p-Aminophenol synthesis in an organic/aqueous system using Pt supported on mesoporous carbons

Kyung-Il Min [a], Jung-Sik Choi [a], Young-Min Chung [b],
Wha-Seung Ahn [a,*], Ryong Ryoo [c], P.K. Lim [d]

[a] *Department of Chemical Engineering, Inha University, Incheon 402-751, Republic of Korea*
[b] *Catalysis Technologies, Corporate R&D Center, SK Corporation, Daejeon 305-712, Republic of Korea*
[c] *Korea Advanced Institute of Science and Technology, Daejeon 305-701, Republic of Korea*
[d] *Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695-7905, USA*

Abstract

The biphasic conversion of nitrobenzene to *p*-aminophenol (PAP) via Pt/C-catalyzed hydrogenation of nitrobenzene and an acid-catalyzed rearrangement of the *N*-phenylhydroxylamine intermediate was studied. The effects of Pt/C catalyst loading, type of carbon support, reaction temperature, acid catalyst concentration, and additives on the reaction rate and PAP selectivity were investigated. At a given catalyst loading, nitrobenzene conversion and PAP selectivity were favored under a high reaction temperature and a high aqueous acid concentration. An increase in Pt/C catalyst loading leads to an increased hydrogenation rate but a lower PAP selectivity. Nitrobenzene conversion and PAP selectivity are both promoted by a small addition of *N,N*-dimethyl-*n*-dodecylamine, which may act as a phase transfer agent or emulsifier. Pt catalysts supported on novel mesoporous carbons – CMK-1 and CMK-3, which have uniform pore diameters of 3 and 4.5 nm – significantly outperform their counterpart supported on activated carbon with micropores. Two percent Pt/CMK-1 shows a catalytic activity equivalent to that of 5% Pt/C, but with significantly better PAP selectivity, i.e., 84% compared to 72%.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Nitrobenzene hydrogenation; *p*-Aminophenol; Biphasic; Mesoporous carbon; Acid-catalyzed rearrangement

1. Introduction

p-Aminophenol (PAP) is an important raw material for the production of acetaminophen, an active ingredient in Tylenol®. The commercial synthesis of PAP [1–4] is typically carried out in a series of continuous stirred tank reactors (CSTRs) in which a biphasic reaction medium is used to accomplish the Pt-catalyzed hydrogenation of nitrobenzene and the acid-catalyzed Bamberger rearrangement of the hydrogenation intermediate product, *N*-phenylhydroxylamine (PHA). The PAP synthesis scheme is shown in Scheme 1.

A biphasic medium is used in PAP synthesis on account of the following three factors: (1) nitrobenzene is essentially insoluble in the aqueous phase; (2) the Pt-catalyzed hydrogenation of nitrobenzene occurs preferentially in the organic phase, in which hydrogen is more soluble; and (3) the Bamberger rearrangement of the PHA intermediate requires an aqueous phase due to the choice of a preferred low-cost acid catalyst, namely, sulfuric acid, which is insoluble in the organic phase. The introduction of an aqueous phase is also designed to allow the polar PHA intermediate to escape from the organic phase and thereby circumvent the major undesired side reaction, namely, the over-reduction of PHA to aniline. In addition to aniline, other side products are also formed in small amounts in PAP synthesis, including *o*-aminophenol (a rearrangement isomer of PAP) and cross-coupling products of amino compounds. Various metal catalysts have been screened for their effectiveness regarding the selective reduction of nitrobenzene to PHA relative to aniline. Mallinckrodt, a commercial PAP producer in the US, employs 5% Pt/C catalyst in its current production process.

Activated carbon has been widely used as a support for precious metal catalysts in the synthesis of fine chemical products [5]. However, the microporous nature of activated

---

* Corresponding author. Tel.: +82 32 860 7466; fax: +82 32 872 0959.
E-mail address: whasahn@inha.ac.kr (W.-S. Ahn).
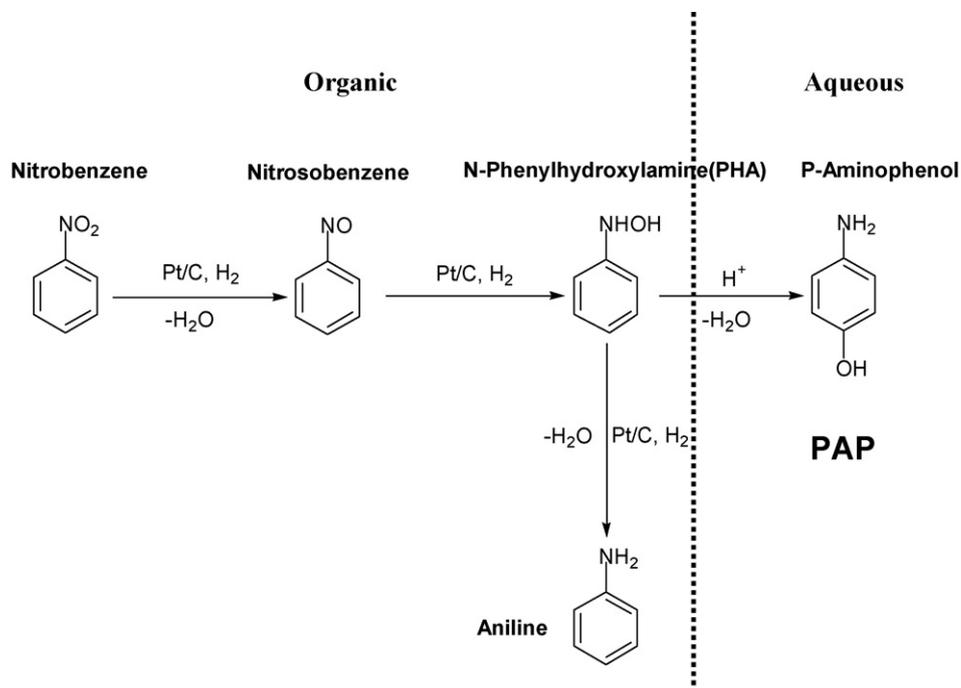
Scheme 1. Biphasic nitrobenzene hydrogenation reactions.

