

Effect of transition metal (Cr, Mn, Fe, Co, Ni and Cu) on the hydrogenation properties of chloronitrobenzene over Pt/TiO₂ catalysts

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Abstract

The influence of transition metal (Cr, Mn, Fe, Co, Ni and Cu) on the hydrogenation properties of chloronitrobenzene (CNB) over Pt/TiO₂ catalyst has been studied in ethanol at 303 K and normal pressure. The hydrogenation of CNB can be carried out over Pt/TiO₂ catalyst. The order of the hydrogenation rate of CNB is $m > p > o$, and the yield of chloroaniline (CAN) is $p > m > o$. The effect of transition metal may be interpreted by electronic effect. Electron deficient species of the second element promote the specific rate constant turnover frequency (TOF) expressed on a per surface Pt atom by activating the nitrogen–oxygen bond. The conversion of CNB is over 99% and chloroaniline is main product on the hydrogenation of CNB over PtM/TiO₂ catalysts. PtFe/TiO₂ catalyst shows the best selectivity of CNB to CAN, and 98.0 mol% for *p*-CAN, 98.5 mol% for *m*-CAN and 98.7 mol% for *o*-CAN, respectively. Both catalytic activity and yield of *p*-CAN increase with addition of Fe over Pt/TiO₂ on the hydrogenation of *p*-CNB.

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1. Introduction

Haloamine is important intermediates for synthesis of organic fine chemicals, such as dyes, drugs, herbicides and pesticides. The main route to these haloamines is through the reduction of the corresponding nitrocompounds, either with metal–acid systems or with hydrogen and a noble metal catalyst. The hydrogenation has been attention for its lower impact on the environment. However, the process of the catalytic reduction is difficult because of extensive dehalogenation. The catalysts of the hydrogenation have been well-studied, such as palladium, platinum, rhodium, nickel and copper chromite catalysts. Platinum-based catalysts have received much attention for minimizing dehalogenation combined with a fast rate of nitro-group reduction [1,2]. To improve the hydrogenation selectivity, special additives (promoters and inhibitors) or modified preparation of platinum catalyst are used [3–7], but none of the cata-

lysts previously proposed are completely satisfactory, each having its own particular limitations.

Transition metal complexes have been studied widely as homogeneous catalysts for the hydrogenation of organic compounds. They have also been used as co-catalyst in a large variety of chemical reactions. Polymer-anchored platinum [8–11], palladium [12] and ruthenium [13–15] homogeneous catalysts modified by transition metal cations and its metal complexes show better catalytic properties on the hydrogenation of α,β -unsaturated aldehydes and chloronitrobenzene. 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 [16].

The aim of the present work is to study the hydrogenation properties of *m*-, *o*- and *p*-chloronitrobenzene (abbreviated as *m*-, *o*- and *p*-CNB) with PtM/TiO₂ catalysts (M = Cr,

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Mn, Fe, Co, Ni, Cu) and to compare the selectivity and activity with the monometallic platinum catalysts in the heterogeneous system.

2. Experimental

The monometallic Pt/TiO₂ 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 KBH₄, filtered with large amount of water, dried at 373 K overnight, and then calcined at 673 K for 4 h. The bimetallic PtM/TiO₂ catalysts (M = Cr, Mn, Fe, Co, Ni and Cu) are also prepared by impregnation, i.e. platinum may be impregnated after the transition metal is impregnated on TiO₂. The preparation process is similar to Pt/TiO₂, and the content of M and Pt is 0.04 and 0.3 wt.%, respectively.

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 2.

A typical hydrogenation procedure is conducted as follows: the catalyst is added into a 50 ml three-necked bottle closed with a self-sealing silicon rubber cap and connected to the vacuum, hydrogen lines and a constant pressure gas burette. The reaction temperature is maintained by a thermostat. After the air in the reactor is replaced with hydrogen, 10 ml of ethanol solution is added. Then 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 course of the reaction is monitored by the hydrogen uptake measured by the constant pressure gas burette. 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. Several experiments using different amounts of catalyst 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

