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Selective hydrogenation of cinnamaldehyde over Pt/ZrO_2 catalyst modified by Cr, Mn, Fe, Co and Ni

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Hydrogenation properties of cinnamaldehyde (CMA) have been studied over Pt/ZrO_2 and PtM/ZrO_2 catalysts (M = Cr, Mn, Fe, Co and Ni) in ethanol at 343 K and 2.0 MPa. The effect of different content of Ni and base has also been investigated over PtNi/ZrO_2 catalyst. With introduction of transition metals to Pt/ZrO_2 catalyst shows a significant influence on the catalytic properties. PtCo/ZrO_2 catalysts show the best yield of cinnamyl alcohol (CMO), and PtNi/ZrO_2 catalyst shows good yield of hydrocinnamaldehyde (HCMA). In the presence of base solution, rate of the hydrogenation of CMA over PtNi/ZrO_2(0.4 wt%) catalyst increases significantly and side reaction is remarkably inhibited. More bare metal atoms situated remote from the interface region on PtNi/ZrO_2 catalyst surface are the reason of good selectivity of HCMA for PtNi/ZrO_2 catalyst.

KEY WORDS: cinnamaldehyde; hydrocinnamaldehyde; phenylpropanol; cinnamyl alcohol; hydrogenation.

1. Introduction

Research in catalytic selective hydrogenation of α, β-unsaturated aldehydes is of great importance in potential industrial applications and theoretical aspects [1–4]. Cinnamaldehyde, a member of α, β-unsaturated aldehydes, and its semi-hydrogenated products such as cinnamyl alcohol and hydrocinnamaldehyde are important fine chemicals and intermediates especially in perfume industry and medicine manufacture. Recently, hydrocinnamaldehyde was found to be an important intermediate in the preparation of pharmaceuticals used in the treatment of HIV [5]. Although various attempts have been made to develop a suitable catalytic system for selective hydrogenation of cinnamaldebyde to hydrocinnamaldehyde [6–9], the selectivity is still an important issue. Platinum catalyst is known to be one of the most effective catalysts for this selective hydrogenation.

Selective hydrogenation of cinnamaldehyde is a difficult process. The hydrogenation of the C = C group is thermodynamically more favorable than the C = O group hydrogenation, but the C = O group of cinnamaldehyde is reduced easily and competes with C = C group. It remains unclear about the key factor to control the selectivity and activity of hydrogenation of cinnamaldehyde, although it is well known as a general rule that the electronic effects and stereo-hindrances predominate the selectivity and activity. The selectivities to hydrocinnamaldehyde and cinnamyl alcohol vary considerably with the method of preparation of the catalyst, the solvent, additives, the process conditions employed and even trace impurities in the reactant [10–15].

The support also plays an important role in the selectivity on the hydrogenation of cinnamaldehyde. Suitable carriers such as carbon, clay, alumina, silica, zirconia, titania supported platinum catalysts have been reported for the hydrogenation of α, β-unsaturated aldehyde. Metals deposited on reducible oxide TiO_2 and ZrO_2 show better catalytic behavior on the selective hydrogenation of chloronitrobenzene and α, β-unsaturated aldehydes [16–23]. It is proposed that the strong metal/support interaction is responsible for this behavior. In this paper, we investigate the catalytic properties of Pt/ZrO_2 catalyst modified by Cr, Mn, Fe, Co and different content of Ni on the hydrogenation of cinnamaldehyde.

2. Experimental

ZrO_2 support is crushed and sieved to obtain a particle size range of 100 ~ 140 meshes, The monometallic Pt/ZrO_2 catalyst is prepared by conventional impregnation with an aqueous solution of hexachloroplatinic acid. The content of platinum is 0.3 wt%. The sample impregnated is reduced by KBH_4, filtered with large amount of water, dried at 373 K overnight, and then calained at 673 K for 4 h. The bimetallic PtM/ZrO_2 catalysts (M = Cr, Mn, Fe, Co and different content of Ni) are also prepared by impregnation, i.e., platinum may be impregnated after the transition metal is impregnated on ZrO_2. The preparation process is similar to Pt/ZrO_2.

