Catal Lett (2008) 126:280–285
DOI 10.1007/s10562-008-9610-6

Influence of Preparation Modes on Pt–Ni/CNTs Catalysts Used in the Selective Hydrogenation of Cinnamaldehyde to Hydrocinnamaldehyde

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Received: 25 June 2008 / Accepted: 3 August 2008 / Published online: 3 September 2008

Abstract Pt–Ni/CNTs catalysts are prepared by different impregnation techniques and different reduction methods (H_2, HCHO, and KBH_4) for the selective hydrogenation of cinnamaldehyde (CMA) to hydrocinnamaldehyde (HCMA) and investigated by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and temperature programmed reduction (H_2-TPR) techniques. The results show that the catalytic selectivity and activity of the Pt–Ni/CNTs catalysts would significantly be improved by using KBH_4 as a reducing agent, due to the electronic synergetic effect of Pt–Ni–B, and 96% for conversion of CMA and 88% for selectivity of HCMA are obtained over Pt–Ni/CNTs catalyst reduced by KBH_4. Furthermore, the hydrogenation rate of CMA and selectivity of CMA to HCMA over Pt–Ni/CNTs catalyst are significantly improved in the presence of trace base or acid promoters again. The best result (92% for conversion of CMA and 96% for selectivity of HCMA) is obtained when NaOAc is used as base promoter.

Keywords Cinnamaldehyde (CMA) · Hydrocinnamaldehyde (HCMA) · Pt–Ni/CNTs catalyst · Selective hydrogenation

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1 Introduction

Cinnamaldehyde (CMA) is a vinylogue of benzaldehyde, and the aldehyde group behaves with catalysts as if it was an aromatic aldehyde. This carbonyl group is reduced easily and competes with saturation of the carbon–carbon double bond [1–3]. The hydrogenation of CMA catalyzed by platinum metal or platinum complex leads usually to a mixture of hydrocinnamaldehyde (HCMA), cinnamyl alcohol (CMO) and phenylpropanol (HCMO). Recently, HCMA is found to be an important intermediate in the preparation of pharmaceuticals used in the treatment of HIV [4]. Although various attempts have been made to develop a suitable catalytic system for selective hydrogenation of CMA to HCMA [5–8], the selectivity is still an important issue, especially under heterogeneous catalysis conditions. Because of the competitive reduction of the aldehyde carbonyl and olefin groups, the selectivity of CMA to HCMA or CMO varies considerably with the method of preparation of the catalyst, the solvent, additives, the process conditions employed and even trace impurities in the reactant [9–14]. A comprehensive review of CMA hydrogenation has been published by Gallezot and Richard [15].

Much interest has been focused on the use of water-soluble homogeneous catalysts, despite the critical drawbacks related to such catalysts. In the case of heterogeneous catalysts, the attainment of high selectivity is more difficult and very dependent on the nature of the aldehyde and requires catalyst modification and promotion [16–18]. However, from the point of view of green chemistry, the development of industrial processes for direct production of organic intermediates using heterogeneous catalysts is an industrially meaningful target, since the catalysts could be easily removed from the reaction mixtures and wastes could be largely diminished. Monometallic-supported catalysts are widely used for this purpose, but bimetallic catalysts show growing attention, as the addition of a second metal can drastically improve the activity and/or selectivity towards the desired product [19–22].

Carbon materials are attractive supports in heterogeneous catalytic processes because of their properties that may be tailored to specific needs [23, 24]. With the discovery and the large-scale synthesis of the carbon nanotubes (CNTs), much attention is being focused on their potential applications to various fields of materials science, such as composite elaboration, electronics, and catalysis [25]. In particular, these materials have excellent electronic properties, good chemical stability, and large surface areas, making them promising supports for advanced catalytic systems.

