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Influence of support and transition metal (Cr, Mn, Fe, Co, Ni and Cu) on the hydrogenation of *p*-chloronitrobenzene over supported platinum catalysts

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Abstract

Hydrogenation properties of *p*-chloronitrobenzene (CNB) have been studied over alumina, zirconium dioxide and titania prepared by different ways supported platinum catalysts in ethanol at 303 K and atmospheric pressure. Pt/TiO_2 catalyst exhibits good catalytic activity and selectivity of *p*-chloroaniline (CAN). The conversion of *p*-CNB is over 99% and *p*-CAN is main product on the hydrogenation of *p*-CNB over TiO_2-supported platinum catalysts. PtM/TiO_2 catalysts (M = Cr, Mn, Fe, Co, Ni, Cu) have also been investigated for the hydrogenation of *p*-CNB to *p*-CAN. A significant influence on the catalytic properties is showed with introduction of transition metals to Pt/TiO_2 catalyst. Both catalytic activity and selectivity of *p*-CAN are all improved. Among all the catalysts, PtFe/TiO_2 catalyst shows the best catalytic activity (TOF, $1.39\,s^{-1}$) and the highest yield of *p*-CAN (98.0 mol%) on the hydrogenation of *p*-CNB.

Keywords: Chloronitrobenzene; Chloroaniline; Hydrogenation

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1. Introduction

There is a growing interest to develop supported metallic catalysts for the selective hydrogenation of a specific function in polyfunctional organic molecules. To achieve this goal the properties of catalyst can be tuned by modifying the dispersion of the metal particle, by alloying or by initiating some kind of interaction between the metal particle and the carrier. The catalysts can be easily removed from the reaction mixtures and wastes could be largely diminished.

Aromatic haloamines are important intermediates in the chemistry of dyes, drugs, herbicides and pesticides. Nitro-submitted aromatic compounds can be effectively reduced to aromatic amines in the presence of various catalysts, including precious metal catalysts. However, where the nitro compound contains an aromatic halogen, reduction of the nitro group without dehalogenation presents a particularly difficult problem [1]. Special catalyst has been proposed as a method of reducing hydrogenolysis of the halogen group [1–6]. Among these catalysts, platinum-based catalysts have received much attention for minimizing dehalogenation combined with a fast rate of nitro-group reduction. To improve selectivity, the catalyst preparations are modified (alloying [7] and metal/support interaction [8], etc.) or specific additives (promoters or inhibitors) [9–13] are used in the reaction system.

Catalytic hydrogenation reactions are influenced by many factors, which include the presence of catalytic activators or poisons, temperature, pressure, solvent agitation and other conditions specific to the particular process. One of the more important considerations is the catalyst support. Suitable carriers such as carbon, alumina, barium carbonate, barium sulfate, calcium carbonate, kieselguhr, silica, titania-supported platinum catalysts have been reported for the hydrogenation of chloronitrobenzene. It has been reported that Pt/TiO_2 catalyst reduced at high temperature is more efficient in preventing dehalogenation. It is proposed [8] that the migration of suboxide TiO_x species ($x < 2$) on to the Pt particles, in a strong metal/support interaction state, is responsible for this behavior. Migrating TiO_x adspecies on Pt activate the N=O bond which becomes highly susceptible to hydrogen attack. However, high selectivity of *p*-chloroaniline accompanies

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low catalytic activity. In our experiment, we prepared different TiO_2 supports and found good catalytic activity and selectivity for TiO_2-supported platinum catalyst.

The aim of the present work is to determine the influence of support on the hydrogenation of chloronitrobenzene (abbreviated as CNB) over supported Pt catalysts. Substrate concentration, reaction temperature and bimetallic effect are also studied on the hydrogenation of CNB over TiO_2-supported Pt catalysts in the liquid phase.

2. Experimental

2.1. Preparation of supported platinum catalysts

Supported platinum catalysts are prepared by conventional impregnation with an aqueous solution of hexachloroplatinic acid. The loading of platinum is 0.3 wt.%. The sample impregnated is reduced by KBH_4, filtered and washed with large amount of water, dried at 373 K overnight, and then calcined at 673 K for 4 h. TiO_2 support is prepared by hydrolyzation of $TiCl_4$, then calcined at 673 K for 2 and 21 h, the platinum catalyst supported over prepared TiO_2 is abbreviated as Pt/TiO_2(I) and Pt/TiO_2(II), respectively. The TiO_2 support of Pt/TiO_2(III) catalyst is purchased from chemical company. The TiO_2 support of Pt/TiO_2(IV) catalyst is prepared by sel–gol. The bimetallic PtM/TiO_2(II) catalysts (M = Cr, Mn, Fe, Co, Ni and Cu) are also prepared by impregnation, i.e. platinum is impregnated after the transition metal is impregnated on TiO_2. The preparation process is similar to monometallic Pt catalyst, and the content of M and Pt is 0.04 and 0.3 wt.%, respectively.