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Table 1
Mean conditions for the characterization of the Pt/ZrO_2 catalysts

Sample	Mean particle size from TEM (nm)	BET(m^2/g)
Pt/ZrO_2	2.0	96.8
PtCr/ZrO_2	3.5	80.9
PtMn/ZrO_2	3.8	79.2
PtFe/ZrO_2	4.0	76.8
PtCo/ZrO_2	4.1	74.8
PtNi/ZrO_2(0.04)	2.8	93.6
PtNi/ZrO_2(0.1)	3.0	92.6
PtNi/ZrO_2(0.2)	3.6	85.3
PtNi/ZrO_2(0.4)	6.7	80.7
PtNi/ZrO_2(0.8)	7.3	75.7

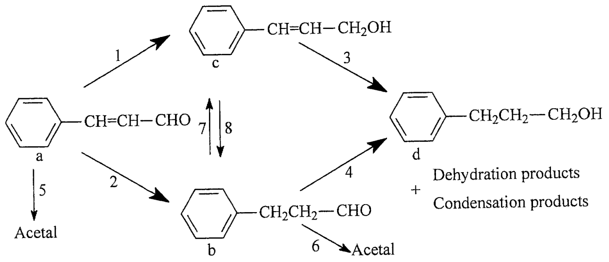
The amount of transition metal is 0.1 wt%.

Surface areas of the support as well as the catalysts are determined by N_2 adsorption at 77 K using the BET method in an OMNISORP 100CX apparatus. Transmission electron microscopy (TEM) is a conventional method to give detailed information about the shapes, mean size and size distribution of metallic dispersions. The size of the platinum metallic particles is checked by TEM using a JEM-200CX apparatus. The results are shown in Table 1.

A typical hydrogenation procedure is conducted as follows: the catalyst (0.18 wt% Pt), 1 ml of cinnamaldehyde (8×10^{-3} mol) and ethanol solution are added into a 50ml stainless steel autoclave. H_2 was charged several times to replace air and the final pressure of H_2 was 2.0 MPa. The hydrogenation reaction is carried out at 343 K for 6 h. 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. With the catalyst amount varied from 0.3 to 0.9 g, the speed of agitation was varied from 600 to 1100 rpm to observe whether the rates of the hydrogenation reactions were dependent on the speed. The test results indicated that the external mass transfer is sufficiently eliminated at the stirring speed higher than 800 rpm.

3. Results and discussion

Hydrogenation of cinnamaldehyde is a complicated process as shown in Scheme 1, and it often yields many by-products. The aim of our study is to achieve high catalytic activity and selectivity to its semi-hydrogenated products. Table 1 lists the results of selective hydrogenation of CMA catalyzed by Pt/ZrO_2 and PtM/ZrO_2 catalysts, respectively, From Table 1, we can see that addition of small amount of transition metals (Cr, Mn, Fe, Co, and Ni) to Pt/ZrO_2 catalyst show different hydrogenation properties. Catalytic activities are all improved except PtCr/ZrO_2 catalyst. PtCo/ZrO_2 and PtFe/ZrO_2 catalysts show good selectivity of CMO, and PtNi/ZrO_2 catalyst shows good selectivity of HCMA. This is an interesting phenomenon, Fe, Co, Ni are elements of the same race, and the property of them are similar but the additions of them have great different influence on the hydrogenation of CMA over PtM/ZrO_2 catalysts (Table 2). The effect of transition metal may be interpreted by electronic effect. Electron deficient species of the second element promote the turnover frequency of Pt atoms by activating the C=O group, so good selectivity of CMO is obtained [24]. This interpretation cannot be applied for PtNi/ZrO_2 catalyst on the hydrogenation of CMA. The effect of Ni over PtNi/ZrO_2 catalyst is investigated on the hydrogenation of CMA as follows.



Scheme 1. Reaction pathways for the hydrogenation of cinnamaldehyde.

No products are observed when zirconia support is tested in cinnamaldehyde hydrogenation.

The effect of different Ni amount is investigated on the hydrogenation of CMA over Pt/ZrO_2 catalyst. The results are listed in Table 3. The main products are HCMA, CMO and HCMO. From Table 3, we can see that PtNi/ZrO_2 catalysts show good selectivity of C=C group. The conversions of CMA and TOF increase with the increasing the Ni amount. We also find the yield of CMO decreases, and the yield of HCMO increases sig-

Table 2
Results of the hydrogenation of CMA over PtM/ZrO_2 catalysts[a]

Catalyst	Conversion (%)	TOF (s^{-1})$\times 10^{-2}$	Yield of products (mol%)			
			HCMA	HCMO	CMO	others
ZrO_2	nil	–	–	–	–	–
Pt/ZrO_2	49.9	1.8	25.5	21.7	42.2	10.6
PtCr/ZrO_2	21.4	0.5	46.5	8.0	1.0	44.5
PtMn/ZrO_2	55.2	1.9	27.4	6.6	52.0	14.0
PtFe/ZrO_2	88.6	3.5	5.4	10.7	83.6	0.3
PtCo/ZrO_2	90.2	3.6	5.3	6.7	88.0	0.0
PtNi/ZrO_2	70.6	2.4	64.3	11.8	7.8	16.1

[a] Reaction condition: 8×10^{-3} mol CMA; reaction temperature is 343 K; P is 2.0 MPa; The amount of catalyst is 0.6 g.