Ni-based catalysts have been proved to be favorable for the hydrogenation of C=C bond in the CMA molecule. In this paper, the major objective is to report the preparation and the characterization of Pt and Ni-decorated CNTs catalysts with good catalytic properties and their implication in hydrogenation reactions. The catalytic properties in the liquid-phase selective hydrogenation of CMA into the corresponding HCMA are examined in mild reaction conditions. The characteristic of the Pt–Ni/CNTs catalysts is also investigated using transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (H_2-TPR) techniques, and their influence on catalytic performance is discussed.

2 Experimental

2.1 Catalyst Preparation

CNTs are prepared according to method described in Ref. [26]. The surface area of CNTs is 110 m^2/g and the average pore diameter value is 22 nm, the pore volume is 0.311 mL/g. The as-prepared carbon nanotubes are subsequently purified by thick nitric acid treatment at 80 °C for 16 h in order to dissolve the residual catalyst which could be contained in their structure during the synthesis process and develop oxygen-containing surface groups, which act as anchoring sites for the precursors before metal impregnation [27]. The solid is filtered and washed several times with distilled water until the pH reached 7, and then dried overnight at 110 °C.

Two different series of bimetallic Pt–Ni/CNTs catalysts are prepared by varying the reduction methods and impregnation modes. In one series, the Pt and Ni metals are introduced simultaneously by co-impregnation with aqueous solutions of $Pt(NH_3)_4Cl_4$ and $Ni(NH_3)_6Cl_2$, and the samples impregnated are reduced by HCHO (70 °C, 6 h), H_2 (400 °C, 4 h), and KBH_4 (80 °C, 2 h), respectively. The catalysts are assigned as Pt–Ni/CNTs (I), Pt–Ni/CNTs (II), and Pt–Ni/CNTs (III), respectively. Pt–Ni/CNTs (V) catalyst is also prepared by co-impregnation while with aqueous solutions of H_2PtCl_6 and $Ni(NO_3)_2$, and reduced by KBH_4 (80 °C, 2 h). Whereas in the other series, the Pt and Ni metals are sequentially introduced, first by impregnation with aqueous solution of $Ni(NO_3)_2$ and second with aqueous solution of $Pt(NH_3)_4Cl_4$, and the sample impregnated is reduced by KBH_4 (80 °C, 2 h). The catalyst is assigned as Pt–Ni/CNTs (IV) and all of the five catalysts with a weight of Pt 0.50 wt% and Ni 0.17 wt%.

Pt/CNTs and Ni/CNTs monometallic catalysts are prepared by conventional impregnation with their aqueous solutions of $Pt(NH_3)_4Cl_4$ or $Ni(NH_3)_6Cl_2$, respectively. The samples impregnated are reduced by KBH_4 (80 °C, 2 h), filtered and washed with large amount of water, dried overnight at 110 °C. The content of Pt and Ni is 0.50 wt% and 0.17 wt%, respectively.

2.2 Catalyst Characterization

2.2.1 Electron Microscopy

TEM is a conventional method to give detailed information about the shapes, mean size, and size distribution of metallic dispersions. The microstructure of the carbon nanotubes supported platinum material is observed by TEM using a JEM-2010 (HR) apparatus operated at 200 kV.

2.2.2 XPS

X-ray photoelectron spectroscopy (XPS) measurements are performed on a VG ESCALAB 2201-XL spectrometer. Non-monochro Mg Ka radiation are used as a primary excitation. The binding energies are calibrated with the C1s level of adventitious carbon (284.6 eV) as the internal standard reference.

2.2.3 H_2-TPR

The reduction properties of the supported Pt catalysts are measured by means of H_2-TPR. Prior to experiments, 50 mg of the catalysts are pre-treated in a He flow at 200 °C for 15 min. When the sample is cooled to −50 °C in flowing He, and then switched to 5 vol.% H_2–He feed purified with deoxidizer and silica gel. The reaction temperature is programmed to rise at a constant rate of 10 °C/min up to 400 °C and the flow-rate is 30 mL/min. Amount of H_2 consumption during the H_2-TPR is measured by a thermal conductivity detector (TCD), and the effluent H_2O formed during H_2-TPR is adsorbed with a 5A molecular sieve. The hydrogen uptakes are quantified using CuO as a standard.