carbon introduces a significant pore resistance to the transport of liquid-phase reactants or product. Pore resistance may significantly affect the selectivity in a liquid-phase reaction that is accompanied by undesirable side reactions, such as the biphasic synthesis of *p*-aminophenol. To reduce the pore resistance for such liquid-phase reactions, it may be desirable to have a support with larger, less tortuous pores than micropores in activated carbon. In this regard, the recent development of a new class of mesoporous carbon molecular sieves, designated as CMK-is [6,7], may provide a low-pore-resistance catalyst support for liquid-phase reactions in general and for the biphasic synthesis of PAP in particular. Being about 10 times larger than the micropores in activated carbon [8–10], the mesopores in CMKs should offer a correspondingly lower pore resistance to a liquid-phase reactant or product [11]. Moreover, the relatively uniform and narrow distribution of the mesopores in CMKs could help optimize the reaction. In the biphasic synthesis of PAP, a CMK catalyst support may provide the added advantage of more intimate contact between the aqueous and organic phases because the CMK carbon is less hydrophobic than the graphitic carbon in activated carbon [12]. Closer contact between the aqueous and organic phases should lend higher selectivity to PAP relative to aniline.

In this work, we investigated the effectiveness of CMK-1 and CMK-3 as catalyst supports for platinum in the biphasic synthesis of PAP, along with a study of various operating parameters in this complex reaction system, such as Pt/C catalyst loading, reaction temperature, acid catalyst concentration, stirring speed, and additives (phase transfer agent, selectivity enhancing agent). CMK-1 has a mean mesopore diameter of 2.7–3.0 nm in a cubic structure, whilst CMK-3 has a larger mean diameter of 4.5 nm in a 2D hexagonal structure. The differences in pore diameters and structures between

CMK-1 and CMK-3 and between CMK-is and activated carbon may lead to performance differences among the supported catalysts in the liquid phase hydrogenation reactions.

2. Experimental

2.1. Preparation of Pt catalysts supported on mesoporous carbon

A mesoporous molecular sieve with an ordered carbon framework designated as CMK-1 was prepared using the procedure of Ryoo et al. [6]. Five grams of dehydrated mesoporous silica in cubic (Ia3d) phase, MCM-48, was well mixed with 6 g of sucrose and 0.7 g of pure sulfuric acid in 30 g of distilled water. The resulting viscous mixture was dried at 373 K in an oven and the oven temperature was subsequently increased to 433 K. The silica host containing partially decomposed sucrose after heating was contacted again with an aqueous solution comprised of 3.75 g of sucrose and 0.4 g of pure sulfuric acid in 30 g of distilled water. After heating to 433 K again, the powder was further heated to 1073–1373 K under vacuum using a fused quartz tube equipped with fritted disks in a vertical furnace. Finally, the carbon-silica composite was washed twice using HF solution at 373 K to remove the silica. The carbon product was then filtered and dried for subsequent use.

Another mesoporous carbon with an ordered carbon framework designated as CMK-3 was synthesized in a similar manner to that employed for the synthesis of CMK-1, except that SBA-15 was used as a silica template used instead of MCM-48 [7].

The mesopore structures of the prepared samples were confirmed by X-ray diffraction analysis using Ni-filtered Cu Kα

radiation (Philips, PW-1700), and the morphology of the samples was examined by SEM (Hitachi, X-650) and TEM (Philips, CM 200). The specific surface area and average pore diameters were determined by N_2 physisorption with the BET method at liquid nitrogen temperature using a Micromeretics ASAP 2000 automatic analyzer. Pt supported on CMK-1 and CMK-3 with a catalyst loading of 1–5 wt% was prepared by the incipient wetness technique using H_2PtCl_6 dissolved in acetone as the metal precursor, which was reduced to platinum under a hydrogen atmosphere at 473 K for 2 h. The metal dispersions were measured using H_2 chemisorption at room temperature.

2.2. Biphasic conversion of nitrobenzene to p-aminophenol

The conversion of nitrobenzene to *p*-aminophenol was carried out at 353 K under a hydrogen atmosphere at atmospheric pressure in a biphasic mixture consisting of nitrobenzene and aqueous sulfuric acid. Pt catalysts supported on activated carbon (commercially available from Aldrich) and mesoporous carbon (prepared as described above) were both used as the hydrogenation catalyst. Pt supported on activated carbon was used in parametric studies, whilst Pt supported on mesoporous carbon was used to show the effect of pore resistance variation on PAP selectivity. The reactor arrangement equipped with a gas burette is basically identical to that described in our earlier work [13].

The typical reaction procedure is as follows: the reactor was charged with 0.04 mol (4.924 g) of nitrobenzene, 60 g of 10% aqueous sulfuric acid, and the desired amounts of catalyst and any additive (DMSO, *N,N*-dimethyl-*n*-dodecylamine). The reactor was placed in a thermostated water-bath and purged with hydrogen for about 10 min and then allowed to equilibrate to the set temperature. Following temperature equilibration, the stirrer was started. The hydrogen uptake of the reaction under 1 atm total pressure was monitored continuously by means of a manometer unit until the reaction reached completion in about 4 h. Upon completion of the reaction, the reaction product mixture was poured into a separating funnel and left standing overnight to achieve complete separation of the aqueous and organic phases. Samples of the aqueous phase were then taken, diluted, and analyzed using a high performance liquid chromatograph (SDV30PLUS, Young Lin) equipped with a 25-cm C_{18} column. The eluent was a 50:50 mixture of methanol and aqueous 0.1 M KH_2PO_4 buffer at a flow rate of 1 mL/min.

