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# Vapour phase catalytic hydrodechlorination of chlorobenzene over Ni–carbon composite catalysts

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## Abstract

Ni–carbon composite catalysts were prepared by a modified carbothermal reduction method using ion exchange resins. The catalysts were characterised by N<sub>2</sub> adsorption, X-ray diffraction and transmission electron microscope. The catalyst activities and selectivities were studied in the hydrodechlorination of chlorobenzene. The catalyst activities depend upon the carbothermal reduction temperature during preparation. These catalysts are found to be more stable and selective in this reaction even in the presence of HCl which is produced during the reaction. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Ni–carbon composite; Carbothermal reduction; Hydrodechlorination; Chlorobenzene

## 1. Introduction

Many chlorinated organic compounds are environmental pollutants because of their carcinogenic and mutagenic activity. These compounds are produced in a broad range of industrial processes. Several methods have been reported for their disposal [1,2]. Catalytic hydrodechlorination (HDC) is one of the best methods for the removal of chlorinated organic compounds, as this method excludes the formation of more toxic dioxin compounds [3].

The catalytic HDC of aromatic and aliphatic chloro compounds using Pd, Pt, Rh and Ni based

catalysts has been reported [4–6]. Most of the work reported has been mainly on Pd based catalysts and the main problem associated with this reaction was deactivation of the catalysts by HCl, which is produced during the reaction [4]. There are a few reports of the use of sulfided Ni or Ni–Mo catalysts for this reaction, and these catalysts are found to be stable, but they require high temperature and pressure [7]. The use of unsulfided supported Ni catalysts in the vapour phase HDC of chloro organic compounds was limited.

We prepared carbon based metal and metal compound catalysts by a novel method called modified carbothermal reduction (CTR) using metal species loaded on ion exchange resins by conventional ion exchange [8]. As metal species are highly dispersed on ion exchange resins, which means that after carbonisation a catalyst with high metal dispersion on

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an amorphous carbon support can be obtained. Recently, we reported carbon based Fe–Pd bimetallic catalysts prepared by the CTR method [9]. These catalysts were found to be selective and active in HDC of chlorobenzene.

In this work, we are reporting the use of Ni–carbon composite catalysts prepared by a modified carbothermal reduction (CTR) method using metal ion exchange resins. Chlorobenzene is used as a model compound in this study, since it represents the halogenated species found in many organic wastes.

## 2. Experimental

The Ni–carbon composite catalysts were prepared by a modified carbothermal reduction method. Firstly, the metal ion exchange resin (spherical shape, chelate type CR11-H<sup>+</sup>, Mitsubishi chemicals, Japan) was taken in a column and the required amount of aqueous Ni(NO<sub>3</sub>)<sub>2</sub> solution was added dropwise from the top of the column. The Ni metal exchanged resin was then filtered, washed and dried at room temperature. Later they were subjected to CTR at a temperature ranging from 400 to 900°C in an N<sub>2</sub> flow (300 ml/min). After CTR the catalyst retained its spherical shape with reduction in size.

X-ray diffraction (XRD) patterns of fresh and used catalysts were recorded on a powder diffractometer (Shimadzu, Type XR2) using Cu K $\alpha$  radiation. The mean crystalline diameters were estimated by Scherrer's equation.

The N<sub>2</sub> adsorption/desorption isotherms at 77 K of the samples were obtained using an adsorption unit (BELSORP 28SP, Nippon Bell, Japan). The BET surface area, total pore volume and average pore radius were obtained from the adsorption isotherms. The Dollimore and Heel method was used to calculate mesopore volume and micropore volume was determined by subtracting the micropore volume from total pore volume.

High-resolution transmission electron microscopy (HRTEM) samples were prepared by grinding catalysts into fine powder by mixing in carbon tetrachloride. A drop of this suspension was placed on a grid supporting a holey-carbon film and dried. Micrographs were obtained using a Topcon microscope

(Topcon EM-002B) equipped with a side entry stage and operating at 200 kV.