2.3 Catalytic Properties Measurement

The hydrogenation reaction of CMA is carried out at low pressure and low temperature, in a stainless steel reactor equipped with a hydrogen inlet, a teflon vessel and a muphet stirrer. A mixture of 0.36 g catalyst, 8.0 mmol CMA, and 19.0 mL C_2H_5OH is placed in the reactor. The reaction temperature is maintained by water bath and the magnetic stirring rate is 1,000 rpm.

Chemical analysis of the products is performed by gas chromatography Perkin-XL equipped with a FID detector and SE-30 capillary column. Reactants and products are identified by comparison with authentic samples. Biphenyl is used as internal standard.

3 Results and Discussion

3.1 Electron Microscopy

The TEM images of Pt–Ni/CNTs (I, II, III, IV, V) are shown in Fig. 1. Figure 1 shows that most of Pt particles over Pt–Ni/CNTs are dispersed more homogeneously on the outer surface of the nanotubes when $Pt(NH_3)_4Cl_4$ is used as the precursor, leading to small diameters on the whole, while the Pt particles have a wide range size of 2–5 nm over Pt–Ni/CNTs (III, IV) catalysts reduced by KBH_4 with a regular spherical distributing and have smaller diameter of 1–3 nm over Pt–Ni/CNTs (I, II) catalysts using HCHO or H_2 as reducers. The Pt particles over Pt–Ni/CNTs (V) catalyst prepared by co-impregnation with the precursor of $Ni(NO_3)_2$ and H_2PtCl_6 show very different distribution with the formation of agglomerate of Pt and Ni particles. Different preparing methods result in different dispersion of Pt particles over CNTs, since different surface property of oxidized CNTs is resulted. It is reported that HNO_3-oxidized CNTs is negative net surface charge [28, 29], which decides that CNTs will adsorb cations in the solution and favor their homogeneous dispersion on the outer surface.

3.2 H_2-TPR

The reducibility of supported platinum catalysts is an important factor influencing its catalytic property. H_2-TPR profiles of the CNTs supported Pt–Ni catalysts are shown in Fig. 2 and values of the H_2 consumption and their peak temperature maxima are listed in Table 1. (Note that the small apparent peak seen with all samples around −50 °C is an artefact caused by the sudden increase in temperature when the temperature ramp is started.)

