# Hydrodechlorination of chlorinated hydrocarbons over metal–carbon composite catalysts prepared by a modified carbothermal reduction method

**N. Lingaiah, Md. A. Uddin, A. Muto and Yusaku Sakata***

*Department of Applied Chemistry, Faculty of Engineering, Okayama University, Okayama, 700-8530, Japan. E-mail: yssakata@cc.okayama-u.ac.jp*

**A highly stable and active Pd–Fe carbon composite catalyst system for hydrodechlorination of chlrohydrocarbons is obtained by a novel modified carbothermal reduction method using ion exchange resins.**

Chlorinated hydrocarbons are one of the most widespread and persistent toxic pollutants. The disposal of these organic wastes is a vital environmental issue. Among the several methods proposed for their destruction, catalytic hydrodechlorination (HDC) is of increasing interest because it excludes the formation of more toxic compounds such as dioxins and has a comparatively low reaction temperature.[1–3] Noble metals are the catalysts of choice for this reaction, which is carried out in either the liquid or the gas phase. Chlorobenzene is usually studied as a model compound for the HDC reaction since it represents the halogen species found in many organic wastes. Deactivation of the catalyst by HCl produced during the reaction is a commonly encountered problem.[4] The development of highly stable and active catalysts for this reaction remains as a challenging task. Recently, more attention has been focused on bimetallic catalysts over monometallic catalysts in order to improve longevity and activity.[5] However, it has been reported that the use of bimetallic catalysts instead of mono-metalic ones can result in a decrease of HDC activity.[6]

In this work we report for first time the preparation of Pd and Pd–Fe carbon composite catalysts by a novel modified carbothermal reduction (CTR) method, and their activity in chlorobenzene HDC. We have been developing a modified carbothermal reduction (CTR) method to prepare highly dispersed and thermally stable metal or metal compound-based carbon composite catalysts.[7] In the CTR process, first an organic ion exchange resin is exchanged with the required metal ions, followed by thermal treatment in the temperature range 500–800 °C. Since the metallic ions adsorbed on the resin are highly dispersed, the catalysts prepared by this method are highly dispersed.

In the preparation of the catalysts, first the required amounts of aqueous solutions of Pd and Fe ($PdCl_2$ and $Fe(NO_3)_3$ precursors used respectively) were added to a commercial chelate type of ion exchange resin (spherical granules) under constant stirring with a magnetic rod. The stirring was continued for about six hours then the solution was filtered and the metal exchanged resin dried at room temperature for about 12 h. The dried samples were then subjected to carbothermal reduction at 800 °C in an $N_2$ flow (300 ml min$^{-1}$) for 3 h. After CTR the catalysts retained their spherical shape but were reduced in size.

The catalyst tests were performed in a fixed bed microreactor at atmospheric pressure as described elsewhere.[8]

The physical characteristics of the catalysts along with their compositions are shown in Table 1, which shows that the surface areas and pore volumes are increased in the bimetallic catalysts in comparison with the corresponding monometallic catalysts. In monometallic catalysts pore blocking due to segregation during the CTR process might be the cause of the decrease in these values. The presence of Fe in the bimetallic catalysts may result in a reduction of the Pd segregation.

The XRD pattern of monometallic Pd/C shows peaks arising from metallic Pd. In bimetallic catalysts, the addition of more iron leads to the formation of $Fe_3C$. In the monometallic Fe/C catalyst, most of the iron exists as $Fe_3C$.

The HDC of chlorobenzene over mono- (Pd, Fe) and bimetallic (Pd–Fe/C) catalysts resulted in the formation of benzene as the only organic product. Percentage conversion values obtained after the catalysts reached steady state conditions at a reaction temperature of 150 °C are presented in Fig. 1. Note that the monometallic Pd/C catalyst shows very low activity at steady state conditions. The Fe/C catalyst does not show any activity in this reaction. In the bimetallic Pd–Fe/C catalysts the addition of Fe to Pd leads to a substantial increase in the activity, even though Fe is inactive for this reaction. The increased activity of the bimetallic catalysts relative to the monometallic catalysts is in contrast to earlier findings, where a decrease in activity in the cases of bimetallic Pd–Sn, Pd–Rh and Pd–Fe catalysts due to the second metal diluting the catalyst surface was reported.[6,9]