All the catalytic reactions were carried out in a previously described fixed bed microreactor over the temperature range 250–400°C [10]. About 0.8 g of catalyst was placed in a quartz tubular reactor (8 mm i.d.) between two quartz plugs and a layer of glass beads above the catalyst bed to ensure that the reactants reached the reaction temperature before contact with the catalyst. Before starting the reaction, the catalyst was pretreated at 450°C for 2 h in hydrogen at a flow rate of 40 ml/min and cooled to reaction temperature. Chlorobenzene (1.2 ml/h) was fed into the reactor using a microfeeder (Hitachi, Japan) and the hydrogen flow was maintained by a mass flow controller. A space velocity of 3360 h<sup>-1</sup> (GHSV) was maintained throughout the reaction study. At the reactor outlet of the reaction products were collected in a cold trap and were analysed by GC with flame ionisation detector.

## 3. Results and discussion

The physico-chemical properties of Ni–carbon composite catalysts are presented in Table 1. The surface area of the catalysts decreased with increasing CTR temperature. A change in crystalline size and pore structure from micro to mesoporous was observed on increasing the CTR temperature from 400 to 900°C. The change in the micropore volume with temperature is due to the increase of nickel ions diffused into inner pores of carbon. It is known that when carbon is used as support, the metal dispersion can be more or less controlled by thermal treatment [11]. The decrease in surface area with increase in CTR temperature might be due to the change in pore structure.

The XRD patterns of the catalysts are presented in Fig. 1. The patterns mainly relate to metallic nickel. The catalysts prepared at low CTR temperatures (400 and 500°C) have poor crystalline structure and the carbon is amorphous. Graphite formation was observed in the catalysts prepared at higher temperatures (600–900°C). The majority of the Ni in the supported catalysts reduced at high temperature. The difficulties associated with reduction of Ni are well

Table 1  
Physico-chemical properties of Ni–carbon composite catalysts

| Catalyst code | CTR temperature <sup>a</sup> (°C) | Metal weight (g(Ni)/g-cat.) | BET surface area (m <sup>2</sup> /g) | Crystalline size <sup>b</sup> (nm) | Micropore (ml/g-cat.) | Mesopore (ml/g-cat.) | Total PV (ml/g-cat.) |
|---------------|-----------------------------------|-----------------------------|--------------------------------------|------------------------------------|-----------------------|----------------------|----------------------|
| Ni 400        | 400                               | 0.257                       | 207                                  | 9.5 (9) <sup>c</sup>               | 0.1588                | 0.0497               | 0.2086               |
| Ni 500        | 500                               | 0.258                       | 392                                  | 11 (93) <sup>c</sup>               | 0.2574                | 0.0552               | 0.3126               |
| Ni 600        | 600                               | 0.272                       | 189                                  | 48                                 | 0.1359                | 0.2046               | 0.3406               |
| Ni 700        | 700                               | 0.283                       | 118                                  | 48 (57) <sup>c</sup>               | 0                     | 0.2859               | 0.2859               |
| Ni 800        | 800                               | 0.267                       | 111                                  | 55                                 | 0.0641                | 0.2714               | 0.3356               |
| Ni 900        | 900                               | 0.282                       | 96                                   | 64 (76)                            | 0.0055                | 0.2966               | 0.3022               |

<sup>a</sup> Heat treatment with 5°C/min to carbonisation temperature and hold for 3 h in N<sub>2</sub> stream.

<sup>b</sup> Calculated using Scherrer's equation ( $K = 1$ ).

<sup>c</sup> Values in the parentheses are calculated from HRTEM.

known [12]. However, the catalysts prepared by modified CTR method have an advantage that metallic nickel forms directly and there is no need for a separate reduction step to obtain metallic nickel as in the case of other preparation methods.

The HDC of chlorobenzene (CB) in the presence of Ni/C catalyst over the temperature range 250–

400°C produced benzene as the only appreciable product.

The HDC of CB activity over the Ni/C catalysts prepared at different CTR temperatures is presented in Fig. 2. It was observed from Fig. 2 that the catalysts prepared at low temperatures (400 and 500°C) show higher CB conversions and the HDC activity decreases to a steady lower value with an increasing CTR temperature in the range 600–900°C. The difference in activities of the Ni/C catalysts prepared at different CTR temperatures might be due to surface changes during the temperature treatment. The catalysts prepared at low CTR temperatures (400 and 500°C) have small crystalline size, high micropore volume and surface area. The Ni/C catalysts prepared by CTR method have an advantage that even at very high Ni content (> 25%), metallic Ni exists with a small crystallite size (9–11 nm). The TEM micrographs of Ni/C catalysts prepared at CTR temperatures of 400 and 500°C are presented in