2.2. Characterization

Surface areas of the supported platinum catalysts were determined by N_2 adsorption at 77 K using the BET method in an OMNISORP 100CX apparatus. The catalysts and crystal sizes of various supports were charactered by XRD (Rigaku-D/max-B automated power X-ray diffractometer, Cu Kα, 45 kV, 40 mA). Dispersion of platinum was measured by H_2 chemisorption, following a procedure described elsewhere [14]. By assuming a stoichiometry for H_2 adsorption on surface platinum atoms (Pt_s) of unity, the dispersion of Pt is given by $D = Pt_s/Pt_t = H/Pt_t$. The sizes of platinum particles were obtained by transmission electron microscopy (TEM). The above results are shown in Table 1.

2.3. Catalytic reaction

Hydrogenations of *m*-, *o*- and *p*-CNB are carried out at 303 K and atmospheric pressure of hydrogen in a thermostated glass reactor closed with silicon rubber cap and connected with hydrogen gas burette. The atmosphere is replaced with hydrogen several times after 0.1 g platinum catalyst is added to the reactor, and then 10 mL of ethanol solution is added. The catalyst is activated under hydrogen with magnetic stirring at 303 K for 1 h before 10 mL ethanol solution of chloronitrobenzene (4×10^{-3} mol of substrate) is injected into the reactor. The hydrogenation consumption is monitored with a graduated gas burette. Chemical analysis of the products is performed by gas chromatography Perkin-XL, equipped with an FID detector and SE-30 capillary column. Reactants and products are identified by comparison with authentic samples. Biphenyl is used as internal standard. Several experiments using different amounts of catalyst and different speed of agitation were carried out in order to determine the diffusion control region in order to eliminate mass transfer limitations during our studies.

3. Results and discussion

It is known that hydrogenation rates are influenced by many factors in catalytic hydrogenation reactions. Catalytic properties of TiO_2, γ-Al_2O_3 and ZrO_2-supported platinum catalysts have been examined for the hydrogenation of *p*-CNB, and the results are listed in Table 2. From Table 2, we can see that Pt/TiO_2(I) catalyst shows the best catalytic property for the hydrogenation of *p*-CNB under normal pressure and 303 K. The hydrogenation rates increase in the order: $Pt/TiO_2(I) > Pt/\gamma\text{-}Al_2O_3 > Pt/ZrO_2$, and the selectivities of *p*-CAN improve in the order: $Pt/TiO_2(I) > Pt/ZrO_2 > Pt/\gamma\text{-}Al_2O_3$. We propose that there is part strong metal/support interaction (SMSI) in Pt/TiO_2(I) catalyst when calcined at high temperature, although the catalyst is not reduced by H_2 at high temperature. Part SMSI is responsible for the good hydrogenation properties of Pt/TiO_2(I) catalyst. In addition, catalytic activity increases with increasing the amount of catalyst, but the yield of *p*-CAN decreases. Different reductants have also influence

Table 1
Characterization of supported platinum catalysts

Sample	Crystal size of various supports from XRD (nm)	H/Pt	BET (m^2/g)	Pt particle size from TEM (nm)
Pt/γ-Al_2O_3	9.6	0.85	100.9	1.3
Pt/ZrO_2	18.8	0.74	55.9	2.3
Pt/TiO_2(I)	14.9	0.56	89.0	1.9
Pt/TiO_2(II)	15.5	0.52	81.6	2.1
Pt/TiO_2(III)	157.4	0.46	6.1	2.7
Pt/TiO_2(IV)	10.3	0.59	110.3	1.6

Table 2
Effect of various supports on the hydrogenation of *p*-CNB over platinum catalyst[a]

