Catalysis Letters Vol. 89, Nos. 3–4, September 2003 (© 2003)

Influence of rare earth (Ce, Sm, Nd, La, and Pr) on the hydrogenation properties of chloronitrobenzene over Pt/ZrO_2 catalyst

Xiaoxiang Han[a], Renxian Zhou[a], Guohua Lai[a,b], Baohua Yue[a], and Xiaoming Zheng[a,*]

[a] *Institute of Catalysis, Zhejiang University, Hangzhou, 310028, P.R. China*
[b] *Zhejiang Chemical College, Hangzhou, 310053, P.R. China*

Received 1 April 2003; accepted 23 June 2003

The effect of rare earths (Sm, Pr, Ce, Nd, and La) on the hydrogenation properties of chloronitrobenzene (CNB) over Pt/ZrO_2 catalyst was studied in ethanol at 303 K and normal pressure. The results show that the hydrogenation of CNB can be carried out over Pt/ZrO_2 catalyst. The order of the hydrogenation rates of CNB is $p > m > o$, and the yield of chloroaniline (CAN) is $p > o > m$. The specific rate constant turnover frequency (TOF) expressed per surface Pt atom increases when the platinum catalyst is modified by rare earth. The conversion of CNB is >99% and CAN is the main product in the hydrogenation of CNB over PtM/ZrO_2 catalysts. The $PtPr/ZrO_2$ catalyst shows the best selectivity of CNB to CAN: 89.4 mol% for *o*-CAN, 94.6 mol% for *m*-CAN and 95.1 mol% for *p*-CAN.

KEY WORDS: rare earths; chloronitrobenzene; chloroaniline; hydrogenation.

1. Introduction

It is known that aromatic halonitro compounds can be effectively reduced to the corresponding haloamine, however, the process is difficult because of extensive dehalogenation [1]. Various catalysts, such as precious metal catalysts and Raney nickel, have been well studied. Of the precious metal catalysts, palladium gives extensive dehalogenation, whereas platinum and rhodium give less. The rhodium catalyst is extremely expensive (about four times the cost of a comparable platinum catalyst). So, platinum-based catalysts have received much attention for minimizing dehalogenation [2–4]. In order to achieve high yields of haloamine, many approaches have been developed either by modified preparation of the catalyst or by use of special additives (promoters and inhibitors) [5–7]. Examples include sulfided platinum catalysts [5], magnesium oxide or magnesium hydroxide—promoted platinum catalysts [8], and platinum group metal modified with a metal selected from the group lead, bismuth and silver [9]. However, none of the catalysts previously proposed is completely satisfactory, each having its own particular limitations.

Rare earths used as promoters have been investigated and utilized in many fields [10]. In our previous research [11], we found that the addition of rare earths in polymer-anchored platinum catalysts decreased catalytic activity for the hydrogenation of *p*-CNB, but they improved the selectivity toward *p*-CAN remarkably. Although platinum catalysts modified by rare earths show good selectivity toward *p*-CAN under mild operating conditions in homogeneous systems, the catalysts separated difficultly from the reaction system. Metals that were deposited on reducible oxide ZrO_2 showed better catalytic behavior on the selective hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols [12,13]. It is proposed that the strong metal/support interaction is responsible for this behavior. In the present work, we have studied hydrogenation properties of chloronitrobenzene with Pt/ZrO_2 catalyst and the effect of rare earths (Ce, Sm, Nd, La, and Pr) in the heterogeneous system.

2. Experimental

ZrO_2 commercial support (A R, $S_{BET} = 39\,m^2/g$, tetragonal system) is crushed and sieved to obtain a particle size range of 140–180 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 impregnated sample is reduced by KBH_4, filtered and washed with large amount of water, dried at 373 K overnight and then calcined at 773 K for 4 h. The bimetallic PtM/ZrO_2 catalysts (M = Ce, Sm, Nd, La, and Pr) are also prepared by impregnation, i.e., platinum is impregnated after the rare earth nitrate (Ce, Sm, Nd, La, and Pr) is impregnated on ZrO_2. The preparation process is similar to Pt/ZrO_2, and the content of M is 1.0 wt%.

