New Direct Hydroxylation of Benzene with Oxygen in the Presence of Hydrogen over Bifunctional Palladium/Platinum Catalysts

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Dedicated to Professor Roger A. Sheldon on the occasion of his 60th birthday.

Abstract: Benzene can be hydroxylated directly to phenol with oxygen in the presence of hydrogen over Pt/Pd containing acid catalysts such as zeolites (BEA, MOR, FER, MFI), acid resins such as Amberlyst, or Nafion/silica composites. The best results were obtained over Nafion/silica composites. As main side products hydroquinone and catechol were found. Various reaction parameters and catalyst preparation methods were optimised.

Keywords: benzene; direct hydroxylation; Nafion-silica composites; oxygen; phenol

Introduction

The conventional industrial process for the production of the important intermediate phenol, the Hock process, is based on the indirect oxidation of benzene via cumene.[1] However, this 3-step process has several disadvantages, the main ones being the formation of acetone as an inevitable couple product, the production of polluted waste-water as well as a low overall yield. The direct hydroxylation of benzene has therefore been attracting great interest and is one of the more challenging subjects in catalysis research at the present time.

Currently, there are several processes for the direct introduction of a hydroxy group on an aromatic ring under investigation. An example is the direct gas-phase oxidation with molecular oxygen or air; unfortunately, this process leads to very low phenol selectivities because of opening of the benzene ring, thus forming maleic acid, or because of the deep oxidation to CO_2. The oxidation of benzene over Cu or Cu/Pd containing catalysts in an acidic medium results in low benzene conversions, and the catalysts have to be regenerated under hydrogen.[2,3] Better results were obtained using molecular oxygen in the presence of palladium and heteropolyacids.[4,5] Another alternative is the use of N_2O over H-[Fe]-MFI or steamed H-[Al]-MFI zeolites. The surface α-oxygen, which is formed upon decomposition of N_2O, was found to react with benzene to phenol, affording conversions of *ca.* 30% and selectivities of over 95%.[6–9] The catalytic activity seems to be related to the Lewis acidity of the catalysts, which unfortunately deactivate rapidly due to strong coking.[9]

Researchers of the Tosoh Company[10–12] used among others Pd/SiO_2, or Pd or $Pt/V_2O_5/SiO_2$ based systems in acetic acid, and Tatsumi et al.[13] investigated the use of palladium containing TS-1 in strong acids such as hydrochloric acid in the direct oxidation of benzene with oxygen and hydrogen. More recently Miyake et al.[14] investigated the influence of the addition of transition metal salts on the performance of a Pt/SiO_2 based catalyst, and found the addition of vanadium compounds to result in the most active systems. In these systems the oxidant hydrogen peroxide is probably formed *in situ* from the oxygen/hydrogen mixture. Miyake et al.[14] proposed this to be followed by a Fenton-type mechanism, in which the hydrogen peroxide produces hydroxyl radicals. Over all of these catalysts only very low phenol yields were obtained, and in all systems homogeneous acids were used, which have to be removed or neutralised after the reaction.

Here, the use of Pd and Pt containing heterogeneous acid catalysts such as zeolites and Nafion-silica composites for the direct hydroxylation of benzene with an O_2-H_2 gas mixture was investigated. The influence of various reaction parameters and the catalytic potential of the Nafion based catalysts were investigated more closely. Nafion is an ionomer with a chemically resistant polymeric backbone and highly acidic sulphonic groups, and has both hydrophobic ($-CF_2CF_2-$) as well as hydrophilic ($-SO_3H$) regions.[15,16] Nafion/silica nanocomposites, produced by the entrapment of nanometer sized Nafion resin particles in a highly porous silica network,

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seem particularly promising as replacements for hazardous conventional strong homogeneous acids such as HCl or H_2SO_4. The ease of separation, reusability and the prevention of salt formation from a neutralising step are further advantages of heterogeneous catalysts.

Results and Discussion

First, a catalyst screening was done, loading a number of different acidic catalysts with palladium and platinum. From earlier experience on the direct epoxidation of propene over Pd/Pt containing TS-1 based systems, it was known that a combination of these noble metals was able to produce hydrogen peroxide *in situ*,[17–19] which was expected to be the intermediate in the direct hydroxylation of benzene. To prevent the use of homogeneous acids as done by Miyake et al.[11,12,14] and Tatsumi et al.[13] different heterogeneous acidic carriers were chosen as the carrier for the noble metals.