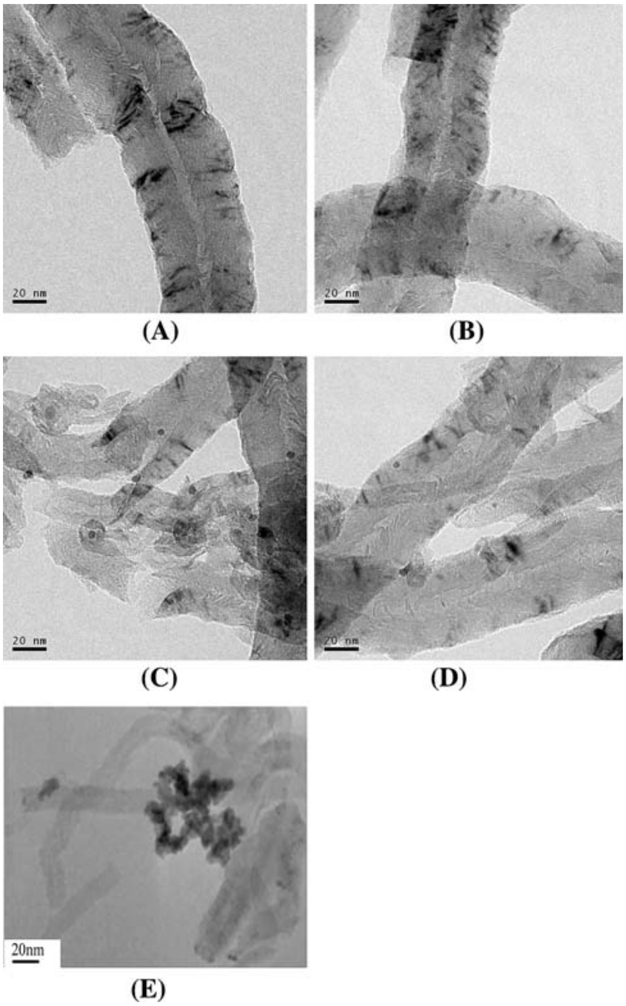

Fig. 1 TEM images of the Pt–Ni/CNTs catalysts (**a**) Pt–Ni/CNTs (I) (**b**) Pt–Ni/CNTs (II) (**c**) Pt–Ni/CNTs (III) (**d**) Pt–Ni/CNTs (IV) (**e**) Pt–Ni/CNTs (V)

From Fig. 2 and Table 1, it can be seen that there is one H_2 consumption peak at the temperature range of −50 to 50 °C representing the reduction of highly dispersed PtO_2 species appears in the Pt–Ni/CNTs (II, III, IV, V) catalysts. A reduction maximum appears at about 20 °C in the catalysts, with a H_2/Pt molar ratio basically equal to the stoichiometry governed by the equation $PtO_2 + 2H_2 \rightarrow Pt + 2H_2O$. However, a big H_2 consumption peak is obtained at about 250 °C in the TPR profile of Pt–Ni/CNTs (I) using HCHO as reducer. On Pt/Al_2O_3 prepared from chlorinated precursor, Marceau et al. [30] indicated the presence of oxy-chlorinated Pt species, which were reduced at 290 °C, while Hwang and Yeh [31] reported that dispersed PtO_xCl_y species were reduced at a higher reduction temperature (350 °C). The high consumption of H_2 ($H_2/Pt = 3.3$) in the TPR profile of Pt–Ni/CNTs (I) is in accordance with that already observed on 5% Pt/ZnO [18] or in Pt/Al_2O_3 [32–36] which was interpreted by the

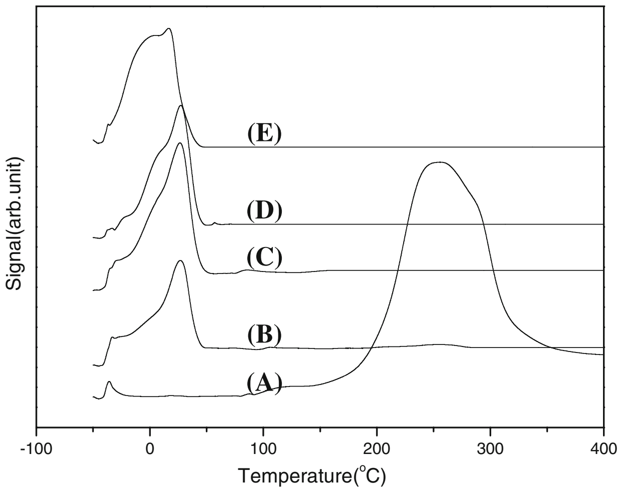

Fig. 2 H_2-TPR profiles of the Pt–Ni/CNT catalysts (**a**) Pt–Ni/CNTs (I) (**b**) Pt–Ni/CNTs (II) (**c**) Pt–Ni/CNTs (III) (**d**) Pt–Ni/CNTs (IV) (**e**) Pt–Ni/CNTs (V)

authors, from EXAFS characterization, by the following equation:

$$[\mathrm{Pt(OH)_4(Cl)_2}]^{2-} + 3\mathrm{H_2} \rightarrow \mathrm{Pt^0} + 4\mathrm{H_2O} + 2\mathrm{HCl} + 2\mathrm{e^-}.$$

In addition, for the Pt–Ni/CNTs (I) catalyst, its XPS analysis confirmed the presence of oxychloride platinum species too, while there is no indication of chlorinated platinum species in the Pt–Ni/CNTs (II, III, IV, V) catalysts using H_2 or KBH_4 as reducers which would reduce the chlorine species to form HCl species because of their stronger reducibility.

