Hydrodechlorination of chlorophenols at low temperature on a novel Pd catalyst[†]

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Pd/mesoporous silica-carbon nanocomposites with 3.2 nm Pd particles, prepared by a simple wetness impregnation method, have demonstrated high activity at 258 K for the hydro-dechlorination of chlorophenols with a high selectivity.

Aryl chlorides are hazardous pollutants that are considered among the most harmful organic contaminants due to their acute toxicity and strong bioaccumulation potential,¹ and therefore, the safe disposal of aryl chloride pollutants has acquired great importance with the ever increasing concern of environmental protection.² Among the various available detoxification techniques, catalytic hydrodechlorination (HDC) is an interesting one that can be employed to treat streams containing concentrated or dilute chlorinated organic pollutants under mild conditions.

Supported Pd catalysts are receiving attention for the treatment of wastewater containing chlorinated organic pollutants, especially in HDC reactions.³ High catalytic performance of Pd catalysts in the HDC of chlorinated aromatics has been observed at ordinary temperature.⁴ However, the HDC at low temperature on Pd catalysts has seldom been reported. The liquid phase catalytic HDC of 2,4-dichlorophenol on Pd/C and Pd/Al₂O₃ was investigated at 273 K.⁵ Limited by the freezing point, the HDC in aqueous solution below 273 K was not feasible. In organic solutions, 10 wt% Pd/C showed almost no activity in the HDC of 4-chlorobiphenyl at 253 K.⁶

Mesoporous silica–carbon nanocomposites (MSCNs) are potentially useful materials for creating a high performance heterogeneous catalyst, because of their unique properties unachievable in traditional materials, with well-controlled pore structures, high surface areas, and large and tunable pore sizes, which facilitate the diffusion of reactant and product inside the pores.⁷ Recently, MSCNs have been used as support materials for metal catalysts in water-mediated coupling reactions of chlorobenzene, without the presence of any phase-transfer catalysts.⁸ The size of the metal particles supported on MSCNs can be controlled on a \sim 3 nm scale, and a higher activity of catalysts than that so far reported in literatures was observed. This may offer an opportunity for establishing novel Pd catalysts with high performance for the HDC of chlorinated aromatics at low temperature. In this work, Pd/MSCN was used for the HDC of 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP), as models of chlorinated organic pollutants. The reaction proceeded within the temperature range of 258–313 K, of which 258 K is lower than the reaction temperature reported in the literature. Meanwhile, the activity of Pd/MSCN was evaluated through different addition modes of triethylamine (Et₃N) into the reaction mass of chlorophenols.

The carrier material, MSCN, with a C : SiO₂ molar ratio of 3.85 : 1, prepared by the method as reported in ref. 7, was impregnated in 0.48 M (0.051 g_{Pd} ml⁻¹) H₂PdCl₄ aqueous solution for 24 h at 298 K, and then dried at 353 K for 8 h in a vacuum oven. The resulting dry solid was reduced under H₂ flow (30 ml min⁻¹) at 473 K for 3 h in a tubular furnace, and finally, 5 wt% Pd/MSCN catalyst, as determined by ICP, was obtained. The same method was employed in preparation of 5 wt% Pd catalyst supported on active carbon (Pd/AC), which was used as a reference sample to compare with Pd/MSCN. The Pd/MSCN catalyst was characterized by XRD, XPS, N₂ adsorption–desorption isotherms and TEM (ESI[†]).

N₂ sorption isotherms of the MSCN exhibit type-IV curves with a very sharp capillary condensation step at P/P_0 0.46–0.80 and an H₁-type hysteresis loop featured by largepore mesoporous materials with cylindrical channels (Fig. 1). A narrow pore size distribution with a mean value of 6.5 nm was calculated from the adsorption branch based on the BJH model. The BET surface area and pore volume of MSCNs were calculated to be 413 m² g⁻¹ and 0.53 cm³ g⁻¹, respectively. After supporting Pd, Pd/MSCN also displays type-IV N₂ sorption isotherms with an H₁-type hysteresis loop. The capillary condensation step shifts slightly to low relative pressure with a wide range of P/P_0 0.44–0.75, resulting



Fig. 1 Nitrogen adsorption–desorption isotherm plots and pore size distribution curves for MSCN and Pd/MSCN.

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from the reduction of the pore size to 6.2 nm. The BET surface area and pore volume of Pd/MSCN were calculated to be $345 \text{ m}^2 \text{ g}^{-1}$ and $0.46 \text{ cm}^3 \text{ g}^{-1}$, respectively. These phenomena can be attributed to 5 wt% Pd supporting inside the channels of the MSCNs, which leads to a partial blocking of the pores.