[b] TOF, specific activity per Pt surface atom (s^{-1}) for the hydrogenation of cinnamaldehyde over supported Pt catatlysts.

[c] Some products with high boiling point could not be determined by GC analysis; HCMA = hydrocinnamaldehyde, HCMO = phenylpropanol; CMO = cinnainyl alcohol.

Table 3
Results of different Ni amount on the hydrogenation of CMA over Pt/ZrO$_2$ catalyst[a]

Ni content (wt%)	Conversion (%)	TOF (s^{-1})× 10^{-2}	Yield of products (mol%)			
			HCMA	HCMO	CMO	others
–	49.9	1.8	25.5	21.7	42.2	10.6
0.04	67.1	2.2	61.8	6.5	13.6	18.1
0.1	70.6	2.4	64.3	11.8	7.8	16.1
0.2	81.9	2.9	68.3	15.6	5.6	10.5
0.4	98.2	3.3	42.4	42.3	0.4	14.9
0.8	99.3	3.5	34.3	53.0	0.1	12.6

[a] Reaction conditions are similar to Table 5.1, the amount of catalyst is 0.6 g.

nificantly with increasing the Ni amount of PtNi/ZrO$_2$ catalyst. However, the addition of HCMO is much higher than the decreasing of CMO when the content of Ni is over 0.2 wt%. So we think the deep hydrogenation of HCMA is carried out. In our experiment, some byproducts are also found on the hydrogenation of CMA over PtNi/ZrO$_2$ catalyst. These products are the formation of diacetals. This was confirmed by mass spectrometric measurements. When the content of Ni is lower 0.2 wt%, the reactions 5 and 6 in Scheme 1 happen. The diacetal is mainly formed by reaction 6 when the content of Ni is over 0.2 wt%.

Based on above experiment results, byproduct of diacetal is formed on the hydrogenation of CMA over PtM/ZrO$_2$ catalyst in ethanol at 343 K and 2.0 MPa. The formation of diacetals is observed when pure alcohol is used as solvent during the hydrogenation of $\alpha\!-\!\beta$ ethylenic aldehydes [16, 25]. This reaction does not occur when a little water is present [26]. Catalytic activities can also be improved in the presence of NaOH [27,28]. So we investigate the hydrogenation properties over PtM/ZrO$_2$ catalysts in the presence of NaOH and H$_2$O. Good hydrogenation properties are found in the presence of 2.5×10^{-5} mol NaOH and 1 ml H$_2$O in our experiment. The effects of different base are also investigated on the hydrogenation of CMA over PtNi/ZrO$_2$ (0.4 wt%) catalyst. The results are listed in Table 4. From Table 4, we can see that catalytic activity and the yield of HCMA are improved significantly on the hydrogenation of CMA over PtNi/ZrO$_2$ (0.4 wt%) catalyst in the presence of NaOH solution. The TOF value increases from 3.3×10^{-2} s^{-1} to 21.8×10^{-2}s^{-1} and the yield of HCMA improves from 42.4 mol% to 90.6 mol%. The main products are HCMA, CMO and HCMO, and we don't find other products in the presence of base. Under reaction condition, Ni/ZrO$_2$ catalyst shows negligible catalytic activity on the hydrogenation of CMA. NiB/ZrO$_2$ catalyst shows low catalytic activity. Using other inorganic base, such as K$_2$CO$_3$ and NaOAc, PtNi/ZrO$_2$(0.4 wt%) catalyst also shows good catalytic activity and yield of HCMA. In order to clarify the effect of support acidity on selectivity, additional experiments are carried out using a PtNi/ZrO$_2$ catalyst treated with 5% aqueous NaOH and 5% aqueous HNO$_3$. The acid-treated PtNi/ZrO$_2$ catalyst contains very strong Brønsted acid sites, while the base-treated PtNi/ZrO$_2$ catalyst has practically no acid sites. As a result, both catalysts show high catalytic activities but they show different catalytic properties: the base-treated PtNi/ZrO$_2$ catalyst shows high selectivity of C=C group, and deep hydrogenation of HCMA is easily carried out. Reaction 6 is easily carried out for the acid-treated PtNi/ZrO$_2$ catalyst. G. Szöllösi et al. [11] have also found that 5% Pt/K-10 catalyst treated by NaOH and 5% Pt/Nafion-H/silica-nanocomposite catalyst show low selectivities of the formation of CMO on the hydrogenation of CMA.

