

Efficient and Selective Hydrogenation of Carboxylic Acid Catalyzed by Ni or Pd on ZSM-5

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Abstract: Efficient and selective catalytic systems, where Ni or Pd is introduced on the silicate material (ZSM-5) having micropore and mesopore structures, have been developed for the reduction of carboxylic acids with H₂ at room temperature. It is found that the catalytic activity depends on the hydrogen pressure, the agitation rate, the nature and the amount of active species. A plausible reaction mechanism for the hydrogenation of carboxylic acids to corresponding alcohols is proposed on the basis of electronic and steric effects in these reactions.

Keywords: Ni, Pd, carboxylic acid, alcohol, ZSM-5, hydrogenation, mechanism

Introduction

The formation of alcohols by the hydrogenation of the carbonyl groups has drawn much interest from both academia and industry [1]. Generally, carboxylic acid derivatives have been reduced to alcohols with various reagents in stoichiometric or catalytic processes. Lithium aluminum hydride or boranes are most commonly used reagents for this reduction but these reagents have severe limitations such as the requirement of anhydrous solvents, hazardous handling, and incompatibility with other functionality [2]. Sodium borohydride is one of the most popular alternatives but does not reduce carboxylic acid derivatives such as nitriles, esters, lactones, and amides [3]. Even though much recent efforts have been made [2], this type of stoichiometric process cannot be adopted in the industry for economic reasons. The development of efficient catalysts and selection of hydrogen source material are important for the reduction of carboxylic acid derivatives in large scale. Even though silanes can be used for the reduction of carboxylic acid derivatives [4], hydrogen has been one of the most versatile reagents in this reaction.

Meanwhile, recent increased concern on the environ-

ment, especially on the ozone layer, has led to extensive research on new alternatives to chlorofluorocarbon (CFC) materials. 2,2,2-Trifluoroethanol (TFEA) has been considered as one of the alternatives to CFC cleaning purposes due to its nondestructive nature for the ozone layer, lower global warming effect than hydrofluorocarbon (HFC) and hydrochlorofluorocarbon (HCFC), high thermal stability, high cleaning power for organic compounds, and miscibility with water. Moreover, TFEA has been used as an intermediate for manufacturing fluorine-containing medicine, pesticides or anesthetics and can be adopted as a starting material for fluoroester and fluoroether, which are in turn utilized to prepare oxygen-containing fluororesins useful for optical fibers and electronic materials.

Even though several preparative methods for TFEA are currently available, hydrogenation of 2,2,2-trifluoroacetic acid (TFAA) is one of feasible candidates for the production of TFEA. Therefore, development of efficient catalysts, especially heterogeneous systems for hydrogenation would be an important key for developing an efficient and economic hydrogenation process of carboxylic acids, especially TFAA.

There has been intense interest in the preparation of ordered mesoporous and macroporous materials composed of polymers, metal oxides, metals, or metallic alloys [5,6]. Metallic species on such porous materials have al-

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so been extensively exploited as active components in catalytic converters [7] and as recyclable heterogeneous catalysts for coupling reactions [8,9]. Recently, much attention has been paid to nanoporous and nanocrystalline materials for their potential application to diverse fields. Both nanoporous and nanocrystalline materials possess an ultrahigh surface-to-volume ratio, which would offer a greatly increased number of active sites for carrying out catalytic reactions [10].

Among the materials having orderly pores, zeolites have been adopted in various fields including solid catalysts or supporters due to their high thermal stability, hydrothermal stability and chemical resistance. Recent research efforts in preparing catalysts have been paid to the preparation of nanoporous or mesoporous materials with a uniform pore distribution to improve the catalytic efficiency [11-17]. Up to date, most of the reported procedures preparing supporters use low molecular weight surfactants as structure-directing agents and auxiliary inorganic precursors for assembly into the mesophase precipitant. These mesoporous materials obtained by use of amphiphilic block copolymers have expanded the areas for their application [18,19].