Hydrogenation of chloronitrobenzene is a complicated process as described elsewhere [17,18], and it often yields many by-products at the same time. As mentioned precisely, catalyst modified by Fe often shows good hydrogenation properties. We investigate the effect of different Fe amount and different addition way of Fe on the hydrogenation of *p*-CNB over Pt/TiO₂ catalyst. The results are listed in Table 1. The conversions of CNB are all over 99%. From Table 1, we can see that Pt/TiO₂ can catalyze the hydrogenation of *p*-CNB at 303 K and normal pressure. We also find catalytic activity increases remarkably when a small amount of Fe is added in Pt/TiO₂ catalyst. The hydrogenation rate of *p*-CNB increases from 38.8×10^{-2} to 73.2×10^{-2} mol H₂ g⁻¹ min⁻¹, but catalytic activity decreases sharply when the content of Fe is higher than 1.0 wt.%. The yields of *p*-CAN are all improved with addition of Fe. Addition way of Fe has significant influence on hydrogenation properties for the hydrogenation of *p*-CNB. The catalytic activity increases slightly with addition of equivalent Fe³⁺ to reaction system catalyzed by Pt/TiO₂ catalyst, but the yield of *p*-CAN is remarkably improved from 92.8 to 98.5 mol%. FePt/TiO₂ catalyst also shows high catalytic activity and yield of *p*-CAN, but which are slightly lower than that of PtFe/TiO₂ catalyst. The reason is probably that Pt active center is partly covered by Fe.

Tables 2–4 list the results of hydrogenation of *p*-, *m*- and *o*-CNB catalyzed by Pt/TiO₂ and PtM/TiO₂ catalysts, respectively. From Table 2, we can see that the additions

Table 1
Effect of different Fe amount and different addition way of Fe on the hydrogenation of *p*-CNB over Pt/TiO₂ catalyst^a

Catalyst	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	<i>p</i> -CAN
Pt/TiO ₂	38.8	0.36	99.5 (110)	1.5	–	92.8
PtFe/TiO ₂ (0.04)	71.2	0.71	99.7 (60)	–	1.2	98.0
Pt/TiO ₂ -Fe(NO ₃) ₃ ^e	44.0	0.50	99.5 (85)	–	–	98.5
FePt/TiO ₂ (0.04) ^f	63.4	0.63	99.6 (67)	–	–	96.8
PtFe/TiO ₂ (0.1)	65.0	0.62	99.7 (65)	1.7	0.6	94.0
PtFe/TiO ₂ (0.4)	73.2	0.72	99.5 (57)	2.0	–	95.8
PtFe/TiO ₂ (1.0)	45.2	0.46	99.7 (90)	2.6	–	96.0

^a Reaction condition: 4×10^{-3} mol *p*-CNB; reaction temperature is 303 K; *P* = 0.1 MPa. The amount of catalyst is 0.1 g.

^b The reaction rate is obtained by measuring the H₂ consumption within the reaction time.

^c TOF, specific activity per Pt surface atom (s⁻¹) for the hydrogenation of *p*-chloronitrobenzene over supported Pt catalysts.

^d Some products with high boiling point could not be determined by GC analysis. AN: aniline; NB: nitrobenzene.

^e Addition of Fe(NO₃)₃ to the reaction system catalyzed with Pt/TiO₂, the amount of Fe is 0.04.

^f Fe may be impregnated after the platinum is impregnated on TiO₂.

Table 2
Results of the hydrogenation of *p*-CNB over PtM/TiO₂ 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	<i>p</i> -CAN
Pt/TiO ₂	38.8	0.36	1.9	99.5 (110)	2.3	0.6	92.8
PtFe/TiO ₂	71.2	0.71	1.7	99.7 (60)	1.2	–	98.0
PtCr/TiO ₂	48.0	0.45	2.0	99.6 (90)	3.2	–	95.7
PtCu/TiO ₂	47.6	0.44	1.8	99.3 (95)	1.7	–	97.4
PtMn/TiO ₂	53.8	0.52	1.9	99.5 (80)	3.0	–	96.3
PtCo/TiO ₂	54.0	0.52	1.8	99.6 (80)	2.2	0.5	96.6
PtNi/TiO ₂	56.8	0.56	1.7	99.5 (75)	1.7	–	97.0

^a Reaction conditions are similar to Table 1.

^b Pt particle size from TEM.