3.3 Catalytic Properties

The hydrogenation of CMA typically produces a mixture of the unsaturated alcohol CMO, the saturated aldehyde HCMA and the saturated alcohol HCMO. Aldol condensation of acetal (ACE) and other unidentified high molecular weight products (OTH) may also be produced in small amounts over some catalysts as shown in Fig. 3. From Table 2, it can be seen that the reducing agents play a critical role for the activity and selectivity of the catalysts, due to have different catalytic active species on the surface of Pt–Ni/CNTs catalysts. The Pt–Ni/CNTs (I) catalyst

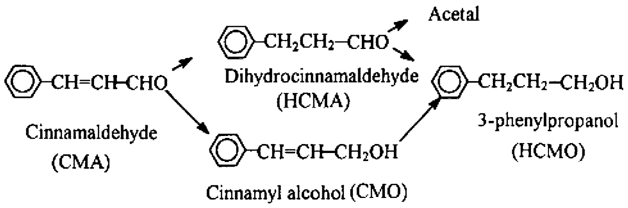

Fig. 3 Hydrogenation mechanism for CMA

using HCHO as reducer shows no activity of catalytic hydrogen and high yield of OTH (by-product), this maybe related to the active component of Pt existing in a state of PtO_xCl_y species while not reduced to metallic Pt. The Pt–Ni/CNTs (II) catalyst exhibits a lower activity of catalytic hydrogen (48% for the hydrogenation conversion) too, and a great deal of by-products of ACE and OTH are produced, which ACE is produced maybe because the promotion effect of the HCl (g) produced partly readsorbed by the CNTs support and remained on the samples after reduced by H_2. The Pt–Ni/CNTs (III, IV, V) catalysts reduced by KBH_4 exhibit good catalytic activity and selectivity for HCMA and the XPS results show that the surface B content is about 0.1 wt% in the three catalysts, thus we suggested that the good effects are also related to the presence of B. To investigate the synergetic effect of Pt, Ni, and B, the hydrogenation property over monometallic Pt/CNTs and Ni/CNTs catalysts reduced by KBH_4 is also examined. From Table 2, it can be seen that the Pt/CNTs shows a lower catalytic activity, while Ni/CNTs has no activity for hydrogenation. Such we can deduce from the results that the high hydrogenation activity and selectivity towards HCMA attributed to the electronic synergetic effect of Pt–Ni–B. Electrons may transfer from B to the vacant d-orbital of metallic Ni for Ni–B particles. Metal catalysts containing boron species, generally called metal boride, have been studied extensively in some reactions, however, their catalytic properties are highly dependent upon the preparation method. The activity and selectivity of NiB and CoB, for instance, can be altered significantly by varying the amount of metal-associated boron [37]. Paul et al. [38] first reported the use of NiB prepared from nickel salt and $NaBH_4$ as hydrogenation catalysts. Narasimhan's group has also published several papers about mixed metal boride

Table 1 H_2 consumption and temperature of TPR peaks for the catalysts

Catalyst	Reduction condition	H_2 consumption (H_2/Pt molar ratio)	Peak temperature (°C)
Pt–Ni/CNTs (I)	HCHO (70 °C, 6 h)	3.3	254
Pt–Ni/CNTs (II)	H_2 (400 °C, 4 h)	2.1	27
Pt–Ni/CNTs (III)	KBH_4 (80 °C, 2 h)	2.3	26
Pt–Ni/CNTs (IV)	KBH_4 (80 °C, 2 h)	2.3	27
Pt–Ni/CNTs (V)	KBH_4 (80 °C, 2 h)	2.5	16