Platinum phase dispersion is measured by H_2 chemisorption, following a procedure described in [14]. By assuming a stoichiometry for H_2 adsorption on surface platinum atoms (Pt_s) of unity, the dispersion of

---

[*] To whom correspondence should be addressed.

Pt is given by $D = Pt_s/Pt_t = H/Pt_t$. The size of the metallic Pt particles is measured by transmission electron microscopy (TEM) using a JEM-200CX apparatus. The agreement with chemisorption is good for the Pt/ZrO_2 parent catalysts. The main characteristics of the catalysts are included in table 1.

Hydrogenation of CNB is carried out at 303 K and normal pressure. A mixture of 0.2 g of platinum catalyst (0.3 wt% Pt) and 10 mL of ethanol solution is placed in a three-necked flask closed with a silicon rubber cap and connected with a hydrogen gas burette. Air in the reactor is replaced by H_2 several times, and 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 hydrogen consumption is monitored with a graduated gas burette. The hydrogenation reaction is initiated immediately by magnetic stirring of the reaction mixture vigorously (800 rpm). The rate of reaction is obtained by measuring the H_2 consumption during the reaction (the H_2 uptake rate per gram of Pt, $R = \text{mol}/\min \text{g Pt}$). Chemical analysis of the products is performed by gas chromatography Perkin-XL, equipped with an FID and an SE-30 capillary column. Reactants and products are identified by comparison with known standards. Biphenyl is used as an internal standard.

3. Results and discussion

In order to ascertain the role of mass transfer, the speed of agitation is varied from 600 to 1100 rpm and the catalyst amount is varied from 0.1 to 0.5 g. In view of the observation that R is independent of the stirring speed and it is varied linearly with the catalyst amount, it can be concluded that the external mass transfer is sufficiently eliminated at the stirring speed of 800 rpm and that the CNB hydrogenation is controlled by the intrinsic kinetics of the reaction.

Hydrogenation of chloronitrobenzene is a complicated process as described in [15,16], and it often yields many by-products. The aim of our study is to achieve high catalytic activity and selectivity toward CAN. We first investigated the effect of Ce content on the hydrogenation properties of *p*-CNB to *p*-CAN catalyzed by $PtCe/ZrO_2$. Figure 1 demonstrates the relation of catalytic activity and yield of *p*-CAN with the content of Ce. The conversions of CNB are all > 99%. From figure 1, it is found that catalytic activity increases when a small amount of Ce is added in the Pt/ZrO_2 catalyst. The hydrogenation rate of *p*-CNB increases from 9.8×10^{-2} to 15.4×10^{-2} mol H_2 g^{-1} min^{-1}, but catalytic activity decreases sharply when the content of Ce is higher than 1.0 wt%. The experiment is repeated three times for $PtCe/ZrO_2$ catalyst with 1.2 wt% Ce. However, yield of *p*-CAN decreases when the content of Ce is lower than 0.5 wt%, and then increases with increasing the content of Ce.

Tables 2, 3, and 4 list the experimental results of the hydrogenation of *o*-CNB, *m*-CNB, and *p*-CNB over PtM/ZrO_2 (the content of M is 1.0 wt%) catalysts respectively. From table 2, we can see that the value of TOF on the hydrogenation of *p*-CNB increases obviously with the introduction of rare earth, and yield of *p*-CAN is also improved for $PtSm/ZrO_2$, $PtCe/ZrO_2$, and $PtPr/ZrO_2$ catalysts. The $PtPr/ZrO_2$ catalyst exhibits the largest TOF and yield of *p*-CAN (95.1 mol%).