Table 3
Results of the hydrogenation of *m*-CNB over PtM/TiO₂ catalysts^a

Catalyst	Reaction rate ($\times 10^{-2}$ mol g ⁻¹ min ⁻¹)	TOF (s ⁻¹)	Conversion (%) (reaction time, min)	Yield of products (mol%)		
				AN	NB	<i>m</i> -CAN
Pt/TiO ₂	57.8	0.53	99.6 (75)	5.4	–	92.0
PtFe/TiO ₂	53.0	0.53	99.8 (80)	1.1	–	98.5
PtCr/TiO ₂	71.4	0.66	99.6 (60)	2.8	–	90.6
PtCu/TiO ₂	42.4	0.40	99.4 (100)	2.1	0.4	93.9
PtMn/TiO ₂	53.4	0.50	99.4 (80)	2.0	–	92.3
PtCo/TiO ₂	54.0	0.50	99.6 (80)	2.2	–	93.3
PtNi/TiO ₂	57.4	0.54	99.4 (75)	1.6	2.7	94.1

^a Reaction conditions are similar to Table 2.

of small amount of transition metals to Pt/TiO₂ catalyst improve obviously catalytic activity and yield of *p*-CNB to *p*-CAN. The hydrogenation rate increases in the order: PtFe/TiO₂ > PtNi/TiO₂ > PtCo/TiO₂ > PtMn/TiO₂ > PtCr/TiO₂ > PtCu/TiO₂ > Pt/TiO₂, and the yield of *p*-CAN increases in the order: PtFe/TiO₂ > PtCu/TiO₂ > PtNi/TiO₂ > PtCo/TiO₂ > PtMn/TiO₂ > PtCr/TiO₂ > Pt/TiO₂.

For the hydrogenation of *m*-CNB, PtM/TiO₂ catalysts show different hydrogenation properties. The results are listed in Table 3. From Table 3, we find that PtCr/TiO₂ catalyst shows the best catalytic activity (the value of TOF is 0.66) and lowest yield of *m*-CAN (90.6 mol%), but the addition of Cu to Pt/TiO₂ decreases the catalytic activity. PtFe/TiO₂ catalyst shows the highest yield of *m*-CAN (98.5 mol%). The addition of transition metal (Mn, Co and

Ni) has no distinct effect on catalytic activity and yield of *m*-CAN.

From Table 4, we can find that the additions of transition metals have also influence on the hydrogenation of *o*-CNB over PtM/TiO₂ catalysts. The addition of small amount of transition metals except Cu increase slightly the catalytic activity of the hydrogenation of *o*-CNB, and has different influence on the yield of *o*-CNB to *o*-CAN. PtFe/TiO₂ and PtCo/TiO₂ catalysts show better yield of *o*-CAN with 98.7 and 97.4 mol%, respectively. For PtNi/TiO₂ catalyst, the catalytic activity is improved but low yield of *o*-CAN is obtained (84.4 mol%).

As indicated above, Pt/TiO₂ catalyst modified by small amount of transition metals (Cr, Mn, Fe, Co, Ni and Cu) exhibits different hydrogenation properties for the

Table 4
Results of the hydrogenation of *o*-CNB over PtM/TiO₂ catalysts^a

Catalyst	Reaction rate ($\times 10^{-2}$ mol g ⁻¹ min ⁻¹)	TOF (s ⁻¹)	Conversion (%) (reaction time, min)	Yield of products (mol%)		
				AN	NB	<i>o</i> -CAN
Pt/TiO ₂	30.0	0.26	99.4 (147)	2.6	0.9	90.1
PtFe/TiO ₂	41.6	0.41	99.7 (105)	–	–	98.7
PtCr/TiO ₂	33.0	0.29	99.5 (135)	3.0	0.4	90.0
PtCu/TiO ₂	26.0	0.23	99.4 (170)	4.8	–	89.6
PtMn/TiO ₂	37.8	0.34	99.5 (115)	2.1	–	90.1
PtCo/TiO ₂	36.0	0.35	99.6 (120)	–	–	97.4
PtNi/TiO ₂	40.0	0.33	99.4 (110)	3.6	0.7	84.4

^a Reaction conditions are similar to Table 1.

