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# Bimetallic Pt-Co catalysis on carbon nanotubes for the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol: Preparation and characterization

Yan Li, Zhen-Guo Li, Ren-Xian Zhou *

*Institute of Catalysis, Zhejiang University, Hangzhou 310028, PR China*

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## Abstract

Carbon nanotubes (CNTs)-based Pt-Co catalysts are prepared by different impregnation techniques and different reduction methods ($H_2$, HCHO and $KBH_4$) for the selective reduction of cinnamaldehyde (CMA) to the corresponding cinnamyl alcohol (CMO). The selectivity and activity of the Pt-Co/CNTs catalysts can be improved significantly by using ammonia as a ligand and $KBH_4$ as a reducing agent because of the synergetic effect of Pt-Co-B. Furthermore, the hydrogenation rate of CMA increases ulteriorly in the presence of trace base and acid promoters.

*Keywords:* Cinnamaldehyde (CMA); Cinnamyl alcohol (CMO); Pt-Co/CNTs catalyst; Selective hydrogenation

## 1. Introduction

α, β-Unsaturated aldehydes are the source materials for many important products in the chemical industry, including polymers and fine chemicals [1,2]. The hydrogenation of α, β-unsaturated aldehydes to the corresponding alcohols is a reaction of relevant importance in the synthesis of various fine chemicals. The selective hydrogenation of the carbonyl group of the above α,β-unsaturated aldehyde, yielding the unsaturated alcohol, remains a challenging task and is of particular interest because of the importance of such alcohols in the fine chemicals industry [1]. Among other factors, selectivity could be enhanced by the electronic effects of the support, the presence of a second metal, and the metal particle sizes and morphology [1].

Cinnamyl alcohol (CMO), an important product of cinnamaldehyde (CMA) hydrogenation, is a source material for cinnamates, which are widely used in the production of perfumes. Selective hydrogenation of CMA is a difficult process, especially under heterogeneous catalysis conditions. Because of the competitive reduction of the aldehyde carbonyl and olefin groups, the selectivities to hydrocinnamaldehyde (HCMA) and CMO vary considerably with the method of preparation of the catalyst, the solvent, additives, the process conditions employed and even trace impurities in the reactant [3–6]. A comprehensive review of CMA hydrogenation has been published by Gallezot and Richard [1].

In general, supported bimetallic catalysts are very interesting materials because one metal can tune and/or modify the catalytic properties of the other metal as a result of both electronic and structural effects [7]. Bimetallic catalysts supported on high surface area carriers, such as, silica and alumina, have attracted considerable attention recently because of their better performance in catalytic reactions which differs significantly from that of the corresponding monometallic counterparts [8]. Pt-Co catalysts have been investigated and characterized by Moraweck et al. [9]. This study has focussed on graphite supported Pt and Pt-Co catalysts and the effects of the use of biphasic solvents and the presence of basic salts on activity and selectivity, the effects of basic media have been reported by Gallezot and Richard [1].

Since the discovery at the beginning of the last decade [10], carbon nanotubes (CNTs) and nanofibers have received an increasing interest both from a fundamental point of view and for potential industrial applications [11–19]. Such applications may include their use as magnetic or sensoring materials, for gas separation and storage, but the most promising seems

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* Corresponding author. Tel.: +86 571 88273272; fax: +86 571 88273290.
*E-mail address:* zhourenxian@zju.edu.cn (R.-X. Zhou).

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to be as catalyst supports [20–22]. Such structures can display unusual behaviors compared to classical supports, especially for liquid-phase reactions, in which diffusion of reactants into the solid matrix and back-diffusion of the products outside the support are significantly influenced by the external size of the particles [23,24]. Furthermore, grain-shaped catalysts can replace homogeneous catalysts, because of their advantages in terms of catalyst and product separation, catalyst recovery and reduction of waste water containing the catalyst. Nanocarbons supported catalysts can exhibit the same properties [25].