Sample	Catalyst amount (mg)	Reaction rate[b] ($\times 10^{-2}$ mol H_2 g^{-1} min^{-1})	TOF[c] (s^{-1})	Conversion, % (reaction time, min)	Yield of products (mol%)[d]		
					AN	NB	*p*-CAN
Pt/γ-Al_2O_3	1000	6.4	0.056	98.7 (70)	7.2	1.1	78.0
Pt/γ-Al_2O_3	500	5.6	0.074	99.0 (110)	5.1	1.6	80.9
Pt/γ-Al_2O_3[e]	500	1.2	0.026	92.1 (320)	4.7	–	89.1
Pt/ZrO_2	500	6.6	0.077	99.8 (130)	6.8	4.6	85.2
Pt/ZrO_2	200	9.8	0.12	99.4 (210)	2.7	1.6	90.4
Pt/ZrO_2[e]	200	Negligible	–	–	–	–	
Pt/TiO_2(I)	200	25.6	0.41	99.3 (80)	5.6	3.6	85.7
Pt/TiO_2(I)	100	38.8	0.64	99.5 (110)	2.3	0.6	92.8
Pt/TiO_2(I)[e]	200	8.5	0.15	99.6 (240)	4.3	–	95.0

[a] Reaction condition: 4×10^{-3} mol *p*-CNB; reaction temperature is 303 K; *P* is 0.1 MPa.
[b] The reaction rate is obtained by measuring the H_2 consumption within the reaction time.
[c] TOF, specific activity per Pt surface atom (s^{-1}) for the hydrogenation of chloronitrobenzene over supported Pt catalysts.
[d] Some products with high boiling point could not be determined by GC analysis; AN = aniline, NB = nitrobenzene.
[e] Catalyst is reduced by hydrazine hydrate.

on both catalytic activity and yield of *p*-CAN. All catalysts reduced by hydrazine hydrate show low catalytic activity and high yield of *p*-CAN. Pt/ZrO_2 catalyst has no catalytic activity, and Pt/γ-Al_2O_3 and Pt/TiO_2(I) also show low catalytic activity, however, the yield of *p*-CAN is improved significantly. The catalyst reduced by KBH_4 exhibits good catalytic activity. In our experiment, we also investigated the effect of K and B. We find that K shows negligible effect. Thus we suggested that good effects are also related to the presence of B [15]. The level of B measured by ICP is 0.027 wt.%.

The hydrogenation properties of different preparation of TiO_2-supported platinum catalysts are also investigated, and the results are listed in Table 3. From Table 3, we can see that different preparation of TiO_2 has significant influence on the hydrogenation of *p*-CNB. Pt/TiO_2(II) shows the best catalytic activity, the value of TOF is 1.45 s^{-1}. Pt/TiO_2(I) shows lower catalytic activity and yield of *p*-CAN. It is interesting that catalytic activity increases significantly when the support is calcined for a longer time (Pt/TiO_2(II) catalyst). The different catalytic activity is related to phase composition of the support from XRD. Pt/TiO_2 catalyst that has certain extent of rutile and anatase phase shows better catalytic behavior. Similar phenomenon was found on the hydrogenation of crotonaldehyde over different phase composition of TiO_2-supported platinum catalyst [16].

Base on above experiment results, we study the influence of substrate concentration and reaction temperature on the hydrogenation of *p*-CNB over Pt/TiO_2(II) catalyst in particular. The results are listed in Tables 4 and 5. In our experiment, we also find that the yield of *p*-CAN increases with increasing the concentration of substrate on the hydrogenation of *p*-CNB. High concentration of substrate probably prevents products from contacting with active sites, which partly inhibits hydrogenolysis of C–Cl bond [17]. From Table 4, we can see that the reaction rate strongly depends on substrate concentration. Under constant hydrogen pressure, reaction temperature and catalyst concentration, the reaction rate equation may be expressed as follows:

$$R = kC^n \tag{1}$$

where R, k, C and n are the reaction rate, rate constant, concentration of *p*-CNB and reaction order, respectively. A plot of $\log R$ versus $\log C$ results in a straight line, and the reaction order "n" is 0.55.

Hydrogenation rate often increases with increasing reaction temperature. In our experiment, we also obtain similar results, but the yield of *p*-CAN decreases (see Table 5). The main reason is that hydrogenolysis rate of the C–Cl bond increases with increasing reaction temperature. The partial hydrogen pressure in the reaction flask at 40 °C will decrease for the evaporation of solvent and a lower hydrogenation rate is observed. At a higher than 40 °C temperature,

Table 3
Hydrogenation of *p*-CNB over TiO_2-supported platinum catalysts[a]

Catalyst	Reaction rate ($\times 10^{-2}$ mol H_2 g^{-1} min^{-1})	TOF (s^{-1})	Conversion, % (reaction time, min)	Yield of products (mol%)		
				AN	NB	*p*-CAN
Pt/TiO_2(I)	38.8	0.64	99.5 (110)	2.3	0.6	92.8
Pt/TiO_2(II)	80.2	1.45	99.7 (50)	4.8	0.7	90.7
Pt/TiO_2(III)	24.2	0.49	99.5 (170)	2.2	–	88.9
Pt/TiO_2(IV)	62.2	0.94	99.6 (70)	4.1	0.5	90.0

[a] Reaction conditions are similar to Table 2. The amount of catalyst is 0.1 g.

