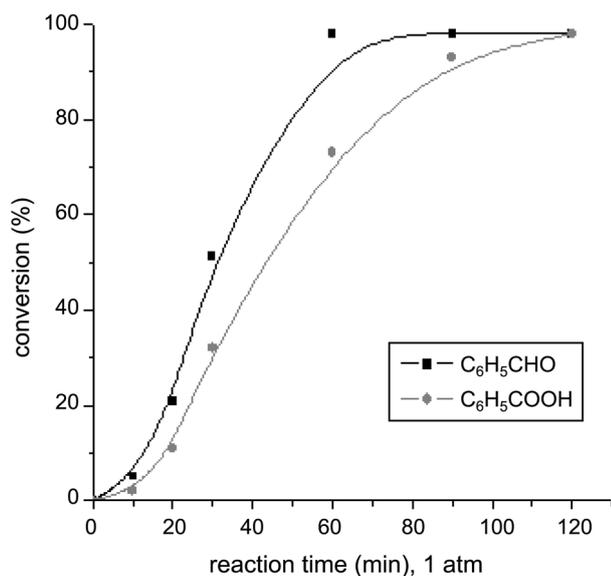


Figure 3. Hammett plot of hydrogenation rates of para-substituted benzoic acids.

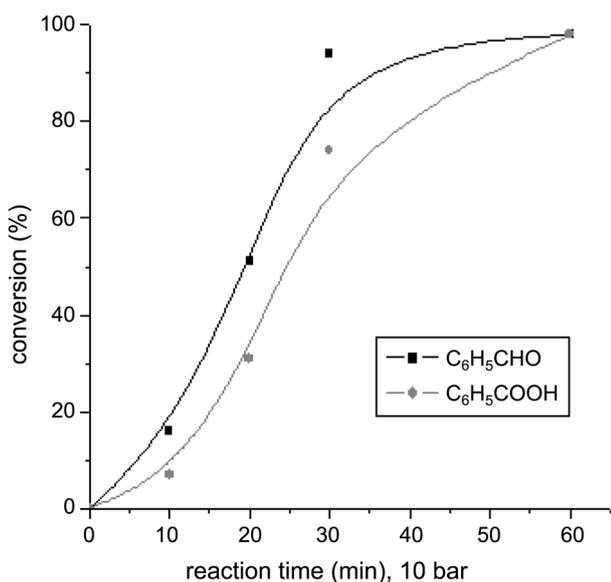
Table 5. Hydrogenation of Carboxylic Acids and Ketones with Ni and Pd catalysts

Entry	Catalyst	Substrate	Reaction Conditions		Reaction Time* (min)
			Temp. (°C)	P <sub>H2</sub> (bar)	
1	ANi-3	<i>p</i> -(NO <sub>2</sub> )PhCOOH	25	10	30
2	ANi-3	<i>p</i> -(Me)PhCOOH	25	10	90
3	Ni	<i>p</i> -(MeO)PhCOOH	25	10	90
4	ANi-3	PhCOMe	25	10	60
5	ANi-3	CH <sub>3</sub> COCH <sub>3</sub>	25	10	90
6	ANi 6-3	<i>p</i> -(NO <sub>2</sub> )PhCOOH	25	10	60
7	ANi 6-3	<i>p</i> -(Me)PhCOOH	25	10	90
8	Pd	<i>p</i> -(MeO)PhCOOH	25	10	120
9	ANi 6-3	PhCOMe	25	10	60
10	ANi 6-3	CH <sub>3</sub> COCH <sub>3</sub>	25	10	60

\*Time required for 95% conversion of the initial substrate.



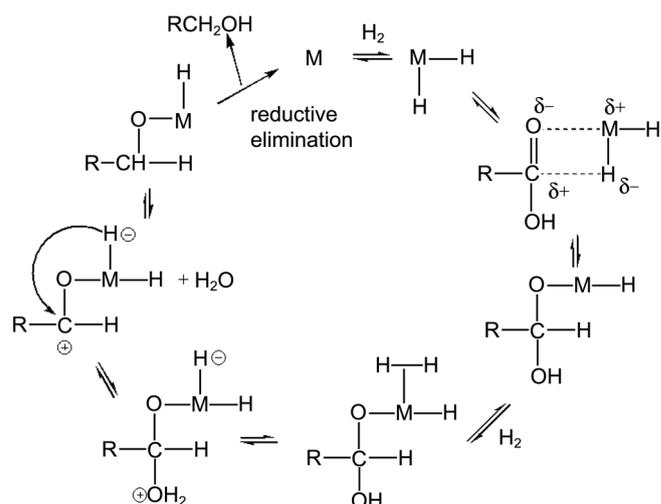
**Figure 4.** Reaction profiles of hydrogenation of benzoic acid and benzaldehyde with ANi 6-3 under 1 bar of hydrogen pressure at 25 °C.



**Figure 5.** Reaction profiles of hydrogenation of benzoic acid and benzaldehyde with ANi 6-3 under 10 bar of hydrogen pressure at 25 °C.

known acidic, and the proton transfer to OH followed by dehydration would proceed reasonably.

In the conventional reduction of carboxylic acids with metal hydrides, stepwise mechanism (carboxylic acids to aldehydes to alcohols) is generally proposed. Several attempts to detect aldehydes, which may be formed if stepwise mechanism is followed, in the liquid-phase reaction products of early stage always failed. No detection of aldehyde indicated that even though the initially formed aldehydes were to be dissociated before being further hydrogenated, they might be immediately coordinated to the active sites of metal again. The general tendency of higher hydrogenation of aldehydes than carboxylic acids would



**Scheme 1.** A plausible mechanism of hydrogenation of carboxylic acids.

help this process to occur. In fact, the hydrogenation rate of benzaldehyde is much faster than that of benzoic acid (entry 2 vs. 8 in Table 4). The 1<sup>st</sup> order rate constants for the hydrogenation of benzaldehyde and benzoic acid were 2.42 min<sup>-1</sup> and 1.49 min<sup>-1</sup> at 1 bar of H<sub>2</sub>, and 4.10 min<sup>-1</sup> and 3.35 min<sup>-1</sup> at 10 bar of H<sub>2</sub>, respectively, as shown in Figure 4 and 5. An induction period could be seen even in the hydrogenation of benzaldehyde under 1 bar of H<sub>2</sub> pressure. Therefore, it may conclude that the rate determining step in this process is the adsorption of hydrogen on the metal or the activation of the metal hydride. This interpretation is further supported by the fact that the hydrogenation rates were dependent on the easiness of hydrogen transfer which was induced by the high hydrogen pressure and the high agitation rate. Finally, the irreversible formation of alcohol by reductive elimination would complete the catalytic cycle.

## Conclusion

Efficient and selective catalytic systems, Ni or Pd on nanoporous carbon, for the hydrogenation of carboxylic acids to related alcohols in acidic solutions have been developed. It was found that the catalytic activity strongly depends on the preparative method of the catalyst. Catalysts prepared by the impregnation of active metallic species into the nanoporous carbon structure of CMK-3 preformed showed the highest activity. The catalytic activity also depended on the hydrogen pressure and the agitation rate as well as the active species. Investigation on the relative hydrogenation rates of various carboxylic acids, aldehydes and ketones clearly showed the electronic and the steric effects on the reaction rates. A plausible reaction mechanism containing an intermediate with molecular hydrogen ligands is proposed.

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