The 2-D hexagonal mesostructures of MSCN and Pd/MSCN samples were confirmed by XRD (ESI[†]). For Pd/MSCN, the face-centered cubic (fcc) Pd lattice is present, as confirmed by several peaks at $2\theta = 40.1, 46.5, \text{ and } 68.0^{\circ}$ in wide-angle XRD patterns (ESI[†]). It is interesting to find by TEM (Fig. 2(A)) a narrow Gaussian distribution of Pd particle size of about 3.2 nm, which is consistent with the results either obtained from H₂ titration or estimated through the Scherrer formula. Compared with the Pd particle size on Pd/AC, as shown in Fig. 2(C), the dispersion of Pd on Pd/MSCN is much higher. The possible reason for the high dispersion of small-size metal particles is the unique hybrid nature of the carrier. In the carrier, the silica and carbon components uniformly disperse on the pore wall to construct a continuous framework.⁷ Pd ions may be selectively adsorbed on the surface of hydrophilic SiO₂, whose silanol groups can interact with the Pd ions, while the inert, hydrophobic component carbon possibly plays a role to separate them. XPS results (ESI⁺) indicate that the intensity of Pd for Pd/MSCN is much stronger than that for Pd/AC, which can be ascribed to higher dispersion of Pd on Pd/MSCN and more Pd atoms exposed to the surface.

The evaluation of the activity of Pd/MSCN for the HDC of 4-CP and 2.4-DCP was carried out under a hydrogen atmosphere within the temperature range of 258-313 K (ESI[†]). The conversion of 4-CP on Pd/MSCN at different temperatures as a function of time is shown in Fig. 3, and the turnover frequency (TOF) for the HDC of 4-CP is listed in Table 1. At 258 K, the TOF for Pd/MSCN is 2.6 min⁻¹, clearly surpassing the TOF for Pd/AC of 0.9 min⁻¹, and it takes 600 min for the HDC of 4-CP on Pd/MSCN to complete in the presence of Et₃N (1.0 equiv. vs. the number of chlorine atoms), which can combine with the HCl formed during the reaction so as to remove Cl species from Pd active sites. This result confirms for the first time that nano-sized Pd particles supported on MSCN are highly active for HDC in the liquid phase at 258 K. Phenol was the only product, and no formation of other species was observed. With raising temperature, the activity of Pd/MSCN for HDC increases obviously, and the TOF reaches 2.8 min^{-1} at 278 K and 25.0 min⁻¹ at 313 K. Under similar conditions, the activity



Fig. 2 TEM images of the mesoporous supported palladium catalysts: fresh Pd/MSCN (A); used Pd/MSCN (B); Pd/AC (C).



Fig. 3 HDC of 4-CP over 5 wt% Pd/MSCN (Pd : Cl = 1 : 100 mol) at 258 and 278 K under ordinary hydrogen pressure (balloon) using Et_3N (1.0 equiv. *vs.* the number of chlorine atoms); 4-CP concentration: 5 mmol per 50 ml methanol solution; sp: the addition of 0.25 equiv. Et_3N *vs.* the number of chlorine atoms per 60 min.

of Pd/AC is low at low temperature, and the TOF is 1.9 min^{-1} at 278 K and 21.7 min⁻¹ at 313 K.

The activity of Pd/MSCN for the HDC of 2,4-DCP is shown in Fig. 4. Considering the conversion of 2,4-DCP to 2-CP and 4-CP, which, in turn, are converted into phenol, occurring on Pd/MSCN, the corresponding TOF is related to the total number of C–Cl bonds transformed and is estimated to be 3.2 min⁻¹ (Table 1), higher than the TOF for the conversion of 4-CP to phenol. This is in contradiction with the fact that the additional Cl substituent is deactivating, ⁹ implying that there may be some factor(s) that will affect the reaction process. The equivalence of the initial 2,4-DCP consumption in the production of 2-CP (5.9 mmol g^{-1} min⁻¹) and phenol (2.7 mmol g^{-1} min⁻¹) to the HDC rate (8.6 mmol g^{-1} min⁻¹) indicates that the reaction proceeds predominantly in a stepwise fashion, converting first to 2-CP and then to phenol. However, a significant amount of 4-CP was formed (with 10% selectivity) on Pd/AC, although its TOF for 2,4-DCP is 1.1 min^{-1} (Table 1).