However, MCM-41, which is a famous silica structure having hexagonally-ordered pores, has amorphous frameworks that are insufficient to withstand the severe process conditions such as the steam regeneration for reactivating catalysts and the exposure to boiling water. Recent significant advances have been addressed with incorporation of crystalline zeolites into the silica frameworks. One of the ideal mesoporous materials for catalysis is the MCM-41 with a crystalline framework such as ZSM-5 or Y-zeolites [20,21]. Even though various preparative methods have been proposed [20-26], the incorporation of a crystalline zeolite having micropores into the mesophase framework without any formation of separate zeolite crystals in the product is still difficult to achieve by conventional techniques.

A recent technique using nano-sized carbon particles proposed by Jacobson [27] made it possible that large zeolite single crystals might grow around carbon particles to fill the pores of inert carbon matrix. Kim [28] improved this method to prepare the mesoporous materials having microporous frameworks, such as MCM-41 and SBA-15, in the type of monolith or thin film as well as powder by using the solid rearrangement process in tetrapropylammonium hydroxide (TPAOH)-impregnated mesoporous precursors. He also reported that this system can be used as a catalyst for thermal cracking of triisopropylbenzene or as a supporter for Mn(III) salen complexes to catalyze the chiral epoxidation of styrene.

In this work, we report that Ni or Pd on ZSM-5 of a bimodal structure having orderly micropores and mesopores can be a much improved and active heterogenized

catalyst for the hydrogenation of carboxylic acids, especially TFAA.

Experimental Section

General Procedure for Preparing ZSM-5

First, SBA-15 silica was synthesized in a shape of powder [11] using tetraethylorthosilicate and amphiphilic PEO-PPO-PEO triblock copolymer (Plunioic P123). A supramolecular silica-surfactant assembly of MCM-41 was also prepared by the reported methods [11,28]. Aluminum was implanted on the surface of mesoporous silica to generate strong acid catalytic sites for the polymerization of phenol and formaldehyde. 1 g of silica was added to a mixed solution of ethanol and dioxane containing 0.2 g of AlCl_3 . The resulting slurry was refluxed for 3 h. The powder collected was dried at 120 °C and calcined at 450 °C for 5 h in the air to yield mesoporous aluminosilicates. The pore volume of the aluminosilicate was filled with phenol and formaldehyde by the incipient-wetness technique. The silica/phenol resin composite was prepared according to the procedure reported in the literature [30]. Various mesoporous aluminosilicates were used as precursors for the synthesis of polymer/silica composites. The resulting mesoporous silica-phenol resin composites were heated under nitrogen flow at a heating rate of 5 °C/min from an ambient temperature to 700 °C and held at this temperature for 7 h to carbonize the phenol resin inside the mesoporous channels. This mesoporous material containing carbon inside was used as a starting material for the synthesis of ZSM-5 crystals. Tetrapropylammonium hydroxide (TPAOH) solution was impregnated on these mesoporous materials, and the mole ratio of TPAOH/ SiO_2 was fixed at 0.1. After evaporation of water, the final mixture was transferred to a Teflon-coated autoclave for further reaction to crystallize ZSM-5 zeolites at 170 °C. Transformation of the amorphous walls of MCM-41 and SBA-15 into the ZSM-5 crystals proceeded at 170 °C for 24 h in the presence of saturated steam. It is essential that water in the autoclave should not be directly contacted with the samples during the crystallization. The solid product was recovered by filtration after being washed with distilled water and dried at 120 °C overnight. The carbon inside was removed from the synthesized material by calcination in the air at 550 °C for 5 h.