Table 2 Influence of reduction methods on the hydrogenation of CMA over Pt–Ni/CNTs catalysts[a]

Catalyst	Reduction condition	Conversion (%)	Selectivity (%)				
			HCMA	HCMO	CMO	ACE	OTH
Pt–Ni/CNTs (I)	HCHO (70 °C, 6 h)	48 (0)[b]	–	–	–	–	100
Pt–Ni/CNTs (II)	H_2 (400 °C, 4 h)	97 (48)	5	15	–	30	50
Pt–Ni/CNTs(III)	KBH_4 (80 °C, 2 h)	96 (96)	88	8	4	–	–
Pt–Ni/CNTs (IV)	KBH_4 (80 °C, 2 h)	95 (95)	88	4	8	–	–
Pt–Ni/CNTs (V)	KBH_4 (80 °C, 2 h)	88 (88)	86	5	9	–	–
Pt/CNTs	KBH_4 (80 °C, 2 h)	48 (48)	57	–	43	–	–
Ni/CNTs	KBH_4 (80 °C, 2 h)	11 (0)	–	–	–	–	100

[a] Reaction condition: 8.0 mmol CMA, 19.0 mL C_2H_5OH, 70 °C, 1.5 h, 2 MPa

[b] Hydrogenation conversion: the percentage of CMA with the reaction of hydrogenation

catalyst, Ru–Sn–B, which was prepared by reducing metal salts with $NaBH_4$ [39]. It was reported that Ru–Sn–B/Al_2O_3 performed better in selective hydrogenation of fatty acid esters to fatty alcohols than Ru–Sn/Al_2O_3 prepared by H_2 reduction. It had been proved that boron species incorporated via $NaBH_4$ reduction played an important role in enhancing the activity and selectivity in this reaction. The role of boron probably lies in changing the electron charge distribution around ruthenium, thereby enhancing its catalytic activity. Such a correlation was suggested earlier in the case of nickel boride catalysts by Schreifels et al. [40], based on X-ray photoelectron spectroscopic studies.

It can also be seen from Table 2 that when the precursor of $Pt(NH_3)_4Cl_4$ is either co-impregnated with $Ni(NH_3)_6Cl_2$ or sequentially impregnated with $Ni(NO_3)_2$ onto the CNTs supports which has negligible different effect on the catalytic properties, while when the precursor of H_2PtCl_6 is co-impregnated with $Ni(NO_3)_2$, the Pt–Ni/CNTs (V) catalyst shows obvious difference in the selective hydrogenation of HCMA with Pt–Ni/CNTs (III, IV) catalysts. This may be the phenomenon of agglomeration in Pt–Ni/CNTs (V) catalyst as seen in TEM image. The stability of the best catalyst of Pt–Ni/CNTs (III) is also investigated, and the results show that in the recycle experiment, the catalytic activity decreases evidently, while the yield of CMO increases. The decreasing of catalytic activity is influenced by many factors on the hydrogenation of CMA. For example, a part of Pt and Ni could be lost when the catalyst is reused. Some intermediates could be also adsorbed on the surface of catalyst and partly cover active center, and which decrease catalytic activity.

The acidity or basicity of the hydrogenation medium can also modify the reactant molecule before its adsorption on the catalytic site. And last, the metal–solvent interaction at the surface of the catalyst forms an electrical double layer where the electrical field is very high and able to orient the approach of the substrate molecule. It is possible to play with the solvent properties to avoid the production of some byproducts [41].

The roles of different organic and inorganic bases/acids as promoters in improving the activity and the selectivity to HCMA of the catalyst are also investigated. The results in Table 3 indicate that trace amount of HAc, HNO_3, NaOH, and NaOAc plays an important role in improving the activity, while organic base such as $(CH_3CH_2)_2NH$ inhibits the reaction. NaOH and NaOAc modify the catalytic activity, probably they can enhance the solubility of hydrogen in ethanol and acid can activate the carbonyl group, but when the acid is strong acidity such as nitrate acid it promotes the yield of by-product of ACE which makes the selectivity of HCMA decreases.