The aim of the present work is to report the preparation and the characterization of Pt and Co-decorated CNTs catalysts and their implication in hydrogenation reactions. The catalytic properties are investigated in the liquid-phase selective hydrogenation of CMA into the corresponding unsaturated alcohol (CMO) in mild reaction conditions. The characteristic of the support and of the catalyst is studied 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 CNTs are subsequently purified by thick nitric acid treatment at 80 °C for16 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-Co/CNTs catalysts are prepared by varying the reduction methods and impregnation modes. In one series, the Pt and Co metals are introduced simultaneously by co-impregnation with aqueous solutions of $Pt(NH_3)_4Cl_2$ and $Co(NH_3)_4Cl_2$, 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-Co/CNTs (I), Pt-Co/CNTs (II) and Pt-Co/CNTs (III), respectively. Pt-Co/CNTs (V) catalyst is also prepared by co-impregnation while with aqueous solutions of $H_2PtCl_6$ and $Co(NO_3)_2$, and reduced by $KBH_4$. Whereas in the other series the Pt and Co metals are sequentially introduced, first by impregnation with aqueous solution of $Co(NO_3)_2$ and second with aqueous solution of $Pt(NH_3)_4Cl_2$, and the sample impregnated is reduced by $KBH_4$. The catalyst is assigned as Pt-Co/CNTs (IV) and all of the five catalysts with a weight of Pt 0.50 wt% and Co 0.17 wt%.

Pt /CNTs and Co/CNTs monometallic catalysts are prepared by conventional impregnation with their aqueous solutions of $Pt(NH_3)_4Cl_2$ or $Co(NH_3)_4Cl_2$, respectively. The samples impregnated are reduced by $KBH_4$, filtered and washed with large amount of water, dried at 110 °C overnight before use. The content of Pt and Co 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

XPS measurement is performed on a VG ESCALAB 2201-XL spectrometer. Non-monochromatic Mg Kα radiation is used as a primary excitation. The binding energy values 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. Then the sample is cooled to −50 °C in flowing He. The feed is then switched to 5 vol% $H_2$ in He, the reduction gas which is purified with deoxidizer and silica gel. The reaction temperature is programmed to rise at a constant rate of 10 °C/min up to 300 °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, 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

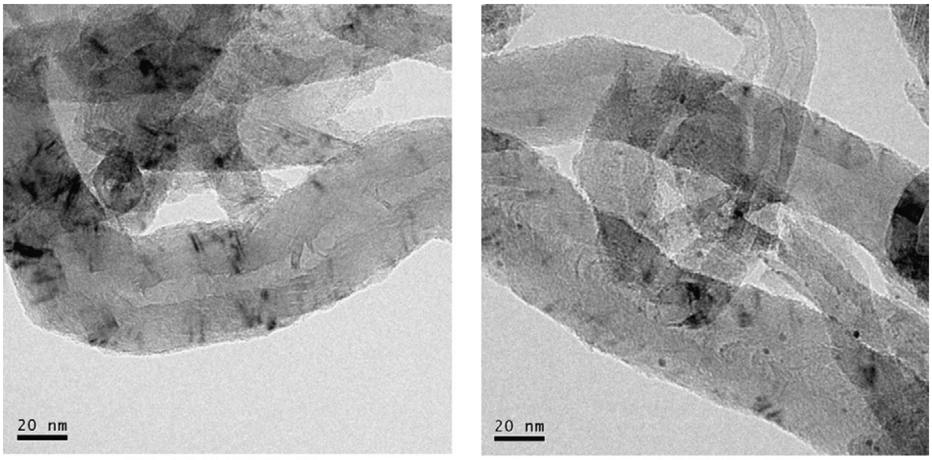
The hydrogenation reaction of CMA is carried out at low pressure and low temperature, in a stainless steel reactor equipped with a hydrogen inlet, a Teflon vessel and a muphet stirrer. A mixture of 0.36 g catalyst, 8.0 mmol CMA and 19.0 ml $C_2H_5OH$ is placed in the reactor. The reaction temperature is maintained by water bath.

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.