3. Results and discussion

3.1. Effects of biphasic reaction parameters on the PAP synthesis

Fig. 1(a) shows H_2 uptake profiles of the nitrobenzene hydrogenation at different catalyst loadings (10–30 mg) of a commercial Pt (5%)/C catalyst purchased from Aldrich. The effect of catalyst loading on the nitrobenzene conversion and PAP selectivity is shown in Fig. 1(b). Nitrobenzene conversions were measured both by H_2 uptake amounts and by a product analysis using HPLC, and the results showed good agreement.
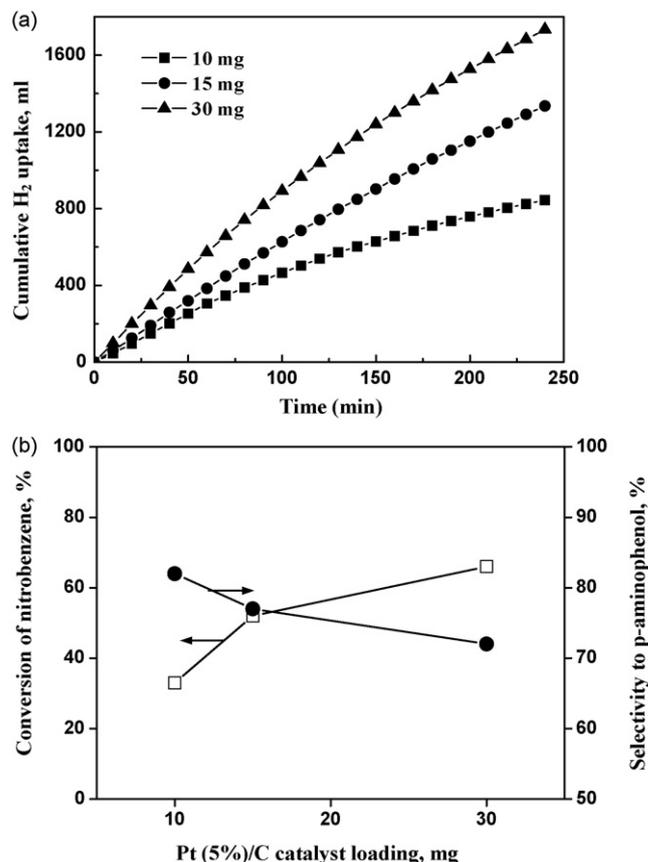

Fig. 1. (a) Cumulative H_2 uptake profiles of nitrobenzene hydrogenation and (b) nitrobenzene conversion and selectivity to PAP with different catalyst loadings (reaction conditions: 40 mmol nitrobenzene, 10% H_2SO_4 solution 60 g, 353 K, 1 atm).

Nitrobenzene conversion was found to increase almost linearly with the catalyst loading, but the PAP selectivity decreased from 82 to 72% when the catalyst loading increased from 10 to 30 mg of Pt (5%)/C. Because the 30 mg catalyst loading gave the highest PAP yield (conversion times selectivity), it was chosen as the standard catalyst loading in all subsequent runs. The decrease in PAP selectivity with an increase in catalyst loading is in accordance with the predicted result and may be rationalized in terms of the increased catalyst loading favoring hydrogenation of the intermediate product, *N*-phenylhydrox-yamine, at the expense of the acid-catalyzed Bamberger rearrangement reaction.