The stability of PtNi/ZrO$_2$ (0.4 wt%) catalyst was also investigated, and the results are summarized in Table 5. In the recycling experiment, three recycles were carried out for the hydrogenation of CMA. It is found

Table 4
Activity and selectivity data of the hydrogenation of CMA over Ni-based (0.4 wt%) catalyst[a]

Catalyst	Base	Conversion (%)	TOF (s^{-1}) × 10^{-2}	Yield of products (mol%)			
				HCMA	HCMO	CMO	others
PtNi/ZrO$_2$[b]	–	98.2	3.3	42.4	42.3	0.4	14.9
PtNi/ZrO$_2$	NaOH	90.5	21.8	90.6	8.9	0.5	0
Ni/ZrO$_2$ [c]	NaOH	nil	–	–	–	–	–
NiB/ZrO$_2$[d]	NaOH	32.8	7.9	72.5	22.2	5.3	0
PtNi/ZrO$_2$	NaOAc	87.7	21.1	92.3	7.7	0	0
PtNi/Zr0$_2$	K$_2$CO$_3$	60.7	14.6	83.6	3.7	12.7	0
PtNi/ZrO$_2$[e]	–	98.6	23.7	53.7	46.3	0	1.6
PtNi/ZrO$_2$[f]	–	91.2	21.4	11.6	36.9	3.4	48.1

[a] Reaction conditions are similar to table 5.1, the amount of catalyst is 0.6 g. The reaction time is 1 h.
[b] The reaction time is 6 h.
[c] The catalyst of Ni/ZrO$_2$ is prepared from NiO/ZrO$_2$ reduced by KBH$_4$.
[d] The catalyst of NiB/ZrO$_2$ is prepared from Ni(NO$_3$)$_2$ supported on ZrO$_2$ reduced by KBH$_4$ solution for 24 h.
[e] The original PtNi/ZrO$_2$(0.4) catalyst was pretreated with a 5 mol/l NaOH solution.
[f] The original PtNi/ZrO$_2$(0.4) catalyst was pretreated with a 5 mol/l HNO$_3$ solution.

Table 5
Stability of PtNi/ZrO_2(0.4wt%) catalyst in the presence of NaOH[a]

Catalyst	Conversion (%)	TOF (s^{-1})× 10^{-2}	Yield of products (mol%)			
			HCMA	HCMO	CMO	others
1	90.5	21.8	90.6	8.9	0.5	0
2	81.3	19.6	91.3	8.1	0.6	0
3	68.3	16.4	92.7	6.9	0.4	0
3[b]	71.2	17.1	90.9	8.5	0.6	0

[a] Reaction conditions are similar to Table 4.
[b] Catalyst is recycled two times, and then reduced by KBH_4 again.

that the catalytic activity decreases, but high yield of HCMA is obtained. 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 (the level of Pt measured by ICP is 0.26 wt%), 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. After PtNi/ZrO_2 (0.4 wt%) catalyst is used for three recycles, the catalyst is reduced by KBH_4 again, filtered and washed with large amount of water, and then dried at 373 K, We find that catalytic activity is partly resumed. The result shows that loss part of B is also a reason of lower catalytic activity.

In order to clarify the process, we study the relation of conversion of CMA and selectivity to each product as functions of the reaction time for PtNi/ZrO_2 (Ni 0.4 wt%) catalyst on the hydrogenation of CMA in the absence of base. The results are listed in figure 1. From figure 1, we can see that PtNi/ZrO_2 (Ni 0.4 wt%) catalyst shows high reaction rate on the hydrogenation of CMA, after 2.5 h the conversion is up to 95%. The conversion of CMA increases monotonously with the reaction time and the highest selectivity to HCMA is obtained in the initial reaction time. As the reaction goes on, the yield of HCMA and CMO decreases, but the yield of HCMO increases, which indicates that the deep hydrogenation of HCMA is carried out. Based on above experiment results, we can think that the two semi-hydrogenated products (HCMA and CMO) are formed on different surface sites and the modifying effect had different influences on these sites. From figure 1, we also find the high yield of byproducts is formed. These products are the formation of diacetals. This was confirmed by mass spectrometric measurements. Reaction 5 is mainly in the initial reaction time, and then reaction 6 happens as the time goes on.