General Procedure for Preparing 10 % Pd or Ni on ZSM-5

2.59 g of $\text{Pd}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ or 4.05 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was completely dissolved into a sufficient amount of distilled water. 10 g of ZSM-5 (Pd catalysts from SBA-15; Ni catalysts from MCM-41) was added to this

Table 1. Hydrogenation of TFAA with Ni or Pd on ZSM-5

Substrate	Catalyst	Reaction Conditions		Reaction Time* (min)
		Temp. (°C)	Pressure (bar)	
CF ₃ COOH	Ni 10 %	25	1	90
			5	30
			10	30
	Pd 2 %	25	1	120
			5	90
			10	60
	Pd 5 %	25	1	90
			5	60
			10	30 (50 mg) ⁺ 20 (100 mg) ⁺
	Pd 10 %	25	1	60
			5	30
			10	20

*time required for 95 % conversion of the initial substrate.

+ amount of total catalyst.

solution. After dried at 100 °C overnight, the resulting solid was calcined at 500 °C for 4 h. The solid was reduced under hydrogen atmosphere at 500 °C for 4 h.

Hydrogenation of TFAA and Carboxylic Acids

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 (at ambient pressure) or a heating media having a temperature controller (at high pressure). After the temperature reached to the pre-set one, hydrogen was introduced in the reactor. The reaction was monitored by taking and analyzing a sample every 10 min.

Hydrogenation of Various Carboxylic Acids

Substrate (carboxylic acid, 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 temperature controller. After the temperature was reached to the preset one, hydrogen was introduced. The reaction was monitored by taking and analyzing a sample every 10 min.

Analysis of Hydrogenation Product

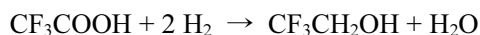
Samples of the reaction products were analyzed by using a Young-In GC 680 A gas chromatograph equipped with a FID and a packed column (HayeSep R, 80/100, 2 m). The flow rates of nitrogen, hydrogen, and air were

0.43, 0.77, and 7.0 cc/s while the injector and detector temperatures were 200 and 250 °C, respectively. The column temperature was programmed from 100 to 200 °C (20 min) with a heating rate of 10 °C for TFAA, benzoic acid and acetic acid. The column temperature was changed from 50 (15 min) to 200 °C (30 min) with a heating rate of 5 °C in the cases of other carboxylic acids.

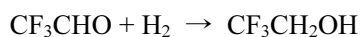
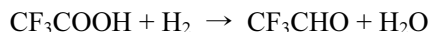
Results and Discussion

In the hydrogenation of unsaturated compounds, various heterogeneous catalysts, such as Raney Ni, and Pd or Pt on charcoal, or homogeneous catalysts, such as RuCl₂(PPh₃)₃ and RhCl(PPh₃)₃, have been usually adopted. Recent extensive review on hydrogenation of polar bonds by ruthenium hydride complexes is one example of active research in this field [31]. Metal hydrides such as LiAlH₄ and NaBH₄ have been also widely used. Recent new environmental legislations for strict limitation of the aromatic contents in fuels, oils and solvents have driven extensive studies on the hydrogenation of aromatic compounds [32]. The effect of stabilizers on the hydrogenation activity has also been another issue in this area [33,34]. Recent issues on the hydrogenation by nano metal or nano metal alloy catalysts have been well reviewed [35]. It is interesting whether the hydrogenation of TFAA to TFEA in an acidic condition can be enhanced based on the information from the foregoing studies.

Hydrogenation of TFAA can be represented by the following equation.



Even though this reaction appears to proceed in a single step, it actually consists of two sequential reactions, depicted by the following equations.



In order to develop a new catalyst for the hydrogenation of TFAA, two features should be considered; formation of water and high acidity of the starting material. Heterogeneous solid catalysts have an advantage in separation and recycle of the catalysts. Various supporters such as active charcoal, silica, zeolite, and MgO have been exploited in many catalytic reactions. New nanoporous carbon having hexagonally ordered mesostructure developed by Ryoo [36] was used as an alternative supporter of charcoal to supply high activities of catalysts toward C-C coupling [37] and epoxidation of alkenes [38].