The reaction was also studied at different temperatures over a temperature range of 313–353 K. Fig. 2(a and b) shows that both nitrobenzene conversion and PAP selectivity increase as the reaction temperature increases from 313 to 353 K. However, the rate of the increase in nitrobenzene conversion and the cumulative hydrogen uptake in the 4 h reaction decreases steadily as the temperature increases. The results may be explained in terms of a rapid increase in the vapor pressure of water with rising temperature, which brought on a corresponding drop in the hydrogen partial pressure in the vapor phase. The total pressure was kept at 1 atm. Both the hydrogenation and the Bamberger rearrangement reaction rate constants would increase with the reaction temperature, but the rapid drop
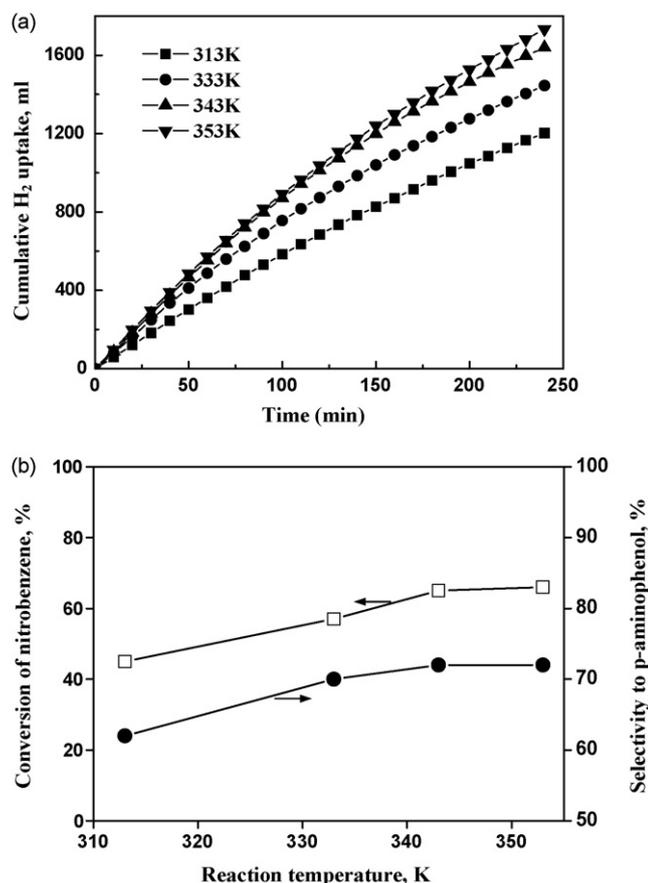
Fig. 2. (a) Cumulative H_2 uptake profiles of nitrobenzene hydrogenation and (b) nitrobenzene conversion and selectivity to PAP at different reaction temperatures (reaction conditions: 40 mmol nitrobenzene, 10% H_2SO_4 solution 60 g, 30 mg catalyst, 1 atm).
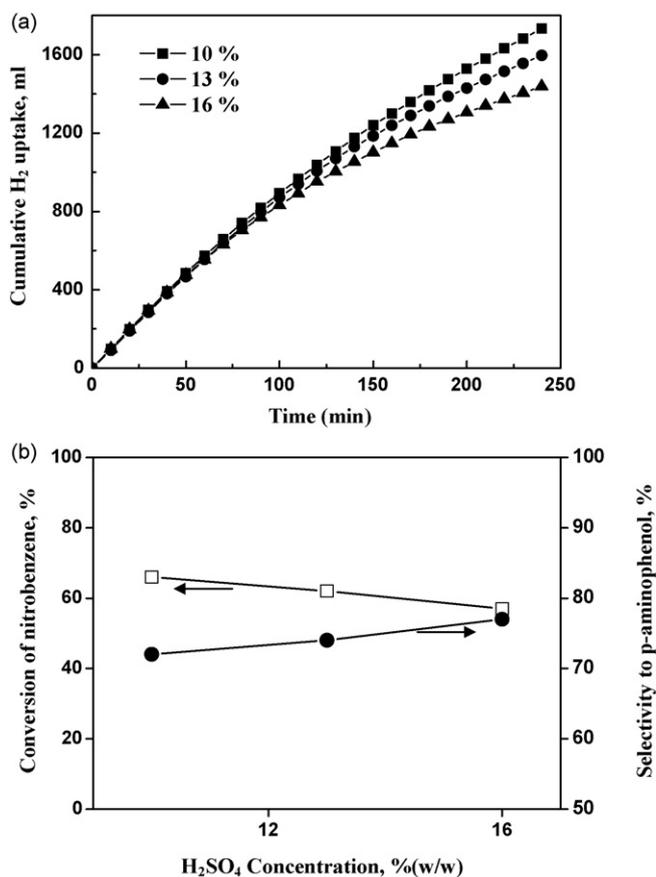
Fig. 3. (a) Cumulative H_2 uptake profiles of nitrobenzene hydrogenation and (b) nitrobenzene conversion and selectivity to PAP at different H_2SO_4 concentrations (reaction conditions: 40 mmol nitrobenzene, H_2SO_4 solution 60 g, 30 mg catalyst, 353 K, 1 atm).

in hydrogen partial pressure would more than offset the higher hydrogenation rate constants to give an increasingly lower cumulative hydrogen uptake value. Thus, the increase in reaction temperature brought on a higher Bamberger rearrangement rate constant and a concomitant decrease in the hydrogen partial pressure, and both effects contributed to an increase in PAP selectivity. The sharp drop in PAP selectivity at temperatures below 343 K indicates that the Bamberger rearrangement reaction in 10% aqueous sulfuric acid solution does not proceed efficiently at temperatures below 343 K.

The effects of the aqueous sulfuric acid concentration on the nitrobenzene conversion rate and PAP selectivity were studied at sulfuric acid concentrations in a 10–16 wt% range. Fig. 3(a) shows the H_2 uptake profiles during the reaction and Fig. 3(b) shows the nitrobenzene conversion in the 4 h reaction and PAP selectivity. An increase in acid concentration leads to an increase in PAP selectivity, which is expected in light of the catalytic role of the acid in the Bamberger rearrangement reaction. The progressive decrease in the hydrogen uptake above 10 wt% acid concentration may be ascribed to the selective conversion of the PHA intermediate to PAP at the expense of aniline.

Many chemical additives of amines and sulfur compounds were screened and found to promote selectivity to PHA relative to aniline, but the overall hydrogenation rates were also found to be impractically low, since most of them easily poison the Pt/ C catalyst [1]. Among the additives, however, dimethylsulfoxide (DMSO) was reported to be promising in terms of enhancing PHA yield without significantly reducing the total hydrogenation rate. Thus, the effect of DMSO concentration on PAP selectivity was investigated in this work. As shown in Fig. 4(a), the introduction of DMSO resulted in a substantial reduction in hydrogen uptake values, whilst PAP selectivity enhancement was noticeable, as illustrated in Fig. 4(b). By the addition of 15 mg of DMSO, the selectivity to PAP increased dramatically from 72% (without DMSO) to 88%. DMSO promotes an increase of the selectivity to PAP by inhibiting the reduction of PHA to aniline [1]. This PAP enhancement was, however, accompanied by a reduction in nitrobenzene conversion from 66 to 47%. A further increase in the amount of DMSO produced little improvement in PAP selectivity, whilst further decreases in the hydrogenation rates were observed.