Table 4
Effect of substrate concentration on the hydrogenation of *p*-CNB over Pt/TiO_2(II) catalyst[a]

Substrate ($\times 10^{-4}$ mol/L)	Reaction rate ($\times 10^{-2}$ mol H_2 g^{-1} min^{-1})	Conversion, % (reaction time, min)	Yield of products (mol%)		
			AN	NB	*p*-CAN
1.31	60.4	99.7 (42)	6.8	4.1	82.3
1.70	68.8	99.5 (48)	4.9	2.0	89.0
2.17	80.2	99.7 (50)	4.8	0.7	90.7
2.67	89.0	99.8 (60)	3.9	0.8	91.6
3.23	99.2	99.6 (65)	1.9	0.6	92.9

[a] Reaction conditions are similar to Table 2.

Table 5
Effect of reaction temperature on the hydrogenation of *p*-CNB over Pt/TiO_2(II) catalyst[a]

Temperature (°C)	Reaction rate ($\times 10^{-2}$ mol H_2 g^{-1} min^{-1})	TOF (s^{-1})	Conversion, % (reaction time, min)	Yield of products (mol%)		
				AN	NB	*p*-CAN
20	55.2	1.05	99.6 (75)	2.3	–	94.9
30	80.2	1.45	99.7 (52)	4.8	0.7	90.7
40	76.8	1.38	99.5 (54)	5.6	2.1	91.7
50	85.0	1.37	99.6 (50)	6.3	1.6	82.5

[a] Reaction conditions are similar to Table 2.

high catalytic activity resumed but selectivity of *p*-CAN decreases sharply. The activation energy was determined for Pt/TiO_2(II) catalyst. The value found, i.e. 11 ± 2 kJ mol^{-1}, is lower than those reported by Coq et al. [17] for the hydrogenation of *p*-CNB over Pt/Al_2O_3 (25 ± 2 kJ mol^{-1}), or by Moreau et al. [18], who found a value of 27 kJ mol^{-1} for CNB hydrogenation over sulfide catalysts.

The stability of Pt/TiO_2(II) catalyst was also investigated, and the results are summarized in Table 6. In the recycling experiment, five recycles were carried out for the hydrogenation of *p*-CNB. It is found that the catalytic activity decrease very slightly, but the yield of *p*-CAN increases. Ninety eight mole percentage of yield of *p*-CAN is obtained when catalyst is used for four recycles. Lower catalytic activity is influenced by many factors on the hydrogenation of *p*-CNB. For example, a part of Pt could be lost when the catalyst is reused (the level of Pt measured by ICP still is 0.28 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 Pt/TiO_2(II) catalyst is used for five 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.

Transition metal complexes have been studied widely as catalysts for the hydrogenation of organic compounds. They have also been used as co-catalyst in a large variety of chemical reactions. The addition of the transition metal ions and metal complexes to the noble metal catalysts can considerably modulate both the activity and the selectivity of the catalysts. Table 7 lists the results of hydrogenation of *p*-CNB catalyzed by Pt/TiO_2(I) catalysts modified by transition metals. From Table 7, we can see that the additions of small amount of transition metals to Pt/TiO_2(I) catalyst improve obviously catalytic activity and yield of *p*-CNB to *p*-CAN. PtFe/TiO_2(I) catalyst exhibits the best hydrogenation rate (the value of TOF is 1.39 s^{-1}) and the highest yield of *p*-CAN (98.0 mol%). The effect of transition metal on hydrogenation properties of supported Pt catalyst may be usually interpreted by electronic effect and/or geometric effect.