Hydrogenation of TFAA in THF with Ni or Pd on ZSM-5 with bimodal microporous and mesoporous structures proved to be quite efficient and selective. TFEA was the only product in this reaction. No aldehyde was observed during the reaction. As shown in Table 1, it was found that the hydrogenation rate depended on the hydrogen pressure and the nature and amount of catalysts. Pd catalysts were more active than Ni (1st order rate constant; 5.4 and 4.9 min⁻¹) as expected even though less Pd was used than Ni in the catalyst. It is generally recognized that H₂ is more easily adsorbed on Pd than on Ni, and the standard reduction potential for M²⁺/M couple in Pd (0.987 V) is much higher than that in Ni (-0.246 V), which implies the easier reduction of Pd²⁺ than Ni²⁺. More metallic species in the reaction and higher hydrogen pressure induced faster hydrogenation rates as expected. The effect of H₂ pressure on the catalytic activity was found a more sensitive factor in the Ni catalysts and the catalysts having low Pd contents. For example, the reaction rate changed from 1.6 min⁻¹ at 1 bar of H₂ to 4.3 min⁻¹ at 10 bar of H₂ with 10 % Ni, from 1.1 to 3.2 min⁻¹ with 2 % Pd, from 2.3 to 4.1 min⁻¹ with 5 % Pd, and from 3.3 to 5.4 min⁻¹ with 10 % Pd. In the lower H₂ pressure, more distinct induction period appeared. This indicated that the induction period might be related with the time of H₂ adsorption.

Since the catalysts of Ni or Pd on ZSM-5 are heterogeneous, these may have practical advantages such as fac-

ile separation from the product solution and reuse. These catalysts retained its initial micro/meso structures inside even under the severely stirred conditions. This meant that ZSM-5 based catalysts had high mechanical strength and attrition resistance, while the structures of ordinary silicates such as MCM-41 were apt to be collapsed during the repeated use [28]. However, the catalyst of 10 % Ni or Pd showed a reduced activity in the second use; the 1st order rate constant with Ni decreased from 1.24 to 1.04 min⁻¹ and that with Pd decreased from 3.25 to 2.6 min⁻¹. In the third use of 10 % Pd catalyst, further activity decrease to 1.67 min⁻¹ and a longer induction period were observed.

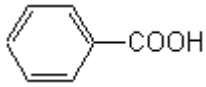
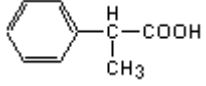
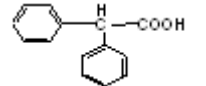
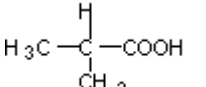
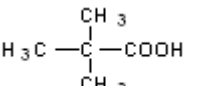



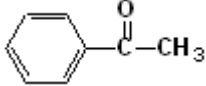
The possible homogeneous catalysis by leached metal ions can be elucidated and excluded by running the reaction with a small amount of Ni(NO₃)₂. It took 60 min with 5 mg of Ni(NO₃)₂ and 180 min with 0.5 mg of Ni(NO₃)₂ when the conversion of TFAA got higher than 95 %, while it took 30 min with Ni on ZSM-5. Since the hydrogenation rate with an expected leaching amount of Ni(NO₃)₂ in the solution was still far lower than that of the heterogenized catalyst, contribution of the heterogenized catalyst to the overall activity could be the major. However, both heterogeneous and homogeneous catalysis might simultaneously occur in this system.

Induction periods were not observed with high metal contents such as 10 % Ni or Pd under high hydrogen pressure, while they were distinct with the same catalytic species of lower metal content under lower hydrogen pressure. Initially, this seemed attributed to the reduction of M(II) to M(0) (M = Ni or Pd). However, since these catalysts were already reduced in the preparative procedures, this assumption might be excluded even though there remained certain possibility of partial oxidation of the catalysts on storage. Therefore, we proposed that adsorption of hydrogen (or activation of hydrogen) or desorption and recoordination of aldehydes, the intermediates of initial hydrogenation, might be the reason for the induction period. Also, since ZSM-5 was so acidic that it could be used as a catalyst for cracking bulky organic molecules [28], the presence of strong acidic sites in the pores of ZSM-5 might play a key role to reduce the induction period in hydrogenation.