The effect of N,N-dimethyl-n-dodecylamine as a possible phase transfer agent or emulsifier in the biphasic conversion of nitrobenzene to p-aminophenol was investigated. The influences of the additive on nitrobenzene conversion and PAP selectivity are shown in Fig. 5(a and b). It is seen that a modest
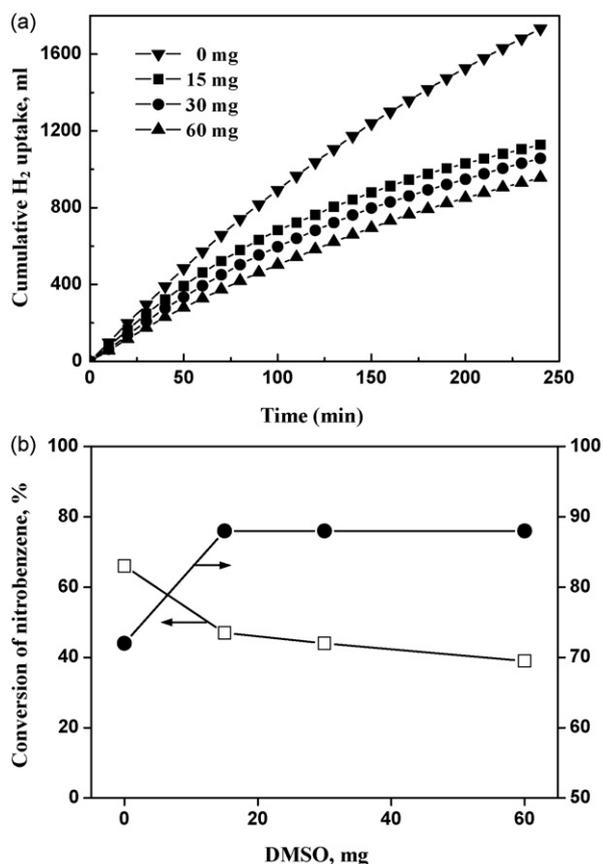
Fig. 4. (a) Cumulative H_2 uptake profiles of nitrobenzene hydrogenation and (b) nitrobenzene conversion and selectivity to PAP with different amounts of DMSO (reaction conditions: 40 mmol nitrobenzene, 10% H_2SO_4 solution 60 g, 30 mg catalyst, 353 K, 1 atm).

Fig. 5. (a) Cumulative H_2 uptake profiles of nitrobenzene hydrogenation and (b) nitrobenzene conversion and selectivity to PAP with different amounts of phase transfer agent (reaction conditions: 40 mmol nitrobenzene, 10% H_2SO_4 solution 60 g, 30 mg catalyst, 353 K, 1 atm).

0.02 g addition of N,N-dimethyl-n-dodecylamine brought about significant increases in both the nitrobenzene conversion (from 66 to 75%) and the PAP selectivity (from 72 to 76%). With greater additions of the additive, the nitrobenzene conversion and PAP selectivity leveled off at around 92 and 82%, respectively. The concurrent increases in nitrobenzene conversion and PAP selectivity in the presence of N,N-dimethyl-n-dodecylamine are noteworthy in that with most other additives, such as DMSO, the effects on nitrobenzene conversion and PAP selectivity tend to be opposing rather than parallel or reinforcing. The finding on N,N-dimethyl-n-dodecylamine may carry industrial significance. It suggests that N,N-dimethyl-n-dodecylamine may act as a phase transfer agent or emulsifier in the biphasic reaction system.

3.2. Performance of Pt/mesoporous carbons (CMK-1, CMK-3) versus commercial Pt/C

Before presenting the kinetic data on Pt supported on mesoporous carbons with respect to the biphasic conversion of nitrobenzene to p-aminophenol, we give some physical characterization data on the mesoporous carbon supports. Fig. 6(a) shows the XRD patterns of the mesoporous carbon CMK-1. Upon removal of the MCM-48 silica template by
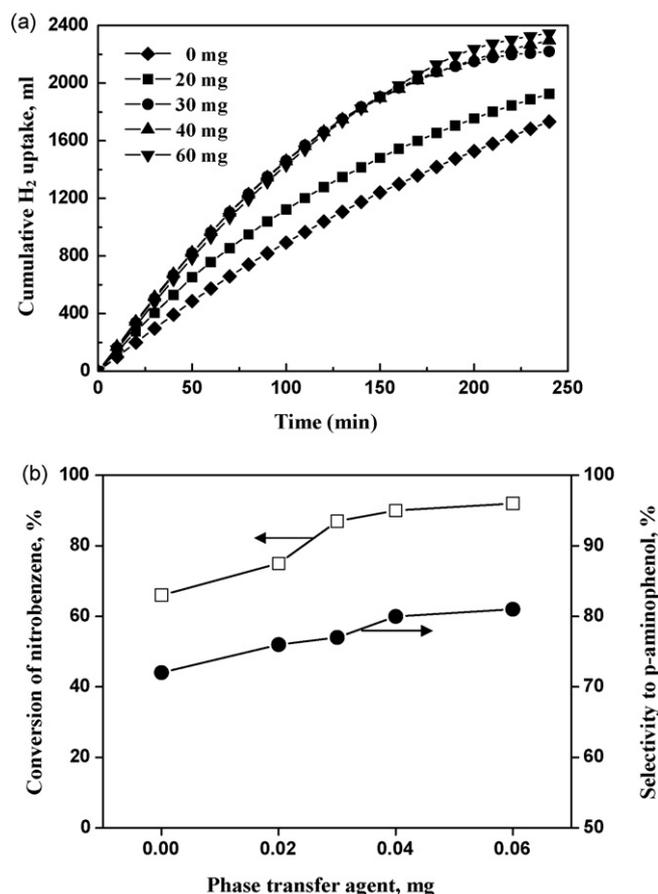
HF, two distinct (1,1,0) and (2,1,0) peaks appeared, reflecting systematic transformation of the pore-filled carbon to a new ordered cubic structure [6]. An argon adsorption–desorption isotherm at 87 K and the corresponding pore-size distribution analysis for CMK-1 gave a sharp inflection characteristic of the capillary condensation with an average pore diameter of 3.0 nm, as shown in Fig. 6(b). The total pore volume was 1.1 cm³/g and the BET surface area of the sample was ca.1350 m²/g. The ordered mesopore structure of CMK-1 was confirmed by a TEM micrograph image and the SEM showed that the porous carbon particles retain the truncated rhombic dodecahedral shape of the MCM-48 template (not shown). The extremely small Pt clusters supported on the CMK-1 carbon are barely visible on the TEM micrograph shown in Fig. 7(a), whereas Pt clusters greater than 2 nm in diameter are observed in the case of the Pt/C sample shown in Fig. 7(b).