The results of the screening experiments are presented in Table 1, alongside the compositions of the several catalysts. Clearly, the best results were obtained over the Nafion/silica composite SAC 13 containing 13% of Nafion, with a maximum phenol yield of 4.25%. In comparison, the highest rate of phenol formation Miyake et al.[12] found was 1.159 mmol/h over $Pt/V_2O_5/SiO_2$, starting from 20 mL of benzene, which would result in a phenol yield after 3 h of *ca.* 1.55%. In a more recent paper, in which Miyake et al.[14] investigated the influence of the addition of transition metals on the phenol formation, reaction rates of up to 0.412 mmol/h were reported, which would result in phenol yields after 3 h of up to only 0.55%. Tatsumi et al.,[13] who investigated the use of palladium containing [Al,Ti]-MFI, found a maximum formation of 96 μmol phenol from 10 mL of benzene after 3 h, i.e., a maximum yield of only 0.86%. Besides these low benzene conversions to phenol these reaction systems suffer from the use of considerable amounts of acids; Miyake et al.[11,12,14] added acetic acid (25 mL to 20 mL benzene), whereas Tatsumi et al.[13] added HCl (5 mL HCl solution to 10 mL of benzene) to the reaction mixture, which would have to be removed after the reaction, resulting in an extra process step, and possible salt formation, which, from an environmental point of view, is undesirable. In contrast, no homogeneous acids were added to the reaction systems investigated here. As side products, resulting from the further oxidation of phenol, hydroquinone, quinone and catechol were found.

In comparison, over the acid zeolites H-FER, H-MOR, H-MFI and H-BEA only small amounts of phenol were formed. The lower rates of phenol formation over these materials might be due to the diffusional constraints caused by the microporosity of the zeolites. To investigate if a stronger acidity would increase the phenol yield, one of the zeolitic materials, the ferrierite, was sulphated with $(NH_4)_2SO_4$ and H_2SO_4. According to Corma et al.[20] and Brown et al.[21] such a sulphation results in the formation of superacid sites. Upon sulphation the amount of phenol formed did indeed increase, showing that the acidity of the catalyst had a strong influence on the activity; over the strong acidic resin Amberlyst there also was a relatively high rate of phenol formation.

The conversion to phenol was also found to be dependent on the amounts of palladium and platinum on the catalysts. Over the BEA and FER type carriers the highest amounts of phenol were formed over the materials with comparably low amounts of Pd and Pt. An increase in the noble metal loading caused a decrease in the phenol yield.

As the best results were obtained over a Nafion/silica composite this type of material was investigated more closely. The catalytic performance of the Pd/Pt/Nafion-silica catalyst could very well be a result of the very strong acidic strength of the sites, combined with the hydrophobic/hydrophilic properties of this material. First, the Nafion content of the composites was varied. The SAC 13 based catalyst (13% Nafion) was clearly superior compared to the other composites materials (see Figure 1). The higher activity of this material

Table 1. Catalyst compositions and results of the catalyst screening experiments for the hydroxylation of benzene with O_2 and H_2. Conditions: batch wise, 1000 kPa O_2, 1000 kPa H_2, 1000 kPa N_2. Catalyst reduction: 5 vol. % H_2 at 150 °C.

carrier	metal content [wt. %]	Si/Al	phenol [mmol]
$Nafion/SiO_2$ SAC 13	0.6% Pd + 0.6% Pt		1.0881
BEA	2.8% Pd + 1.8% Pt	12.5	0.0035
BEA	0.4% Pd + 0.4% Pt	12.5	0.0216
FER	3.0% Pd + 0.3% Pt	9.0	0.0085
FER	0.6% Pd + 0.4% Pt	9.0	0.0846
FER, $(NH_4)_2SO_4$	0.5% Pd + 0.4% Pt	9.0	0.0433
FER H_2SO_4	0.4% Pd + 0.2% Pt	9.0	0.2032
MOR	1.6% Pd + 0.5% Pt	7.5	0.0088
MFI	2.4% Pd + 1.2% Pt	30.0	–
Amberlyst 15	1.0% Pd + 0.01% Pt		0.0619
Amberlyst 15	2.5% Pd + 1.2% Pt		0.2274

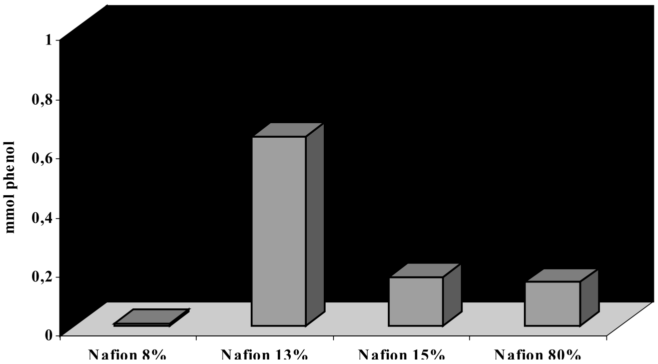

Figure 1. Influence of the Nafion content in the composite on the phenol formation. Conditions: solvent 15 g methanol + 5 g H_2O, batchwise, 1000 kPa O_2, 1000 kPa H_2, 1000 kPa N_2. Catalyst: Pd/Pt/Nafion/SiO_2, 0.5 wt. % Pd + 0.5 wt. % Pt, reduced under 5 vol. % H_2.