Preparation by the CTR method may result in a different morphology of the catalyst surface. SEM–EDX images of Pd and Fe for a cross-sectional view of a cylindrical granule of the bimetallic 2Pd–2Fe/C catalyst are shown in Fig. 2. It can be seen from Fig. 2(a) that the majority of the Pd is present on the surface whereas most of the iron [Fig. 2(b)] is dispersed inside the catalyst particle. During the CTR the Pd might be

**Table 1** Physical characteristics of the mono- and bimetallic Pd–Fe carbon composite catalysts

| Catalyst code | Fe content/ g $g_{cat}^{-1}$ | Pd content/ g $g_{cat}^{-1}$ | $S_{BET}$/m$^2$ g$^{-1}$ | $V_p$/ml $g_{cat}^{-1}$ | XRD Peak |
|---|---|---|---|---|---|
| 2Pd | 0 | 0.069 | 140 | 0.071 | Fe, $Fe_3C$ |
| 4Pd | 0 | 0.11 | 209 | 0.149 | Pd |
| 2Pd2Fe | 0.036 | 0.068 | 331 | 0.331 | Pd |
| 2Pd4Fe | 0.079 | 0.06 | 333 | 0.334 | Pd |
| 2Pd8Fe | 0.111 | 0.054 | 370 | 0.377 | Pd, Fe, $Fe_3C$ |
| 2Fe | 0.29 | 0 | 200 | 0.327 | Pd, Fe, $Fe_3C$ |
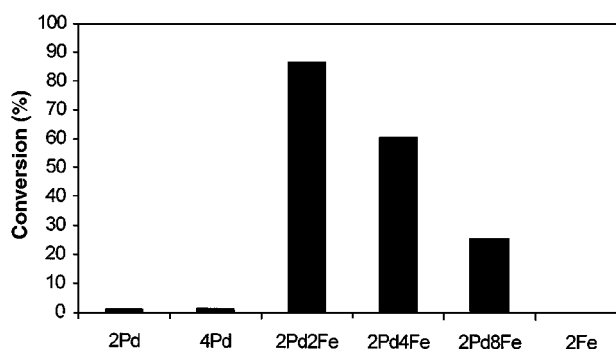


**Fig. 1** Hydrodechlorination of chlorobenzene on monometallic Pd and Fe and bimetallic Pd–Fe carbon composite catalysts (reaction temperature: 150 °C; space velocity: 7680 h$^{-1}$).
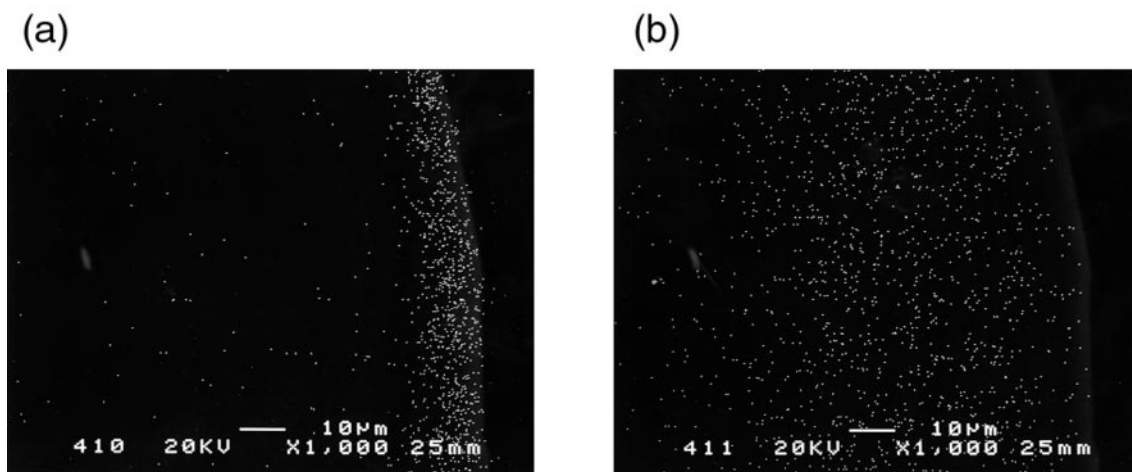
**Fig. 2** SEM-EDX images of a cross-sectional view of a spherical granule of the 2Pd–2Fe/C catalyst [(a): EDX of Pd; (b): EDX of Fe].

transported to the surface. Similar behavior has been observed for other bimetallic catalysts.