From table 3, we can see that the addition of rare earths in the Pt/ZrO_2 catalyst improves catalytic activity and yield of *m*-CNB to *m*-CAN. The $PtLa/ZrO_2$ catalyst exhibits the largest TOF and the $PtPr/ZrO_2$ catalyst exhibits the best yield of *m*-CAN. From table 4, we can find that the addition of rare earth to the Pt/ZrO_2 catalyst increases the catalytic activity of the hydrogenation of *o*-CNB remarkably, and has a different influence on the yield of *o*-CNB to *o*-CAN. The addition of Pr and Ce in the Pt/ZrO_2 catalyst increases the yield of *o*-CAN, whereas the addition of

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

Sample	H/Pt[a]	Mean particle size from TEM (nm)	Observation from TEM
Pt/ZrO_2	0.74	2.3	–
$PtPr/ZrO_2$	0.58	3.9	Some large particles
$PtNd/ZrO_2$	0.69	3.2	–
$PtLa/ZrO_2$	0.67	3.6	Some large particles
$PtSm/ZrO_2$	0.63	3.7	Some large particles
$PtCe/ZrO_2$	0.67	3.3	–

[a] By assuming a stoichiometry for H_2 adsorption on surface platinum atoms (Pt_s) of unity, the dispersion of Pt is given by $D = Pt_s/Pt_t = H/Pt_t$.

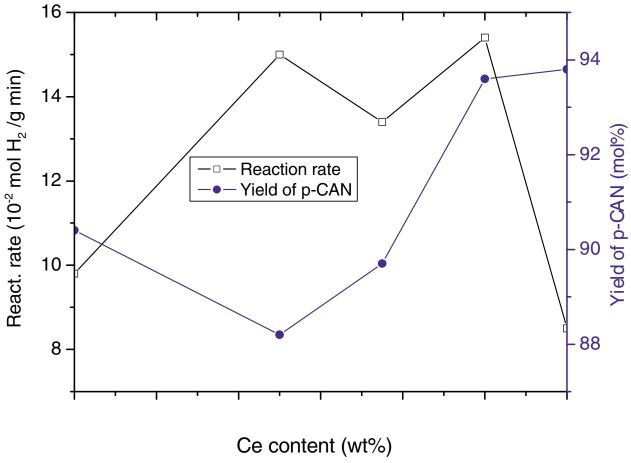

Figure 1. The effect of Ce content on the hydrogenation of *p*-CNB to *p*-CAN catalyzed by $PtCe/ZrO_2$.

Table 2
Results of the hydrogenation of *p*-CNB over PtM/ZrO_2 (M = Pr, Nd, La, Sm, Ce) catalysts[a]

Catalyst	Reaction rate[b] $(\mathrm{mol\,g^{-1}\,min^{-1}}) \times 10^{-2}$	TOF[c] (s^{-1})	Conversion (%), (React. time, min)	Yield of products (mol%)[d]		
				AN	NB	*p*-CAN
Pt/ZrO_2	9.8	0.20	99.4(210)	2.7	1.6	90.4
$PtPr/ZrO_2$	17.8	0.48	99.7(120)	2.5	–	95.1
$PtNd/ZrO_2$	14.0	0.31	99.5(150)	4.6	1.5	89.1
$PtLa/ZrO_2$	17.8	0.47	99.6(120)	4.9	–	89.4
$PtSm/ZrO_2$	14.2	0.34	99.2 (145)	2.1	1.5	93.7
$PtCe/ZrO_2$	15.4	0.36	99.3(135)	3.5	–	93.6

[a] Reaction condition: 4×10^{-3} mol *p*-CNB; reaction temperature is 303 K; P is 0.1 MPa; the amount of catalyst is 0.2 g.

[b] The reaction rate is obtained by measuring the H_2 consumption within the reaction time, i.e., average rate.

[c] TOF, specific activity per Pt surface atom (s^{-1}) for the hydrogenation of *p*-chloronitrobenzene over supported Pt catalysts with 50% conversion of CNB.