The XRD patterns of the mesoporous carbon CMK-3 prepared from SBA-15 silica is shown in Fig. 8(a); the peaks can be assigned to (1,0,0), (1,1,0), and (2,0,0) diffractions of a hexagonal structure [7]. The nitrogen adsorption–desorption isotherm at 77 K and the corresponding pore-size distribution analysis for CMK-3 indicate a narrow pore-size distribution centered at 4.5 nm, as shown in Fig. 8(b). The total pore volume
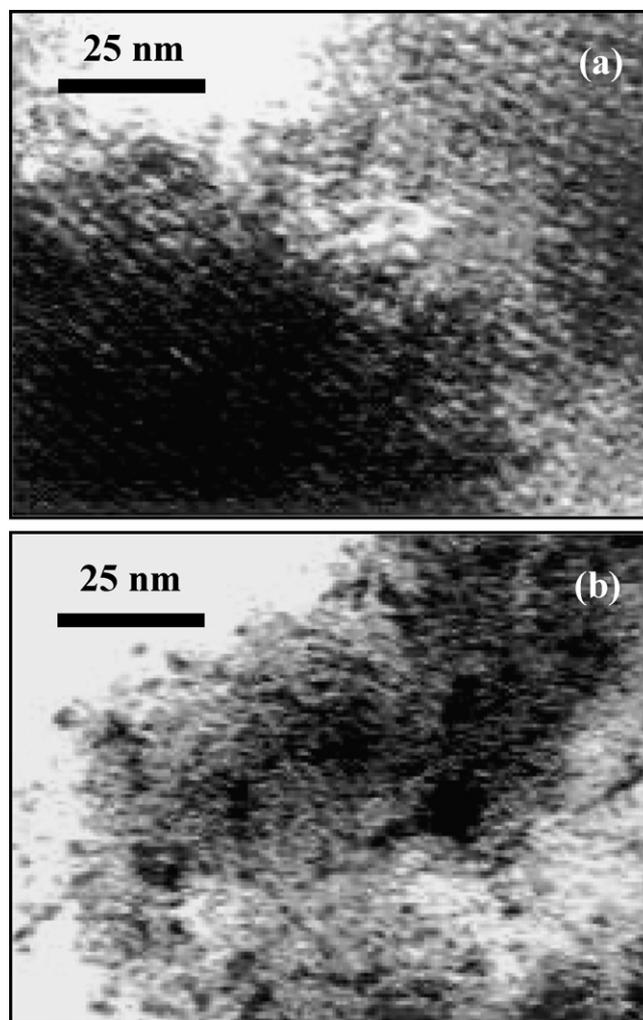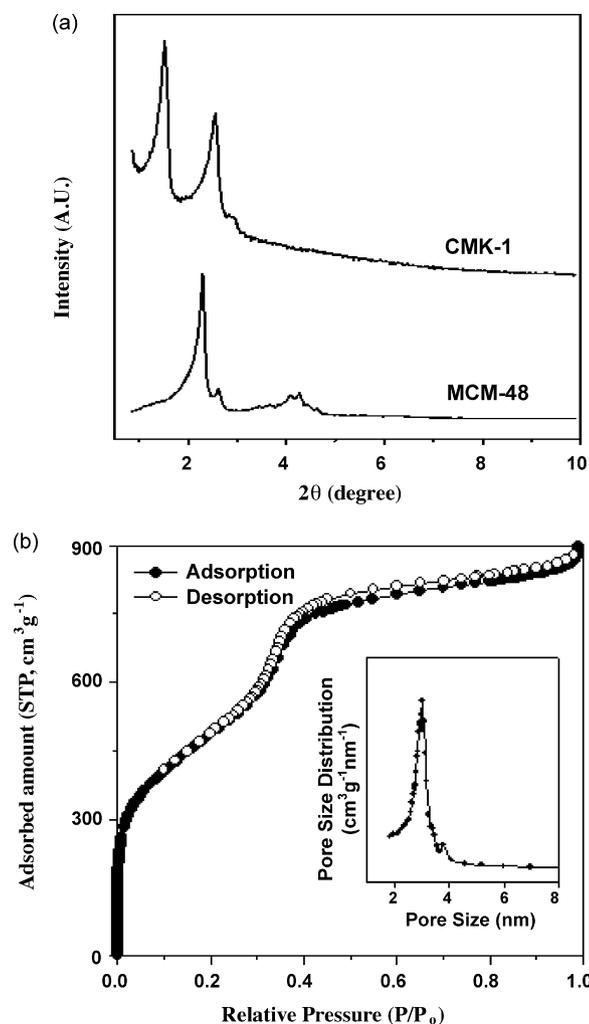
Fig. 6. (a) XRD patterns of CMK-1 and its silica template MCM-48 and (b) argon adsorption–desorption isotherm of CMK-1.