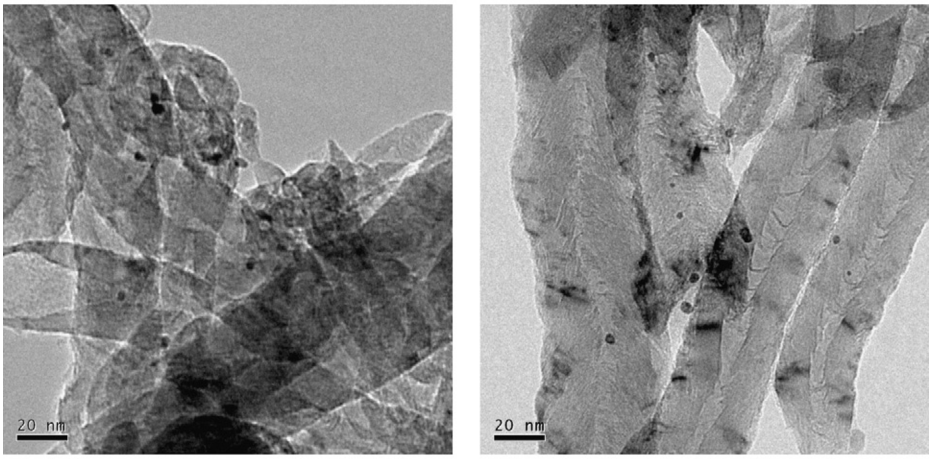
## 3. Results and discussion

### 3.1. Electron microscopy

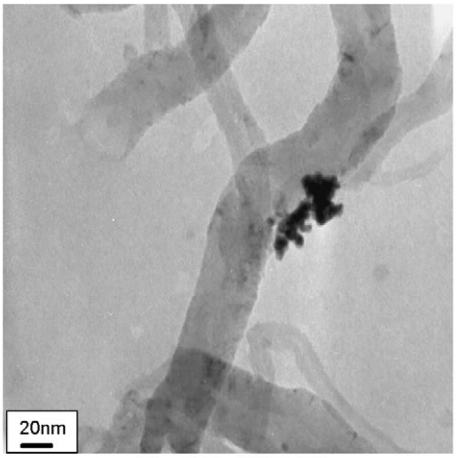
The TEM images of Pt-Co/CNTs (I–V) are shown in Fig. 1. Fig. 1 shows that most of Pt particles over Pt-Co/CNTs are dispersed more homogeneously on the outer surface of the nanotubes when the solution of $Pt(NH_3)_4Cl_2$ is used as the precursor,



(A) Pt-Co/CNTs (I) (B) Pt-Co/CNTs (II)



(C) Pt-Co/CNTs (III) (D) Pt-Co/CNTs (IV)



(E) Pt-Co/CNTs (V)

Fig. 1. TEM images of the Pt-Co/CNTs catalysts.

leading to small diameters on the whole, while the Pt particles have a wide range size of 2–5 nm over Pt-Co/CNTs (III, IV) catalysts reduced by $KBH_4$ with a regular spherical distributing and have smaller diameter of 1–3 nm over Pt-Co/CNTs (I, II) catalysts using HCHO or $H_2$ as reducers. The Pt particles over Pt-Co/CNTs (V) catalyst prepared by co-impregnation with the precursor of $Co(NO_3)_2$ and $H_2PtCl_6$ show very different distribution with the formation of agglomerate of Pt and Co 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.

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-Co/CNTs (I) | HCHO (70 °C, 6 h) | 3.3 | 250 |
| Pt-Co/CNTs (II) | $H_2$ (400 °C, 4 h) | 1.64 | 22 |
| Pt-Co/CNTs (III) | $KBH_4$ (80 °C, 2 h) | 2.4 | 31 |
| Pt-Co/CNTs (IV) | $KBH_4$ (80 °C, 2 h) | 2.2 | 22 |
| Pt-Co/CNTs (V) | $KBH_4$ (80 °C, 2 h) | 2.2 | 17 |

### 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-Co 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.)

From Fig. 2 and Table 1, it can be seen that there is one $H_2$ consumption peak at the temperature range of −50 °C to 350 °C representing the reduction of highly dispersed $PtO_2$ species appears in the CNTs supported Pt-Co catalysts.