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

Table 3
Results of the hydrogenation of *m*-CNB over PtM/ZrO_2 (M = Pr, Nd, La, Sm, Ce) catalysts[a]

Catalyst	Reaction rate $(\mathrm{mol\,g^{-1}\,min^{-1}}) \times 10^{-2}$	TOF (s^{-1})	Conversion (%), (React. time, min)	Yield of products (mol%)		
				AN	NB	*m*-CAN
Pt/ZrO_2	5.8	0.14	99.5(340)	1.4	10.7	82.2
$PtPr/ZrO_2$	13.0	0.43	99.8(160)	2.0	1.3	94.6
$PtNd/ZrO_2$	11.2	0.31	99.6(180)	2.1	2.7	88.4
$PtLa/ZrO_2$	15.2	0.55	99.3(140)	3.0	3.4	91.4
$PtSm/ZrO_2$	13.6	0.38	99.7(155)	1.1	2.6	93.4
$PtCe/ZrO_2$	12.8	0.42	99.4(160)	2.0	2.1	94.1

[a] Reaction conditions are similar to table 2.

La, Sm, and Nd decreases the yield. Among all PtM/ZrO_2 catalysts, $PtLa/ZrO_2$ exhibits the best catalytic activity and the worst yield of *o*-CAN; $PtPr/ZrO_2$ exhibits the best yield of *o*-CAN.

As indicated above, the catalytic activities increase remarkably with the addition of rare earth (Ce, Sm, Nd, La, and Pr) in the Pt/ZrO_2 catalyst for the hydrogenation of CNB, especially for *o*-CNB. Among the catalysts, $PtPr/ZrO_2$ exhibits the best selectivity of *o*-, *m*- and *p*-CNB to their corresponding CAN products. From table 1, we can see that the value of H/Pt decreases and the size of Pt particle increases with the introduction of rare earth. In most of the bimetallic formulations, the activity is enhanced at low H/Pt ratio. Similar results have previously been reported by Galvagno *et al.* [17] for nitrobenzene hydrogenation over PtSn/nylon catalysts, and Coq [18] for *p*-CNB hydrogenation over Pt/Al_2O_3 catalysts. They suggested that large Pt particles would decrease the activity of hydrogenolysis of the C–Cl bond, and that CAN is easily desorbed from the Pt surface. The special rate constant (expressed per surface Pt atom basis as a

Table 4
Results of the hydrogenation of *o*-CNB over PtM/ZrO_2 (M = Pr, Nd, La, Sm, Ce) catalysts[a]

Catalyst	Reaction rate $(\mathrm{mol\,g^{-1}\,min^{-1}}) \times 10^{-2}$	TOF (s^{-1})	Conversion (%), (React. time, min)	Yield of products (mol%)		
				AN	NB	*o*-CAN
Pt/ZrO_2	4.4	0.08	99.1(480)	8.9	2.6	84.9
$PtPr/ZrO_2$	9.2	0.22	99.3(245)	5.1	3.0	89.4
$PtNd/ZrO_2$	8.0	0.15	99.2(280)	8.0	8.1	82.3
$PtLa/ZrO_2$	11.6	0.25	99.5(200)	7.5	4.7	78.6
$PtSm/ZrO_2$	9.0	0.24	99.4(235)	10.2	5.2	81.9
$PtCe/ZrO_2$	9.8	0.22	99.4(225)	7.7	–	87.1

[a] Reaction conditions are similar to table 2.