Fig. 7. TEM images of (a) 5% Pt/CMK-1 and (b) 5% Pt/C.

was 1.3 cm^3/g and the BET surface area of the sample was ca.1520 m^2/g.

Fig. 9 shows H$_2$ uptake profiles of the reaction runs with 1, 2, and 5 wt% of Pt supported on CMK-1 and 5% of Pt supported on activated carbon. The corresponding steady-state H$_2$ uptake rates over the first 100 min of the reaction, the nitrobenzene conversion in the 4 h reaction, and the PAP selectivity are summarized in Table 1. It is seen that the nitrobenzene conversion increased from 53 to 81% as Pt loading was increased from 1 to 5% on CMK-1, accompanied by decreased selectivity to PAP from 88 to 72%. The 2% Pt/CMK-1 showed a

Table 1
Performance comparison of Pt/CMK-1 with commercial Pt (5%)/C

Catalyst	Conversion of nitrobenzene (%)	H$_2$ uptake rate (mL/min)	Selectivity to PAP (%)
Pt (5%)/C	66	10.0	72
Pt (1%)/CMK-1	53	7.4	88
Pt (2%)/CMK-1	67	11.0	84
Pt (5%)/CMK-1	81	15.6	72

Reaction conditions: 40 mmol nitrobenzene, 10% H$_2$SO$_4$ solution 60 g, 30 mg catalyst, 353 K, 1 atm.

catalytic activity equivalent to that of commercially available 5% Pt/C, but with significantly improved PAP selectivity, i.e., 84% compared to 72%. At the same 5% Pt-metal loading, the steady-state H$_2$ uptake rate for Pt/CMK-1 was 56% higher than that of commercial 5% Pt/C, with the total H$_2$ uptake being ca. 20% higher.

Selected H$_2$ chemisorption studies on these catalyst samples indicated a sorption stoichiometry ratio of about 1.5 H/Pt for 2% Pt/CMK-1, which corresponds to a platinum dispersion remarkably close to 100%. The high level of Pt dispersion was maintained up to 5 wt% Pt loading, which gave a sorption stoichiometry ratio of 1.3 H/Pt. In contrast, 5% Pt/C (Aldrich) yielded a sorption stoichiometry ratio of only 0.8 H/Pt. Evidently, the improved performance of Pt/CMK-1 relative to Pt/C is due in part to its substantially higher level of Pt dispersion. The difference in Pt dispersion was also clearly evident in Fig. 7.

The effect of stirring speed was studied with 5% Pt/C, 2% Pt/CMK-1, and 2% Pt/CMK-3; the results are summarized in Table 2. It is seen that nitrobenzene conversion and PAP selectivity both increase with stirring speed for all three supported catalysts, but the PAP selectivity increase was more
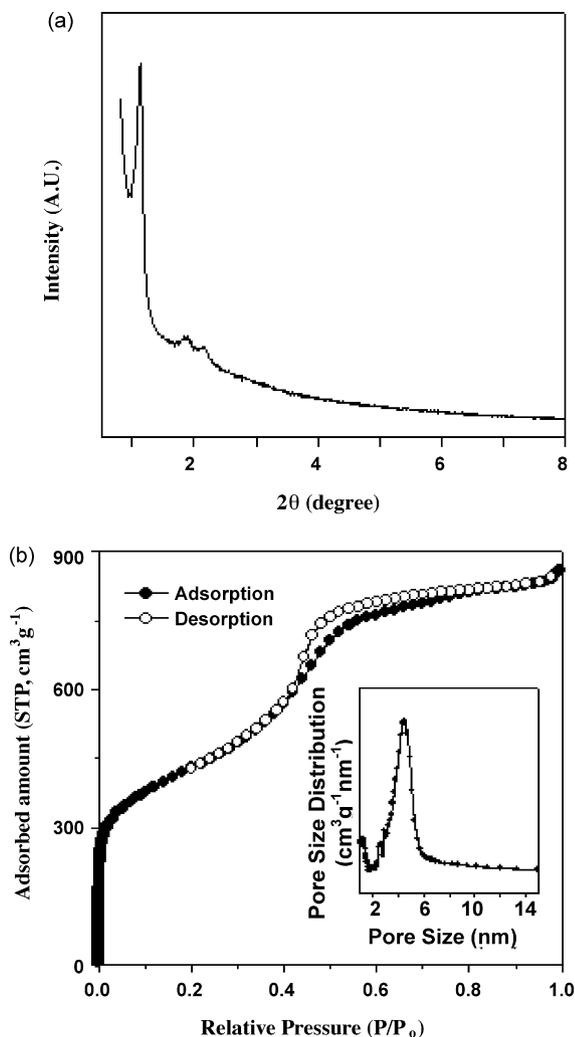
(a)

(b)

Fig. 8. (a) XRD pattern and (b) nitrogen adsorption–desorption isotherm of CMK-3.

Fig. 9. Cumulative H_2 uptake profile of nitrobenzene hydrogenation with different Pt loadings of CMK-1 (reaction conditions: 40 mmol nitrobenzene, 10% H_2SO_4 solution 60 g, 30 mg catalyst, 353 K, 1 atm).

having larger pore size, pore volume, and surface area, performs better than Pt/CMK-1 at 500 rpm, under which hydrogen transport to the catalyst active sites and transport of PHA to the aqueous phase are more difficult.