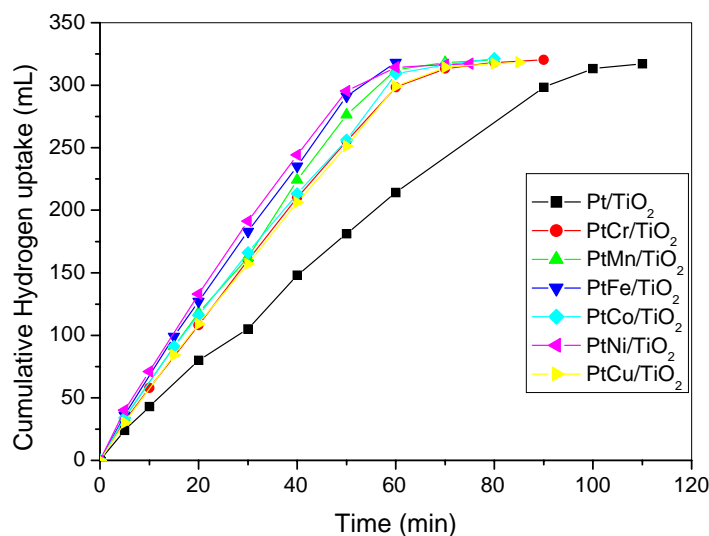


Fig. 1. Cumulative hydrogen uptake profiles of catalytic hydrogenation of *p*-CNB over PtM/TiO₂ catalysts.

hydrogenation of CNB. Among the catalysts, PtFe/TiO₂ exhibits the best yield of *o*-, *m*- and *p*-CNB to their corresponding CAN products. The high catalytic activity is also found for PtFe/TiO₂ catalysts on the hydrogenation of *p*-CNB. The effect of transition metal may be usually interpreted by electronic effect and/or geometric effect. As reported by literature, most of the bimetallic formulations the activity is enhanced at low M/Pt ratio, i.e. good hydrogenation properties is found on large Pt particles. Such behavior was also reported by Galvagno et al. [19] for nitrobenzene hydrogenation over PtSn/nylon catalysts and Coq [20] for *p*-CNB hydrogenation over Pt/Al₂O₃ catalysts. It was explained in part by a re-dispersion of the Pt particles. This interpretation cannot be applied in the present work for on the one hand the starting Pt/TiO₂ catalyst had a mean particle size of 1.9 nm, on the other hand these Pt particles did not change in size when adding the second metal (see Table 2). 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/TiO₂ catalyst shows better catalytic activity than that of catalysts. Ionic and electron deficient Fe species would be the active centers for N=O activation in these bimetallic formations. 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/TiO₂ 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. Fig. 1 gives the kinetic curves of hydrogenation of *p*-CNB catalyzed by PtM/TiO₂ catalysts. From Fig. 1, we find that platinum catalysts modified by transition metal show similar catalytic behavior on the hydrogenation of *p*-CNB. The catalytic activities are all higher than Pt/TiO₂ catalyst is used alone. The hydrogen

consumption is lined with reaction time at the start of reaction. Comparison of the results with Tables 2–4 reveals that the rates of hydrogenation of CNB are greatly affected by the position of substituent groups for the hydrogenations of CNB catalyzed by Pt/TiO₂. The rates of the hydrogenations increase in the order: *m* > *p* > *o*, and the yields of CAN increase in the order: *p* > *m* > *o*. However, when metal catalysts such as Ni, Pd, Pt and Ru are used for hydrogenation of nitrobenzene derivatives, the hydrogenation rates usually increase in the order: *o* > *m* > *p* [21]. The different effect may be related with the special nature of support TiO₂. The strong metal/support interaction state of Pt/TiO₂ is responsible for the good catalytic activity on the hydrogenation of CNB. Our results also indicate that different catalytic process is found on the hydrogenation of *o*-, *m*- and *p*-CNB.

4. Conclusions

Pt/TiO₂ catalyst can catalyze the hydrogenation of CNB at 303 K and normal pressure. The conversions of CNB are all over 99%. The order of hydrogenation rate of CNB is *m* > *p* > *o*, and the yield of CAN is *p* > *m* > *o*. Both catalytic activities and yields of *p*-CAN are all improved over Pt/TiO₂ catalysts with the introductions of transition metal 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 the second metal improves the yield of *p*-CAN from 92.8 to 98.0 mol% at high *p*-CNB conversion. For the hydrogenation of *m*-CNB, only PtCr/TiO₂ shows good catalytic activity. PtFe/TiO₂ catalyst shows 98.5 mol% of *m*-CAN. There are no distinct effect on the catalytic activity and yield of *m*-CAN for Pt/TiO₂ catalyst modified by Ni, Co and Mn. The catalytic activity increases slightly on the

hydrogenation of *o*-CNB over PtM/TiO₂ catalysts. However, only PtFe/TiO₂ and PtCo/TiO₂ show good yield of *o*-CAN with 98.7 and 97.4 mol%, respectively. The content of Fe in PtFe/TiO₂ catalyst has significant influence on catalytic properties for the selective hydrogenation of *p*-CNB. Both catalytic activity and yield of *p*-CAN increase with addition of Fe.

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