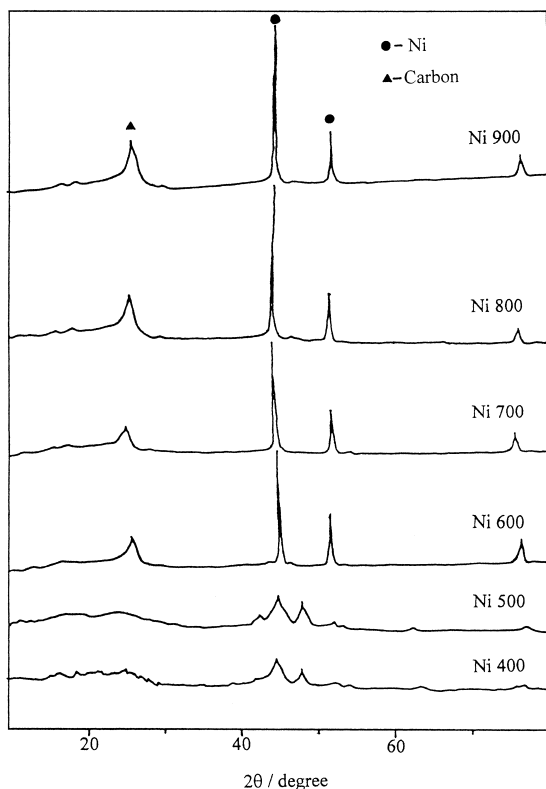


Fig. 1. X-ray diffraction patterns of Ni–carbon composite catalysts as a function of CTR temperature.

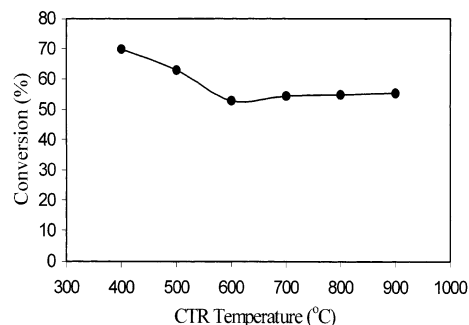


Fig. 2. Conversion of chlorobenzene over Ni/C catalysts prepared at various CTR temperatures (reaction temperature, 350°C; GHSV, 3360 h<sup>-1</sup>).