For the Pt-Co/CNTs (II) catalyst, the TPR profile is well explained by assuming the reduction of small $PtO_2$ particles containing a core made of metal platinum since $H_2$/Pt was smaller than the stoichiometry governed by the equation $PtO_2 + 2H_2 \rightarrow Pt^0 + 2H_2O$. While the Pt-Co/CNTs (I) catalyst presents a large peak of $H_2$ consumption appearing at a higher temperature, 250 °C. 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) is in accordance with that already observed on 5% Pt/ZnO [32] or in Pt/$Al_2O_3$ [33,34] which was interpreted by the authors, from EXAFS characterization, by the following equation: $\ulcorner Pt(OH)_4(Cl)_2 \lrcorner^{2-} + 3H_2 \rightarrow Pt^0 + 4H_2O + 2HCl + 2e-$.The other catalysts present a reduction maximum at about 20 °C, with a $H_2$/Pt ratio basically equal to 2. However, for the Pt-Co/CNTs (I) catalyst using HCHO as reducer, its XPS analysis shows a shift of Pt $4f_{7/2}$ towards lower binding energies which may because of the effect of electron donation from the ligand of chlorine compared with the Pt-Co/CNTs (II, III) catalysts using $H_2$ or $KBH_4$ as reducers, and after the catalyst is ulteriorly reduced by hydrazine hydrate, the chlorine ion is detected in the solution which deeply confirms the presence of oxychloride platinum species, while there is no indication of chlorinated platinum species in the Pt-Co/CNTs (II, III)catalysts using $H_2$ or $KBH_4$ as reducers which would reduce the chlorine species to form HCl species because of their stronger reducibility.

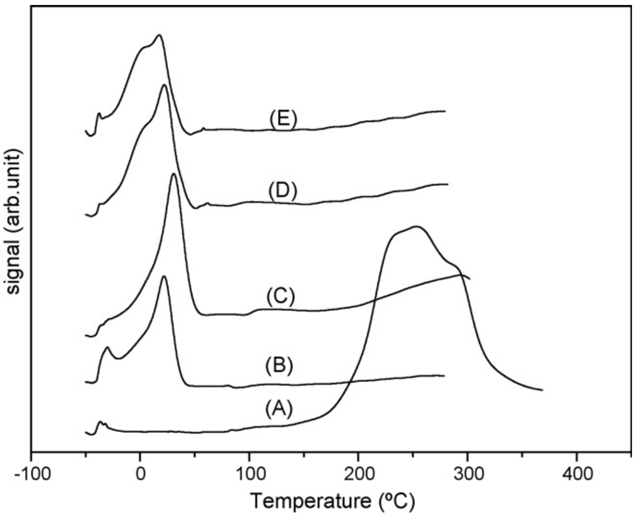


Fig. 2. $H_2$-TPR profiles of the Pt-Co/CNT catalysts (A) Pt-Co/CNTs(I) (B) Pt-Co/CNTs (II) (C) Pt-Co/CNTs (III) (D) Pt-Co/CNTs (IV) (E) Pt-Co/CNTs (V).

### 3.3. Catalytic properties

The hydrogenation of CMA typically produces a mixture of the desired unsaturated alcohol CMO, the undesired 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 over some catalysts as shown in Fig. 3. Different reduction methods have also influence on both catalytic activity and selectivity, as seen in Table 2. The Pt-Co/CNTs (I) catalyst using HCHO as reducer shows low catalytic hydrogen activity and high yield of OTH, this maybe related to the active component of Pt exist in a state of $PtO_xCl_y$ species while not reduced to metallic Pt. For the Pt-Co/CNTs(II) catalyst, its catalytic hydrogen activity is not high too (48.7% for the hydrogenation conversion), and yield a great deal of by-product of ACE. 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-Co/CNTs (III–V) catalysts reduced by $KBH_4$ exhibit good catalytic activity and selectivity for CMO. The XPS results show that the surface B content is about 0.1 wt% in the three catalysts, thus we suggest that good

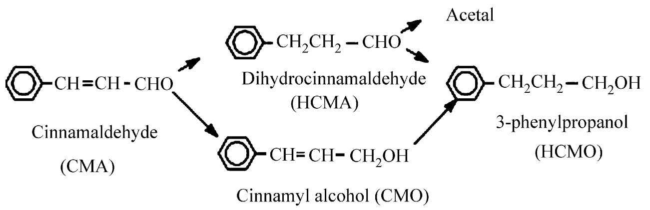


Fig. 3. Hydrogenation mechanism for CMA.