4. Conclusions

The conversion of nitrobenzene to *p*-aminophenol via Pt/C-catalyzed hydrogenation and acid-catalyzed rearrangement in a biphasic reaction scheme was studied. The biphasic reaction was favored under a high reaction temperature (over the 313–353 K range) and a high aqueous acid concentration (over the 10–16 wt% range). An increase in Pt/C catalyst loading resulted in an increased hydrogenation rate but PAP selectivity decreased as conversion increased. DMSO promoted selectivity to PAP by inhibiting the reduction of PHA to aniline; however, this PAP enhancement was accompanied by a reduction in nitrobenzene conversion. Nitrobenzene conversion and PAP selectivity were both promoted by a small addition of *N,N*-dimethyl-*n*-dodecylamine, which may act as a phase transfer agent or emulsifier.

Pt catalysts supported on novel mesoporous carbons – CMK-1 and CMK-3, which have uniform pore diameters of 3 and 4.5 nm – significantly outperform their counterparts supported on activated carbon, which is characterized by micropores of an average diameter of 0.3 nm. Two percent Pt/CMK-1 shows a catalytic activity equivalent to that of 5% Pt/C, but with significantly improved PAP selectivity. These enhancements in

pronounced for 2% Pt/CMK-1 and 2% Pt/CMK-3 as the stirring speed was increased from 500 to 900 rpm. Evidently, with reduced pore resistance in Pt/CMK-1 and Pt/CMK-3, a higher stirring speed promotes interfacial mixing between the organic and aqueous phases. In addition, the mesopore structure with a hydrophilic surface in CMKs results in more efficient transportation of PHA to the aqueous phase and raises the PAP selectivity more than in the case of Pt/C.

The results in Table 2 also show that Pt/CMK-1 and Pt/CMK-3 essentially provide comparable performance at 700 and 900 rpm conditions in terms of PAP yield. However, Pt/CMK-3,
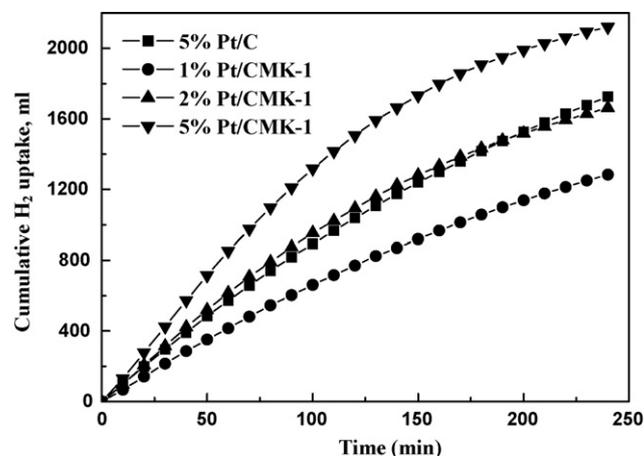
Table 2
Catalytic performance of Pt (2%)/CMK-1, -3 for nitrobenzene hydrogenation at different stirring speeds

Catalyst	Pt (5%)/C commercial		Pt (2%)/CMK-1		Pt (2%)/CMK-3	
rpm	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
900	66	72	67	84	73	81
700	62	69	62	76	66	73
500	28	60	27	61	36	64

Reaction conditions: 40 mmol nitrobenzene, 10% H_2SO_4 solution 60 g, 30 mg catalyst, 353 K, 1 atm.

activity are believed to be a consequence of an increased metal dispersion and a concurrent reduction in pore diffusion resistance in the mesoporous structure of CMK-1 and CMK-3. The results provide confirmation of some of the expected advantages of using mesoporous carbon as a catalyst support in liquid-phase reactions.

Acknowledgements

References

[1] P.N. Rylander, I.M. Karpenko, G.R. Pond, Ann. N.Y. Acad. Sci. 172 (1970) 266.

[2] S.L. Karwa, R.A. Rajadhyaksha, Ind. Eng. Chem. Res. 26 (1987) 1746.

[3] P.N. Rylander, I.M. Karpenko, G.R. Pond, U.S. Patent 3,715,397 (1973).

[4] P.N. Rylander, Catalytic Hydrogenation in Organic Synthesis, Academic Press, New York, 1979, p. 325.

[5] L.R. Radovic, C. Sudhakar, in: H. Marsh, E.A. Heintz, F. Rodriguz-Reinoso (Eds.), Introduction to Carbon Technologies, University of Alicante, Spain, 1997, p. 103.

[6] R. Ryoo, S.H. Joo, S. Jun, J. Phys. Chem. B 103 (1999) 7743.

[7] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 122 (2000) 10712.

[8] Z. Guo, G. Zhu, B. Gao, D. Zhang, G. Tian, Y. Chen, W. Zhang, S. Qiu, Carbon 43 (2005) 2344.

[9] W.S. Ahn, K.I. Min, Y.M. Chung, H.K. Rhee, S.H. Joo, R. Ryoo, Stud. Surf. Sci. Catal. 135 (2001) 313.

[10] P. Dibandjo, F. Chassagneux, L. Bois, C. Sigala, P. Miele, J. Mater. Chem. 15 (2005) 1917.

[11] A.B. Stiles, Catalyst Supports and Supported Catalysts, Butterworth Publishers, Boston, 1987, p. 136.

[12] T.W. Kim, I.S. Park, R. Ryoo, Angew. Chem. Int. Ed. 42 (2003) 4375.

[13] Y.M. Chung, W.S. Ahn, P.K. Lim, J. Catal. 173 (1998) 210.