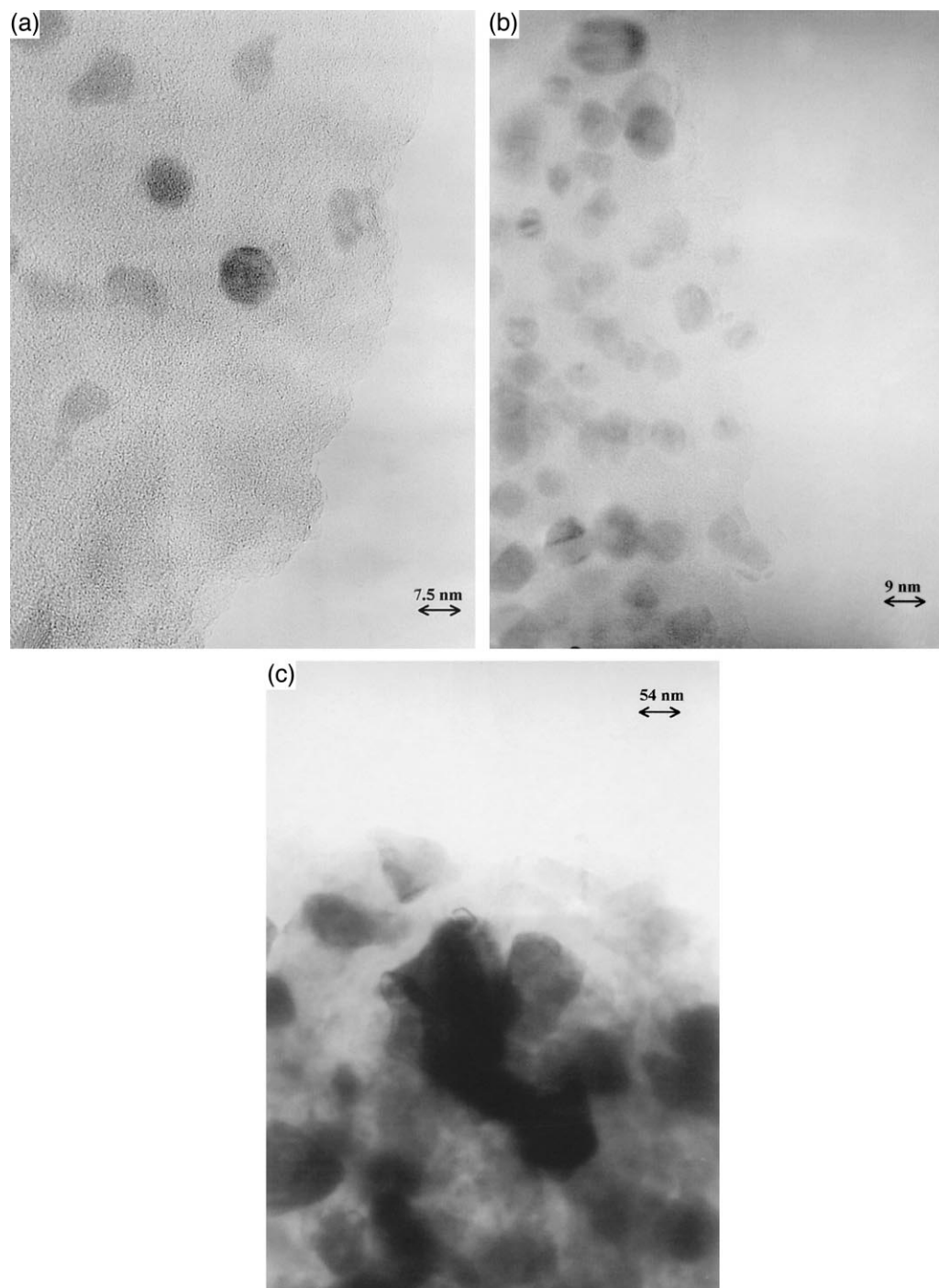


Fig. 3. HRTEM images of Ni-carbon composite catalysts prepared at CTR temperatures of (a) 400°C (1 cm = 7.5 nm); (b) 500°C (1 cm = 9 nm) and (c) 700°C (1 cm = 54 nm).

Fig. 3a and b, respectively. Metallic Ni exists as small particles of fairly uniform size well distributed over carbon in the case of the catalyst prepared at lower CTR temperatures (400 and 500°C) as shown in Fig. 3a and b. Metallic Ni particle sizes calculated from TEM and Scherrer's equation are in good agreement. The higher activity for these catalysts might be due to the high dispersion of Ni on amorphous carbon. The small crystalline size, higher surface area and presence of carbon as an amorphous phase in these catalysts support the high dispersion of Ni. With an increase in the CTR temperature, there is a clear shift in crystallite size and pore structure. At higher CTR temperatures the Ni may have occupied a large number of carbon pores resulting in a significant increase in crystallite size. A constant activity was observed in the case of catalysts prepared at CTR temperature from 600 to 900°C. Catalysts prepared at higher CTR temperatures have a different morphology. These high temperatures treated catalysts all show similar crystallite sizes and pore structure. The TEM micrograph (Fig. 3c) shows the formation of large clusters of Ni. The TEM findings clearly demonstrate the change in pore structure and crystallite size with changing in the CTR temperature from 400 to 900°C. It has been reported that in hydrogenation over Ni on activated carbon the loss of hydrogenation activity for the catalysts treated at high temperature (> 450°C) was not mainly due to metal sintering but instead to the carbon surface species produced by the precipitation of bulk dissolved carbon [13]. In the present case, a

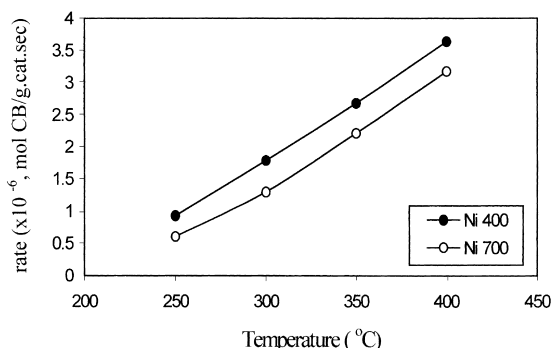


Fig. 4. Effect of reaction temperature on HDC of chlorobenzene over Ni/C catalysts prepared at CTR temperatures of 400 and 700°C (reaction temperature, 250–400°C; GHSV, 3360 h<sup>-1</sup>).