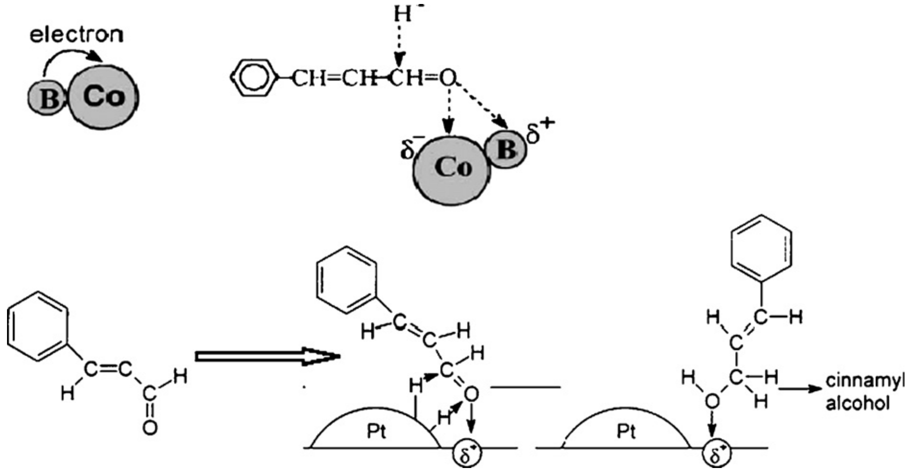


Fig. 4. Hydrogenation mechanism of CMA over Pt-Co/CNTs catalysts reduced by $KBH_4$.

effects are also related to the presence of B [35]. To investigate the synergetic effect of Pt, Co and B, the hydrogenation property is also carried out over monometallic Pt/CNTs and Co/CNTs catalysts reduced by $KBH_4$, the Pt/CNTs shows low catalytic activity and Co/CNTs shows absence activity for hydrogenation. Such we can deduce from the results that the high hydrogenation activity and selectivity towards CMO attributed to the synergetic effect of Pt-Co-B. Electrons may transfer from B to the vacant d-orbital of metallic Co for Co-B particles [36] and form the electron positive center to adsorb the carbonyl group through a vertical C=O atop geometry as described in Fig. 4. Metal catalysts containing boron species, generally called metal boride, have been studied extensively in some reactions. Paul et al. [37] first reported the use of NiB prepared from nickel salt and $NaBH_4$ as hydrogenation catalysts. Narasimhan's group has published several papers about mixed metal boride catalyst, Ru-Sn-B, which was prepared by reducing metal salts with $NaBH_4$ [38–40]. 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. [41] based on XPS studies.

It also can be seen from Table 2 that when the precursor of $Pt(NH_3)_4Cl_2$ solution is either co-impregnated with $Co(NH_3)_4Cl_2$ solution or sequentially impregnated with $Co(NO_3)_2$ solution onto the CNTs supports which have negligible different effect on the catalytic properties, while when the precursor of $H_2PtCl_6$ solution is co-impregnated with $Co(NO_3)_2$ solution, the Pt-Co/CNTs (V) catalyst shows obvious difference in the selective hydrogenation of CMO with Pt-Co/CNTs (III, IV) catalysts. This may be the phenomenon of agglomeration in Pt-Co/CNTs (V) catalyst as seen in TEM image. The stability of Pt-Co/CNTs (III) catalyst is also investigated, and the results show that in the recycle experiment, the catalytic activity decreases evidently, while the yield of HCMA increases. Lower catalytic activity is influenced by many factors on the hydrogenation of CMA. For example, a part of Pt could be lost when the catalyst is reused, and results in decreasing in the number of active sites for hydrogen of the Pt surface. Some intermediates could be also adsorbed on the surface of catalyst and partly cover active center, and which decrease catalytic activity.

The roles of different organic and inorganic bases and acids as promoters in improving the activity and the selectivity to CMO of the catalyst are also investigated. The results in Table 3 indicate that trace amount of HAc, $HNO_3$ and NaAc play an

Table 2
Influence of preparation methods on the hydrogenation of CMA over Pt-Co/CNTs catalysts[a]

| Catalyst | Reducer | Conversion (%) | Selectivity (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | HCMA | HCMO | CMO | ACE | OTH |
| Pt-Co/CNTs (I) | HCHO (70 °C, 6 h) | 54.7 (3.5)[b] | – | – | 6.3 | – | 93.7 |
| Pt-Co/CNTs (II) | $H_2$ (400 °C, 4 h) | 96.7 (48.7) | 2.0 | 4.8 | 13.6 | 30.0 | 49.6 |
| Pt-Co/CNTs (III) | $KBH_4$ (80 °C, 2 h) | 87.4 (87.4) | 4.7 | 2.9 | 92.4 | – | – |
| Pt-Co/CNTs (IV) | $KBH_4$ (80 °C, 2 h) | 85.9 (85.9) | 4.7 | 2.1 | 93.3 | – | – |
| Pt-Co/CNTs (V) | $KBH_4$ (80 °C, 2 h) | 85.7 (85.7) | 21.5 | 3.3 | 75.3 | – | – |
| Pt/CNTs | $KBH_4$ (80 °C, 2 h) | 48.2 (48.2) | 56.7 | – | 43.3 | – | – |
| Co/CNTs | $KBH_4$ (80 °C, 2 h) | 11.5 (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 sum of the conversion for HCMA, HCMO, CMO and ACE.