Since NaOAc plays an important role in improving the selective hydrogenation of CMA to HCMA, the influence of addition amount of NaOAc is also studied. Figure 4 shows that the conversion increases as the amount of NaOAc increases at first, and reaches the best (92%) when the NaOAc amount is 0.05 mmol. The selectivity towards HCMA increases obviously and there is no yield of CMO with the addition of NaOAc. Highest selectivity of 97% is obtained when NaOAc amount is 0.075 mmol.

Table 3 Influence of bases and acids on the hydrogenation of CMA over Pt–Ni/CNTs (III) catalyst[a]

Base/Acid	Conversion (%)	Selectivity (%)				
		HCMA	HCMO	CMO	ACE	OTH
–	63	78	5	17	–	–
NaOH	92	94	4	2	–	–
$(CH_3CH_2)_2$ NH	76	86	5	9	–	–
NaOAc	92	96	4	–	–	–
HAc	100	61	30	9	–	–
HNO_3	89	84	3	6	7	–

[a] Reaction condition: 8.0 mmol CMA, 19.0 mL C_2H_5OH, 0.05 mmol base/acid, 60 °C, 1.5 h, 1.5 MPa

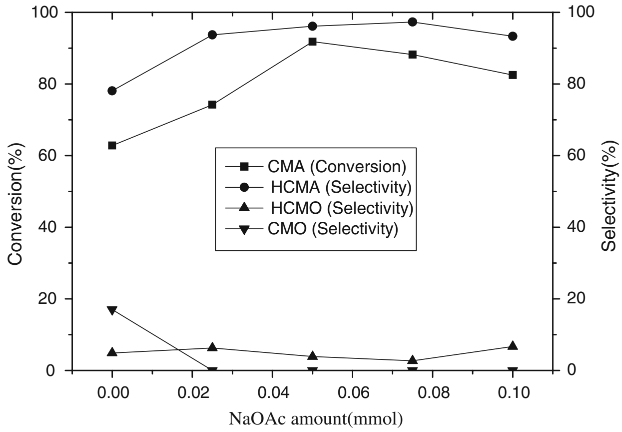

Fig. 4 The hydrogenation of CMA over Pt–Ni/CNTs (III) catalyst with different amount of NaOAc at a reaction condition of 8.0 mmol CMA, 19.0 mL C_2H_5OH, 60 °C, 1.5 h, 1.5 MPa

4 Conclusions

Pt–Ni/CNTs catalysts are prepared by different impregnation techniques and different reduction methods (H_2, HCHO, and KBH_4) for the selective hydrogenation of CMA to HCMA and investigated by TEM, XPS, and H_2-TPR techniques. The results show that the catalytic selectivity and activity of the Pt–Ni/CNTs catalysts would significantly be improved by using KBH_4 as a reducing agent, due to the electronic synergetic effect of Pt–Ni–B, and 96% for conversion of CMA and 88% for selectivity of HCMA are obtained over Pt–Ni/CNTs catalyst reduced by KBH_4 and by co-impregnation with aqueous solutions of $Pt(NH_3)_4Cl_4$ and $Ni(NH_3)_6Cl_2$. In addition, the roles of different organic and inorganic bases/acids as promoters in improving the activity and the selectivity to HCMA of the catalyst are also investigated. We found that the hydrogenation rate of CMA and selectivity of CMA to HCMA over Pt–Ni/CNTs catalyst can significantly be improved in the presence of trace base or acid promoters. The best result (92% for conversion of CMA and 96% for selectivity of HCMA) is obtained when NaOAc (0.05 mmol) is used as base promoter.

Acknowledgment We gratefully acknowledge the financial support from the Natural Science Foundation of Zhejiang, China (No.Y407350)

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