Taking the solubility of H₂, which has no significant change within the range of 258–313 K, the temperature dependence of the initial reaction rate can be used to generate apparent activation energies. The associated E_a value (with 95% confidence limits; ESI†) of the HDC of 4-CP is 15.6 kJ mol⁻¹ within this temperature range on Pd/MSCN, markedly lower than the value (40.8 kJ mol⁻¹) obtained on Pd/AC (Table 1), and even lower than the value (24.8 kJ mol⁻¹) that has been quoted for the HDC of 4-CP promoted by Pd on carbon cloth over the temperature range 303–358 K.¹⁰ This comparison indicates that nano-sized Pd catalyst supported on MSCN is highly active for the HDC of chlorophenols.

When Et₃N is added in batches of 0.25 equiv. vs. the number of chlorine atoms per 60 min for the HDC of 4-CP, the conversion of 4-CP on Pd/MSCN is promoted greatly within the range of the amount of Et₃N added equivalent to the formed HCl during the HDC, and the TOF at 258 K increases up to 4.9 min⁻¹ from 2.6 min⁻¹. Meanwhile, the corresponding E_a is 15.2 kJ mol⁻¹ within the range of 258–313 K (ESI†), almost as same as the value for the HDC with one batch addition of Et₃N. This phenomenon indicates that Pd atoms could interact with Et₃N so as to be unavailable to

Table 1	Metallic	size and	the catalytic	performance	of hydrodec	hlorination	of chlorophenols
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Sample	D _p /nm	$S_{\rm BET}/{ m m}^2~{ m g}^{-1}$	$V_{t}/m^{3} g^{-1}$	d _{Pd} /nm ^a	$E_{ m a}/{ m kJ}~{ m mol}^{-1b}$	TOF/min ^{-1c}			
						4-CP			2 4 DCB
						258 K	278 K	313 K	2,4-DCP 258 K
MSCN Pd/MSCN Pd/AC	6.5 6.2 3.4	413 345 727	0.53 0.46 0.21	3.2 5.1	15.6 (15.1) 40.8	2.6 (4.9) 0.9 (2.2)	2.8 (6.7) 1.9	25.0 (26.5) 21.7	3.2 (3.3) 1.1 (2.7)

^{*a*} Particle size, calculated from the H₂ chemisorption. ^{*b*} Activation energy for the hydrodechlorination of 4-CP. ^{*c*} The turnover frequency, the number of molecules transformed per surface metal atom and per minute, and the values of the total number of C–Cl bonds transformed in the case of 2,4-DCP; the values within parenthesis obtained by the addition of 0.25 equiv. Et₃N *vs.* the number of chlorine atoms per 60 min for 4-CP, and 0.1 equiv. Et₃N, per 30 min for 2,4-DCP.



Fig. 4 The HDC of 2,4-DCP over 5 wt% Pd/MSCN (Pd : Cl = 1 : 100 mol) at 258 K under ordinary hydrogen pressure (balloon) using Et₃N (1.0 equiv. *vs.* the number of chlorine atoms); 2,4-DCP concentration: 5 mmol per 50 ml methanol solution; sp: the addition of 0.1 equiv. Et₃N *vs.* the number of chlorine atoms per 30 min.

reactant molecules. For 2,4-DCP, however, the batch addition of Et₃N affects the HDC to a small extent, which implies that 2,4-DCP molecules adsorb more competitively on the active sites than Et₃N does. The different effect of Et₃N on the HDC of 4-CP and 2,4-DCP stems from the fact that Pd atoms favor reacting with the electron-deficient benzene ring of 2,4-DCP. By raising the temperature to 278 K, this inhibition effect of Et₃N on the HDC of 2,4-DCP disappears. In the case of the Pd/AC catalyst, the HDC of both 4-CP and 2,4-DCP is inhibited obviously by Et₃N, even at 278 K. Therefore, the Pd/MSCN catalyst, with smaller size Pd particles, interacts more strongly with chlorophenols than Pd/AC, and presents a high activity for the HDC of chlorophenols. Without Et₃N, Pd catalysts will deactivate and the reaction rate lowers quickly, because of the strong adsorption of the formed chlorine species on the active sites. For the recycling study, the HDC reaction of 4-CP was performed maintaining the same reaction conditions as described above, and up to five successive runs

were tested. The TOF for used Pd/MSCN was 2.4 min⁻¹, almost the same as that of the fresh one. The Pd content of the used catalyst, after run 5, was 4.9 wt%. A low Pd leaching amount (less than 0.3% of Pd content of catalyst) was detected by ICP analysis of the catalyst-free liquor. The mesostructure stayed unchanged, and the dispersion of Pd particles was still high (Fig. 2(B)).

In conclusion, a new and stable Pd/MSCN of 3.2 nm Pd particles has been prepared successfully using a simple procedure. For the HDC of chlorophenols at 258 K, this novel Pd catalyst presents higher activity and selectivity than other Pd catalysts so far reported in the literature.

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