Table 6
Stability of Pt/TiO_2(II) catalyst[a]

Cycle	Reaction rate ($\times 10^{-2}$ mol H_2 g^{-1} min^{1})	TOF (s^{-1})	Conversion, % (reaction time, min)	Yield of products (mol%)		
				AN	NB	*p*-CAN
1	80.2	1.45	99.7 (52)	4.8	0.7	90.7
2	71.6	1.38	99.6 (57)	3.0	0.6	95.1
3	62.4	1.16	99.7 (65)	0.9	–	93.6
4	60.4	1.22	99.7 (67)	1.6	–	98.0
5	53.0	1.01	99.7 (77)	0.9	0.3	94.0
5[b]	57.4	1.10	99.6 (70)	3.2	0.4	92.8

[a] Reaction conditions are similar to Table 2.
[b] Catalyst is recycled four times, and then reduced by KBH_4 again.

Table 7
Results of the hydrogenation of *p*-CNB over PtM/TiO_2(I) catalysts[a]

Catalyst	Reaction rate ($\times 10^{-2}$ mol g^{-1} min^{-1})	TOF (s^{-1})	TEM[b] (nm)	Conversion, % (reaction time, min)	Yield of products (mol%)		
					AN	NB	*p*-CAN
Pt/TiO_2	38.8	0.64	1.9	99.5 (110)	2.3	0.6	92.8
PtFe/TiO_2	71.2	1.39	1.7	99.7 (60)	1.2	–	98.0
PtCr/TiO_2	48.0	0.85	2.0	99.6 (90)	3.2	–	95.7
PtCu/TiO_2	47.6	0.85	1.8	99.3 (95)	1.7	–	97.4
PtMn/TiO_2	53.8	1.00	1.9	99.5 (80)	3.0	–	96.3
PtCo/TiO_2	54.0	1.02	1.8	99.6 (80)	2.2	0.5	96.6
PtNi/TiO_2	56.8	1.12	1.7	99.5 (75)	1.7	–	97.0

[a] Reaction conditions are similar to Table 2.
[b] Pt particle size from TEM.

As reported by literature, catalytic activity is enhanced at low M/Pt ratio for most of the bimetallic catalysts, i.e. good hydrogenation properties are obtained on large Pt particles. Such behavior was also reported by Galvagno et al. [19] for nitrobenzene hydrogenation over PtSn/nylon catalysts and Coq [17] for *p*-CNB hydrogenation over Pt/Al_2O_3 catalysts. It was explained in part by a redispersion of the Pt particles. This interpretation cannot be applied in the present work for Pt particles in Pt/TiO_2(I) and PtFe/TiO_2(I) catalysts had a mean particle size of 1.7–2.0 nm (see Table 7). We prefer the second interpretation proposed by Galvagno et al. [19], suggesting that the tin species on the N–O bond, which becomes more reactive towards the attack by chemisorbed hydrogen. PtFe/TiO_2 catalyst shows better hydrogenation properties than that of catalysts. Ionic and electron deficient species act as Lewis sites. These sites interact with the lone electron pair of the oxygen atom of the N=O group, polarizing the bond, and favoring its hydrogenation by hydridic hydrogen adsorbed on the Pt metal. It is well known that copper metal catalysts usually show better catalytic properties on the selective hydrogenation of various organic compounds. However, copper metal catalysts are easily poisoned by sulfide and chloride. In our experiment, PtCu/TiO_2 catalyst shows low catalytic activity, which may be related to the chlorine from the hydrogenolysis of the C–Cl bond and/or from hexachloroplatinic acid. The presence of B is also responsible for its lower catalytic activity. Similar phenomenon was reported on the hydrogenation of crotonaldehyde over cobalt–copper catalyst reduced by $NaBH_4$ [20].

4. Conclusions

TiO_2, γ-Al_2O_3 and ZrO_2-supported platinum catalysts can catalyze the hydrogenation of *p*-CNB to *p*-CAN at 303 K and normal pressure. TiO_2-supported platinum catalysts show good hydrogenation properties. Different preparation of TiO_2-supported platinum catalyst shows different hydrogenation properties. Pt/TiO_2(II) catalyst shows the best catalytic activity (TOF is 1.45 s^{-1}) and good yield of *p*-CAN, and also has good stability. The yield of *p*-CAN increases with increasing the concentration of substrate on the hydrogenation of *p*-CNB over Pt/TiO_2(II) catalyst. Both catalytic activities and yields of *p*-CAN are all improved over Pt/TiO_2(I) catalyst with the introductions of transition metals(M = Cr, Mn, Fe, Co, Ni, Cu) on the hydrogenation of *p*-CNB. 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 nitrogen–oxygen bond. Addition of Fe improves the yield of *p*-CAN from 92.8 to 98.0 mol% at high *p*-CNB conversion.

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