Wunder and Phillips,[10] in their studies on Pd–Fe supported on graphite, proposed that the iron exists on the surface and the Pd in the bulk. In conventional methods of preparation the iron is present initially as hematite which is later reduced to magnetite and metallic iron during the catalyst runs. During this process most of the iron migrates to the surface.

The TEM data show that in the case of the monometallic Pd/C catalyst the Pd forms large clusters (particle size about 56 nm). The low values of BET surface area and pore volume also suggest the aggregation of Pd. TEM of the bimetallic 2Pd2Fe/C catalyst depicts highly dispersed small particles (about 14 nm) of the bimetallic ensembles. The surface migration of Pd and the formation of small Pd–Fe bimetallic particles may be responsible for the substantial increase in activity in the bimetallic catalysts.

Upon the addition of more Fe to Pd a decrease in activity in the conversion of chlorobenzene was observed. In the high Fe containing catalyst 2Pd–8Fe/C it also observed from SEM–EDX of Pd and Fe that the Pd is present on the surface, similar to other catalysts, but the density of Fe in the catalyst is high, diluting the Pd. Another reason for the low activity reported earlier is that the less active metal Fe, which is present in large amounts, migrates to the surface in the HCl atmosphere generated during the reaction.[6]

Comparisons were made of the highly active 2Pd–2Fe/C catalyst with a catalyst prepared by a conventional impregnation method, with a similar composition, on carbon. The results show that the bimetallic catalyst prepared by modified CTR method possesses higher activity (87% conversion) than the catalyst prepared by the the conventional method (53% conversion).

The advantage of the CTR method over conventional methods of preparation for carbon based catalysts is that the metal ions are well dispersed on the ion exchange resin and this leads to the formation of bimetallic ensembles from a single step, whereas in conventional methods there is a need for separate treatments to obtain the bimetallic ensembles.

This method of preparation can be applied to the preparation of a variety of mono- and bimetallic carbon composite catalysts with varying metal contents.

Time on stream analysis results for 2Pd/C and 2Pd–2Fe/C catalysts, at a reaction temperature of 200 °C, are shown in Fig.
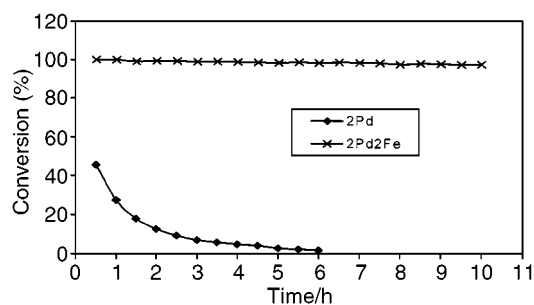


**Fig. 3** Hydrodechlorination of chlorobenzene: time on stream analysis (reaction temp: 200 °C; space velocity: 7680 $h^{-1}$).

3. It can be seen that the activity of monometallic 2Pd/C steadily decreased with time, whereas the bimetallic 2Pd–2Fe/C catalyst exhibited fairly constant conversion throughout the period of study. The bimetallic catalysts prepared by the modified CTR method revealed high activity with higher stability in the HDC reaction.

## Notes and references

1 E. N. Balko, E. Zybylski and F. Von Trentini, *Appl. Catal. B.*, 1993, **2**, 1.

2 F. Gioia, E. J. Gallagher and V. Familetti, *J. Haz. Mater.*, 1994, **38**, 277.

3 A. Gampine and D. P. Eyman, *J. Catal.*, 1998, **179**, 315.

4 B. Coq, G. Ferrato and F. Figueras, *J. Catal.*, 1986, **101**, 434.

5 A. G. Fendler, D. Richard and P. Gallezot, *Stud. Surf. Sci. Catal.*, 1998, **41**, 171.

6 P. Bodnaviuk, B. Coq, G. Ferrato and F. Figueras, *J.Catal.*, 1989, **116,** 459.

7 Y. Sakata, A. Muto, Md. Azhar Uddin and K. Harino, *J. Mater. Chem.*, 1996, **6**, 1241.

8 P. S. Sai Prasad, N. Lingaiah, P. Kanta Rao, F. J. Berry and L. Smart, *Catal. Lett.*, 1995, **35**, 345.

9 N. Lingaiah, Ph.D thesis, Osmania University, Hyderabad, India, 1995

10 R. W. Wunder and J. Phillips, *J. Phys. Chem.*, 1996, **100**, 14 430.