turnover frequency) increases by one order of magnitude when the Pt dispersion decreases from 1.0 to 0.09 in the hydrogenation of *p*-CNB over the Pt/Al$_2$O$_3$ catalyst [18]. This behavior is interpreted in terms of a transition state bearing a weak negative charge, which more effectively stabilized on the large Pt particles. This interpretation cannot be completely applied in the present work because these Pt particles did not change markedly in size when adding rare earth. The surface area and the average pore size have been examined. Additions of rare earth have small influence on the change of surface area and the average pore size of the ZrO$_2$ (surface area and average pose size varied from 39.0 to 37.6 m^2/g and 6.1 to 6.7 nm for ZrO$_2$ modified by 1.0 wt% Ce); thus, we believe that electronic effect may play an important role for the good hydrogenation properties for the Pt/ZrO$_2$ catalyst modified by rare earth. Rare earth could give electrons, and which the electrons transfer from rare earth to Pt [19]. It is very likely that the electron species of rare earths promote the turnover frequency of Pt atoms by activating the nitrogen–oxygen bond. In our experiment, we also investigated the effect of K and B. We found that K shows an effect that can be neglected. However, the catalyst reduced by KBH$_4$ shows better catalytic activity than the catalyst reduced by H$_2$ or hydrazine hydrate. Thus we suggested that good effects are also related to the presence of B [20]. The level of B measured by ICP is 0.027 wt%. The results in tables 2, 3 and 4 reveal that the rates of CNB hydrogenation over Pt/ZrO$_2$ are greatly affected by the position of substituent groups. Hydrogenation rate increases in the order: $p > m > o$, and the yield of CAN increases in the order: $p > o > m$. These differences are due to the different electron cloud densities between the C–Cl bond, which affects the rate of hydrogenolysis of the C–Cl bond. The conjugative effect between Cl and NO$_2$ increases the bond energy of C–Cl in *o*- and *p*-CNB, which decreases the hydrogenolysis of the C–Cl bond. Inductive and steric effects increase the rate of hydrogenolysis of the C–Cl bond in *o*-CNB. Figure 2 gives the kinetic curves of hydrogenation of CNB catalyzed by Pt/ZrO$_2$. These curves show that the catalytic hydrogenations of *o*-, *m*- and *p*-CNB proceed differently, the initial hydrogenation rate for *p*-CNB being higher than that of *m*- and *o*-CNB. Figure 3 also gives the kinetic curves of hydrogenation of *p*-CNB catalyzed by PtM/ZrO$_2$ catalysts. From figure 3, we find that platinum catalysts modified by rare earth show similar catalytic behavior on the hydrogenation of *p*-CNB.

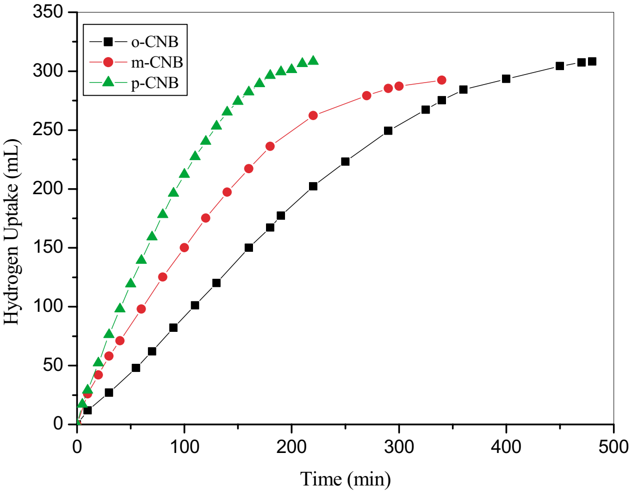

Figure 2. Cumulative hydrogen uptake profiles of catalytic hydrogenation of chloronitrobenzene over Pt/ZrO$_2$ catalyst.

4. Conclusions

The Pt/ZrO$_2$ catalyst can catalyze the hydrogenation of CNB at 303 K and 1 atm. The conversions of CNB are all >99%. The order of hydrogenation rate of CNB is $p > m > o$, and the selectivity of CAN is $m > p > o$. Catalytic activities are all improved over PtM/ZrO$_2$ catalysts with the introductions of rare earth on the hydrogenation of CNB. For the hydrogenation of *p*-CNB, PtSm/ZrO$_2$, PtCe/ZrO$_2$, and PtPr/ZrO$_2$, catalysts show good selectivity of *p*-CNB to *p*-CAN. The PtPr/ZrO$_2$ catalyst exhibits the highest TOF of 0.48 s^{-1} and yield of *p*-CAN (95.1 mol%). For the hydrogenation of *m*-CNB, both catalytic activity and selectivity of *m*-CNB to *m*-CAN increase remarkably over PtM/ZrO$_2$ catalysts. The catalytic activity is also improved on the hydrogenation of *o*-CNB over PtM/ZrO$_2$ catalysts. However, only PtPr/ZrO$_2$ and PtCe/ZrO$_2$ show good selectivity of *o*-CNB to *o*-CAN with 89.4 mol% and 87.1 mol%, respectively. The content of Ce in the PtCe/ZrO$_2$ catalyst has significant influence on the