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

| Base/acid | Conversion (%) | Selectivity (%) | | | | |
|---|---|---|---|---|---|---|
| | | HCMA | HCMO | CMO | ACE | OTH |
| – | 77.7 | 5.1 | 1.3 | 93.6 | – | – |
| NaOH | 63.2 | 7.4 | 1.9 | 90.7 | – | – |
| $(CH_3CH_2)_2$ NH | 61.4 | 8.9 | 1.9 | 89.2 | – | – |
| NaAc | 87.2 | 6.9 | 1.4 | 91.8 | – | – |
| HAc | 80.9 | 8.4 | 2.3 | 89.4 | – | – |
| HNO3 | 96.0 | 11.0 | 4.6 | 63.5 | 20.9 | – |

[a] Reaction condition: 8.0 mmol CMA, 19.0 mL $C_2H_5OH$, 2 mmol base/acid, 60 °C, 1.5 h, 1.5 MPa.

important role in improving the activity, while organic base such as $(CH_3CH_2)_2NH$ and strong alkali NaOH inhibit the reaction. NaAc modifies the catalytic activity, probably it 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 CMO decreases. Another important find is the consistent variety tendency of the selectivity of the HCMA and HCMO, it has been reported by Tong et al. [42] that HCMO is produced exclusively from the hydrogenation of HCMA and not CMO in the two parallel routes of the hydrogenation mechanism for CMA shown in Fig. 3. So when the solvents favor the selective hydrogenation of HCMA, the yield of HCMO increases.

Since NaAc plays an important role in improving the selective hydrogenation of CMA to CMO, the influence of addition amount of NaAc is also studied. Fig. 5 shows that the conversion of CMA increases as the amount of NaAc increases at first, and reaches the best (87.2%) when the NaAc amount is 0.05 mmol. The selectivity towards CMO increases in accord with increasing amount of NaAc. Highest selectivity of 96.5% has been obtained when NaAc amount is 0.10 mmol.

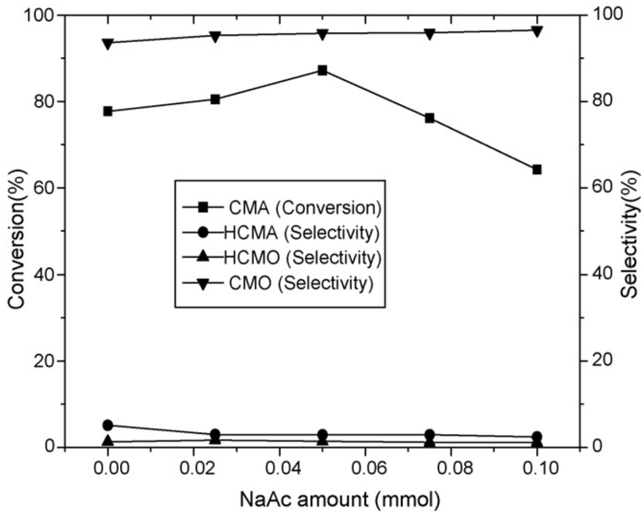


Fig. 5. The hydrogenation of CMA over Pt-Co/CNTs (III) catalyst with different NaAc amount.

## 4. Conclusions

We have developed very active and selective catalysts for hydrogenation of CMA to CMO under mild conditions. High activity and selectivity are obtained on the Pt-Co/CNTs (III) catalyst which is reduced by $KBH_4$ and the metals are introduced onto CNTs supports by co-impregnation with their ammines, we have demonstrated that the performance mainly ascribes to the synergetic effect of Pt-Co-B. Finally, the hydrogenation rate of CMA and selectivity of CMA to CMO increase significantly in the presence of NaAc over the Pt-Co/CNTs (III) catalyst probably it can enhance the solubility of hydrogen in ethanol.

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