Higher agitation rate improves the hydrogenation rate, which represents the importance of hydrogen diffusion to the active site of catalyst.

In order to investigate the reaction mechanism of the catalytic hydrogenation of TFAA, various carboxylic acids were employed, and the hydrogenation results were summarized in Tables 2 and 3. Generally, electron-withdrawing substituents adjacent to the COOH group accelerated the reaction rates (entry 1,2,5) but sterically bulky substituents reduced the reaction rates as expected (entry 5,6,7). It was harder to reduce ketones than car-

Table 2. Hydrogenation of Various Carboxylic Acids and Ketones with Ni Catalysts

Entry	Substrate	Catalyst	Reaction conditions		Reaction time* (min)
			Temp. (°C)	Pressure (bar)	
1	CF ₃ COOH	Ni 10 %	25	1	90
				5	60
				10	30
2		Ni 10 %	25	10	60
3		Ni 10 %	25	10	120
4		Ni 10 %	25	10	90
5	CH ₃ COOH	Ni 10 %	25	10	60
6		Ni 10 %	25	10	120
7		Ni 10 %	25	10	150
8		Ni 10 %	25	10	30
9		Ni 10 %	25	10	90
10		Ni 10 %	25	10	90
11		Ni 10 %	25	10	60
12	CH ₃ COCH ₃	Ni 10 %	25	10	60

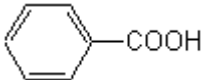
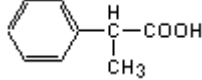
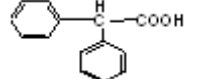
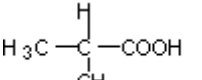
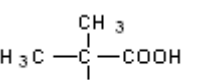
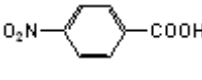
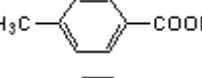
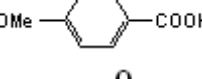
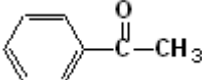
* time required for 95 % conversion of the initial substrate.

boxylic acids with Pd catalysts possibly because of the steric reason (entry 12). However, the reduction rates of ketones were as fast as those of corresponding carboxylic acids with the Ni catalysts (Table 1). Sterically bulky substituents might prevent the substrate from coordinating to the metal, and hydride transfer to the carbonyl carbon might be retarded. Substitution of protons with phenyl groups in the acetic acid (entry 5) showed mixed electronic and steric effects. Due to bulkiness of the phenyl group, the hydrogenation rate decreased initially (entry 3) but further introduction of another phenyl group (entry 4) induced the increase of hydrogenation rate possibly due to the electron-withdrawing nature of

phenyl group.

Pure electronic effect could be shown by using several para-substituted benzoic acids (entry 8~11). Hammett plot [39] clearly shows the cationic character of the active intermediate in Figure 1. The reaction rate of hydrogenating benzoic acid with an electron-withdrawing group is faster than that with an electron-donating group. Hydride transfer to the carbonyl carbon having cationic character would be the rate-determining step and a plausible reaction mechanism with an intermediate containing a molecular hydrogen ligand was proposed to explain the observed experimental results (Scheme 1). Presence of molecular hydrogen ligands was proposed to

Table 3. Hydrogenation of Various Carboxylic Acids and Ketones with Pd catalysts

Entry	Substrate	Catalyst	Reaction conditions		Reaction time* (min)
			Temp. (°C)	Pressure (bar)	
				1	60
1	CF ₃ COOH	Pd 10 %	25	5	30
				10	20
2		Pd 10 %	25	10	30
3		Pd 10 %	25	10	60
4		Pd 10 %	25	10	60
5	CH ₃ COOH	Pd 10 %	25	10	30
6		Pd 10 %	25	10	90
7		Pd 10 %	25	10	120
8		Pd 10 %	25	10	30
9		Pd 10 %	25	10	60
10		Pd 10 %	25	10	90
11		Pd 10 %	25	10	60
12	CH ₃ COCH ₃	Pd 10 %	25	10	60