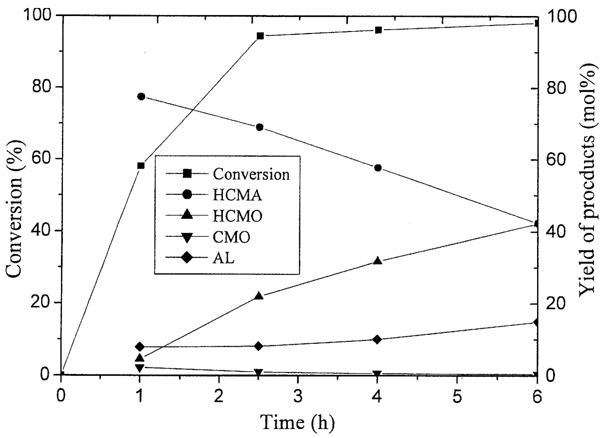


Figure 1. The conversion of CMA and the selectivity to each product as functions of the reaction time for PtNi/ZrO_2 (Ni 0.4 wt%).

As indicated above, Pt/ZrO_2 catalyst modified by small amount of transition metals (Cr, Mn, Fe, Co and Ni) shows different hydrogenation properties for the hydrogenation of CMA. Among the catalysts, PtCo/ZrO_2 catalyst shows the best catalytic activity and yield of CMO. PtNi/ZrO_2 catalyst shows the best yield of HCMA. The effect of transition metal may be usually interpreted by electronic effect and/or geometric effect. As reported by literature, good hydrogenation properties are found on large Pt particles. Such behavior was also reported by Galvagno et al. [24] for nitrobenzene hydrogenation over PtSn/nylon catalysts and Coq [29] for 2-butenal hydrogenation over Pt/Al_2O_3 catalysts. This interpretation cannot be completely applied in the present work for these Pt particles did not change markedly in size when adding small amount of transition metal (see Table 1). Particle size of the metal has an essential effect on the selectivity. Galvagno and coworkers [14, 30] have found that the selectivity to cinnamyl alcohol increases with Ru particle size on carbon support, reaching a value of about 60% on the least dispersed samples. In contrast to this, Arai and coworkers [31, 32] have found that the small platinum particles (about 1 nm) on alumina obtained at reduction temperature of 303 K have a high selectivity to cinnamyl alcohol. It has been reported [33] that the hydrogenation of the C = C group took place on bare metal atoms situated remote from the interface region and the hydrogenation of the C = O group took place at the metal-support interface. The metal particle size may play a role only by determining the ratio between the metal atoms situated at the interface region and of those far from the support. So we suppose the good yield of HCMA for PtNi/ZrO_2 catalyst is that there are more bare metal atoms situated remote from the interface region on PtNi/ZrO_2 catalyst surface. The second interpretation proposed by Galvagno et al. [34] and Richard et al. [35], suggesting that the deposition of electron deficient centers on the platinum surface, which tend to adsorb C = O groups through the unshared electron pairs of carbonyl oxygen. Ionic and electron deficient metal species for PtM/ZrO_2 catalyst acting as Lewis acid that activate the C = O group towards addition of the hydrogen chemisorbed on the platinum. The good catalytic properties are related with the presence of B [32, 36, 37]. NiB/ZrO_2 catalyst shows certain catalytic activity. Under our catalytic preparation, cobalt boride, iron boride and nickel boride is easily formed in the presence of $NaBH_4$. These boron compounds also have influence on hydrogenation properties on the hydrogenation of CMA. The good effects are also related to the special nature of support ZrO_2. The strong metal/support interaction state of Pt/ZrO_2 is responsible for the good catalytic activity on the hydrogenation of CMA.

4. Conclusions

Pt/ZrO_2 catalyst can catalyze the hydrogenation of CMA at 343 K and 2.0 MPa. Catalytic activities are all improved with the addition of small amount of transition metal to Pt/ZrO_2 catalyst except Cr. $PtCo/ZrO_2$ and $PtFe/ZrO_2$ catalysts show better selectivity of CMO, and $PtNi/ZrO_2$ catalyst show better selectivity of HCMA. Conversion of CMA increases with increasing the amount of Ni over $PtNi/ZrO_2$ catalyst on the hydrogenation of CMA. In the presence of base, the hydrogenation rate increases significantly and side reaction is remarkably inhibited. The effect of transition metal may be interpreted by electronic effect. Electron deficient species of the second element promote the turnover frequency of Pt atoms by activating the $C=O$ bond. The main reason of good yield of HCMA is that there are more active sites for the hydrogenation of $C=C$ group on $PtNi/ZrO_2$ catalyst surface.

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