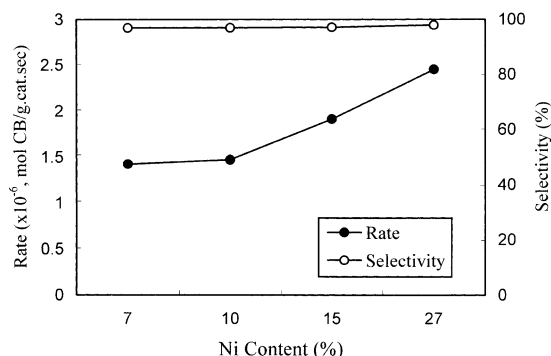


Fig. 5. Effect of Ni metal content in HDC of chlorobenzene over Ni/C catalysts prepared at CTR temperature 800°C (reaction temperature, 350°C; GHSV, 3360 h<sup>-1</sup>).

similar reasoning cannot be ruled out as the graphite phase was observed in the catalysts treated at high CTR temperature (600–900°C).

The rates of HDC of chlorobenzene on the Ni/C catalysts prepared at different CTR temperature (400 and 700°C) are presented in Fig. 4. The activity of the catalysts increased with increase in reaction temperature. There are no significant database on the effect of reaction temperature in HDC of chloroaromatics over a catalyst in a one-step operation, because most of the catalysts initially deactivate in this reaction. The linear relationship between conversion and reaction temperature in Fig. 4 suggests that the catalysts are not deactivated by the interaction of HCl with the surface of the catalyst.

The activity of HDC of CB on the catalysts with varying nickel content prepared at a CTR tempera-

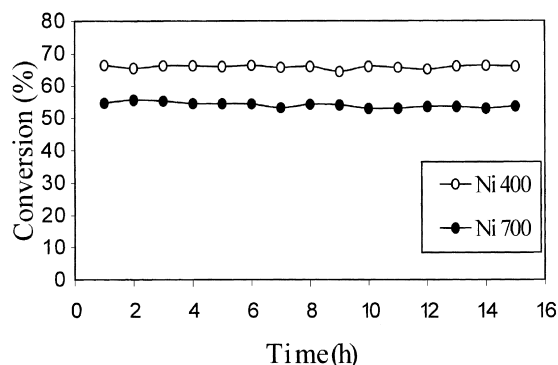


Fig. 6. Time-on-stream analysis: hydrodechlorination of chlorobenzene over Ni/C catalysts (reaction temperature, 350°C; GHSV, 3360 h<sup>-1</sup>).

ture of 800°C are reported in Fig. 5. The data indicate that the activity rises with the increase in Ni metal content. Suzdorf et al. reported in their study on Ni/Al<sub>2</sub>O<sub>3</sub> in HDC of CB that the activity of the catalysts increased with an increase in the metal content [14]. Our results are in good agreement with their findings.

The change in conversion of chlorobenzene with time at a reaction temperature of 350°C was studied on Ni/C catalysts prepared at different CTR temperatures. The profiles in Fig. 6 show the results of time on stream analyses of the catalysts prepared at CTR temperatures of 400 and 700°C only for the sake of clarity. It can be seen that there is no appreciable deactivation over time on all the Ni/C catalysts prepared by the CTR method at different temperatures, where a loss of HDC activity with time has been reported for palladium, platinum, rhodium, bulk nickel and Ni/SiO<sub>2</sub> catalysts in the conversion of chlorinated aromatic reactants [4–6,15].

Catalyst deactivation in HDC reaction has been attributed mainly to the presence of HCl generated in the reaction by the formation of a stable surface chloride species and the reaction can then essentially be viewed as a cycle of chlorination/dechlorination of the surface [6]. The analysis of fresh and used catalysts by X-ray diffraction did not reveal any significant structural changes. It indicates that Ni/C composite catalysts are stable in the HCl and chlorobenzene atmosphere.

#### 4. Conclusions

An increase in the size of pore structure and crystallite size occurs with change in the CTR tem-

perature from 400 to 900°C during the preparation of Ni/C composite catalysts. In the case of catalysts prepared at lower CTR temperatures (400 and 500°C) metallic Ni exists as small particles of fairly uniform size well distributed over carbon and these catalysts shows high activity in HDC of chlorobenzene. Increasing the Ni content and reaction temperature increased the HDC reaction rate. The Ni/C composite catalysts prepared by a modified CTR method are highly stable in HCl and chlorobenzene atmosphere.

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