* time required for 95 % conversion of the initial substrate.

avoid an unstable oxidation state of metal. M(IV) is the oxidation state with full oxidative addition of two mole of H₂, which is less stable than M(II) proposed in this mechanism. Another advantage of molecular hydrogen intermediates is as follows; molecular hydrogen is known to be acidic and proton transfer to OH followed by dehydration would proceed reasonably [40]. Acidic sites in the pore of ZSM-5 would help this step to proceed. Aldehydes initially formed can be dissociated before further hydrogenation, but these have to coordinate to the metal again to explain the absence of aldehydes in the system. However, several attempts to detect aldehydes in the reaction products of early stage failed. Since no aldehydes were detected in the reaction products of early stage, dissociated aldehydes, if any, might

remain near the active site and coordinate to the active site again immediately. The higher hydrogenation tendency of aldehydes than carboxylic acids would help this process to occur. In fact, the hydrogenation rate of benzaldehyde was much faster than that of benzoic acid (entry 2 and 13 in Table 3) even though the completion times for both reactions under 10 bar were almost same. For example, the 1st order rate constants of hydrogenating benzaldehyde and benzoic acid were found 2.73 and 1.71 min⁻¹ under 1 bar, and 5.0 and 4.5 min⁻¹ under 10 bar, respectively. As shown in Figures 2 and 3, no induction period could be seen even in the hydrogenation of benzaldehyde under 1 bar of H₂. Therefore, it could be concluded that the induction period was not related to the adsorption rate of aldehydes on the metal. However,

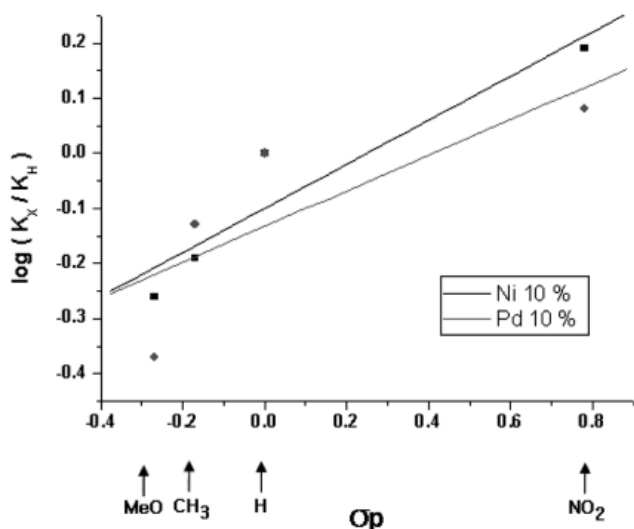


Figure 1. Hammett plots of hydrogen rates of para-substituted carboxylic acids.

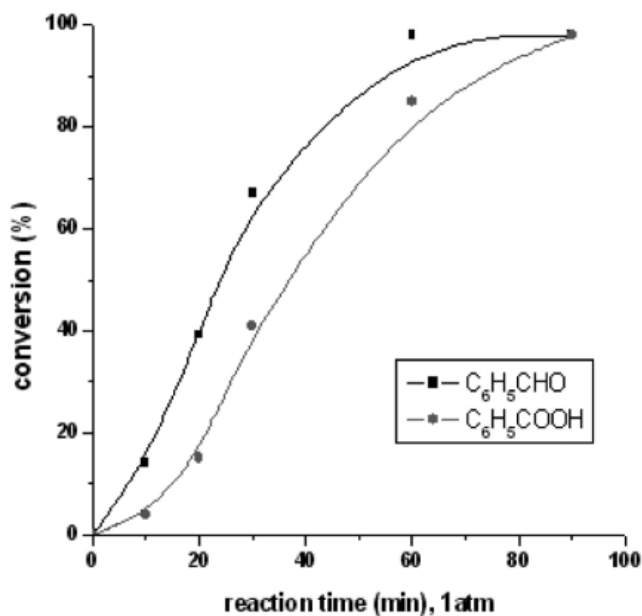


Figure 2. Reaction profiles of hydrogenation of benzoic acid and benzaldehyde with Pd 10% catalyst under 1 bar of hydrogen pressure at 25 °C.