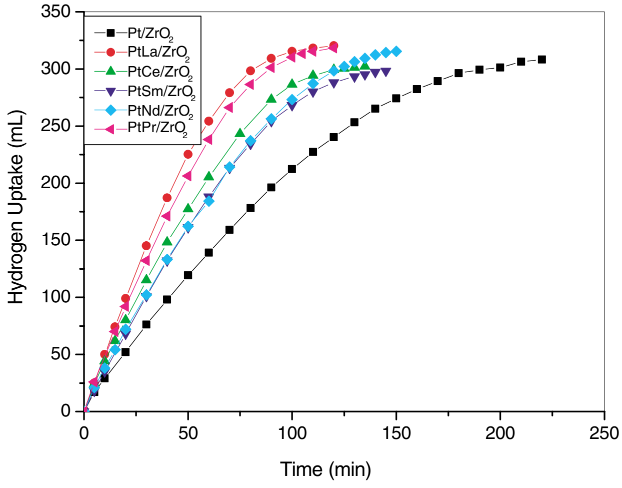

Figure 3. Cumulative hydrogen uptake profiles of catalytic hydrogenation of *p*-chloronitrobenzene over the Pt/ZrO$_2$ catalyst.

catalytic properties for the selective hydrogenation of *p*-CNB, and yield of *p*-CAN increases with increasing amount of Ce.

References

[1] R. Baltzly and A.P. Phillips, J. Am. Chem. Soc. 68 (1946) 261.

[2] J.R. Kosak, U.S. Patent 4,020,107 (1977) to E.I. du Pont de Nemours and Co.

[3] L. Cerveny, I. Paseka, V. Struckly and V. Ruzicka, Collect. Czech. Chem. Commun. 47 (1982) 853.

[4] S. Galvagno, A. Donato, G. Neri and R. Pietropaolo, J. Mol. Catal. 42 (1987) 379.

[5] H. Greenfield and F.S. Dovell, J. Org. Chem. 32 (1967) 3670.

[6] J.R. Kosak, N.Y. Ann. Acad. Sci. 172 (1970) 175.

[7] G.C. Bond, D.E. Webster, N.Y. Ann. Acad. Sci. 158 (1969) 540.

[8] L. Spiegler, U.S. Patent 3,073,865 (January 1963) to E.I. du Pont de Nemours and Co.

[9] S.G. Hindin, U.S. Patent (May 1972) to Engelhard Minerals & Chemicals Co.

[10] X. Guangxian and X. Jime (eds.), *New-Frontiers in Rare Earth Science and Applications* (Science Press, Beijing 1985); K. A. Gschneider, Jr., Industrial Applications of Rare Earth Elements, Am. Chem. Soc. (1981).

[11] X.X. Han, R.X. Zhou, X.M. Zheng and H. Jiang, J. Mol. Catal. A 193 (2003) 103.

[12] B. Coq, P.S. Khumbar, C. Moreau, P. Moreau and M. Warawdekar, J. Mol. Catal. 85 (1993) 215.

[13] B. Coq, P.S. Khumbar, C. Moreau, P. Moreau and F. Figueras, J. Phys. Chem. 98 (1994) 10180.

[14] H.X. Li, W. Wang, H. Li and J.F. Deng, J. Catal. 194 (2000) 211.

[15] J.R. Kosak, in *Catalysis in Organic Chemistry*, W.H. Jones (ed.), (Academic Press, New York, 1980) p. 107.

[16] W. Pascoe, in P.N. Rylander, H. Greenfield and R.L. Augustine (eds.), *Catalysis of Organic Reactions* (M. Dekker, New York, 1988) p. 121.

[17] S. Galvagno, A. Donato, G. Neri and R. Poetrpaolo, J. Mol. Catal. 42 (1987) 379.

[18] B. Coq, A. Tijani and F. Figuéras, J. Mol. Catal. 68 (1991) 331.

[19] K. Christman and G. Ertl, Surf. Sci. 60 (1976) 365.

[20] X.P. Yan, M.H. Liu, H.F. Liu and H.Y. Liew, J. Mol. Catal. A 169 (2001) 225.