the fact that the hydrogenation rates are dependent on the hydrogen pressure indicates that the hydrogen transfer, the hydrogen adsorption or the activation of hydrogen on the metal is still important and seems related to the induction period. This conclusion was supported by the results that benzoic acid and benzaldehyde showed similar hydrogenation rates under 10 bar, but benzaldehyde showed a much faster rate than benzoic acid under 1 bar. These findings and the presence of strong acidic sites on ZSM-5 supporter strongly indicated that the coordinated carboxylic acid was successively transformed without dissociation as shown in Scheme 1. Finally irre-

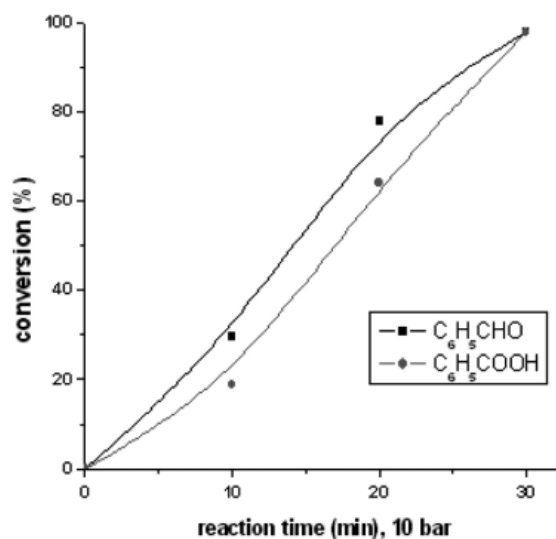
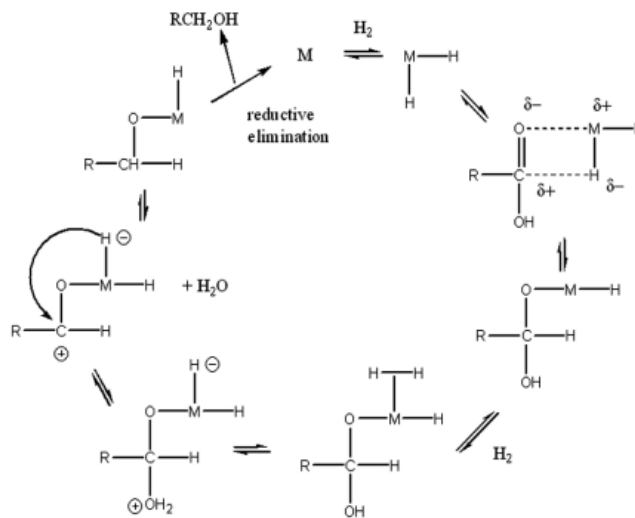


Figure 3. Reaction profiles of hydrogenation of benzoic acid and benzaldehyde with Pd 10% catalyst under 10 bar of hydrogen pressure at 25 °C.



Scheme 1. A plausible mechanism of hydrogenation of TFAA.

versible formation of alcohol by reductive elimination would complete the catalytic cycle.

Conclusion

Efficient and selective catalytic systems, Ni or Pd on the ZSM-5, for the production of TFEA by the hydrogenation of TFAA have been developed. It was found that the catalytic activity depended on preparative methods. Catalysts prepared by the impregnation of catalytically active species after carbonization showed the highest activity. The catalytic activity also depended on the hydrogen pressure, the agitation rate, and the nature of active species. Hydrogenation of various carboxylic acids and ketones clearly showed the electronic and ster-

ic effects on the reaction rate and a plausible reaction mechanism containing an intermediate of molecular hydrogen ligand was proposed. The induction period appeared to be related to the adsorption or the activation of hydrogen on the metallic species and successive transformation of carboxylic acid without dissociation was indicated.

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