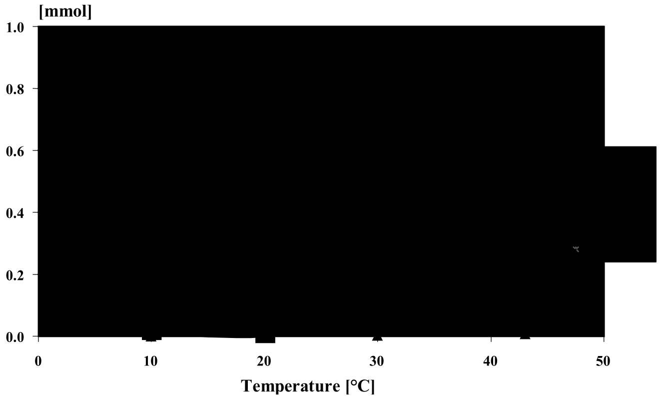

Figure 2. Influence of the reaction temperature on the catalytic performance; HQ: hydroquinone, Q: quinone, CAT: catechol. Conditions: semi-continuous, 1.3 L/h H_2, 1.3 L/h O_2, 1.4 L/h N_2, 700 kPa. Catalyst: Pd/Pt/SAC 13, 0.5 wt. % Pd + 0.5 wt. % Pt, reduced under 5 vol. % H_2.

Table 2. Influence of the solvent on the phenol formation. Conditions: batch wise, 1000 kPa O_2, 1000 kPa H_2, 1000 kPa N_2. Catalyst: Pd/Pt/SAC 13, 0.5 wt. % Pd + 0.5 wt. % Pt, reduced under 5 vol. % H_2.

solvent	yield [%]	selectivity[a] [%]
no solvent	< 0.1	100
water	4.2	41
water/methanol (3:1)	4.2	56
water/methanol (1:3)	2.5	54
methanol	0.5	70
ethanol	0.2	100
2-propanol	< 0.1	100
acetone	–	–

[a] Based on organic products in the liquid phase.

compared to the other composites was not a result of the BET surface area or the cumulative pore volume, as the surface area ranged from 15 m^2/g for SAC 80 to 158 m^2/g for SAC 15 (pore volume 36 cm^3/g), 92 m^2/g for SAC 13 (pore volume 21 cm^3/g), up to 270 m^2/g for SAC 5. The better catalytic performance of the SAC 13 based catalyst was probably caused by a higher dispersion of the Nafion resin over the silica matrix, resulting in an optimal distribution of the strong acid sulphonic groups over the catalyst for the hydroxylation.

Previous experience on the direct epoxidation of propene with H_2/O_2 over TS-1 based systems showed a higher propylene oxide yield upon the addition of alkali halides such as NaBr to the reaction mixture.[17–19] Therefore, the influence of the addition of NaBr on the phenol yield was investigated. The addition of small amounts of NaBr resulted in an increase in the phenol yield. Without NaBr yields of only 0.5% were obtained, whereas the addition of 0.5 mmol/L NaBr resulted in yields of up to 4.2%. This could be a result of a promoting or stabilising effect of the bromide ion, as was also reported by Gosser[22–24] for the preparation of hydrogen peroxide over palladium containing catalysts. The addition of higher amounts of NaBr resulted in a strong decrease of the phenol yield: upon addition of 60 mmol/L NaBr the yield dropped to only 0.2%, which was very likely due to a decrease of the number of acid sites by an ion-exchange of the proton with sodium, which again stresses the importance of strong acid sites for the hydroxylation of benzene.

Following these first catalyst screening experiments the reaction parameters such as the temperature were optimised for the SAC 13 based carrier, as the highest phenol yields were obtained over this material. As can be seen in Figure 2 the highest amounts of phenol were formed at temperatures between 30 and 40 °C, with an increasing formation of higher oxidised compounds, especially hydroquinone, at increasing temperatures. At temperatures below 20 °C only very low phenol yields were found.

There was a strong influence of the solvent used (see Table 2): the phenol yield was found to increase with the polarity of the solvent in the order acetone < 2-propanol < ethanol < methanol < water, which was somewhat surprising, as the solubility of benzene decreases in these solvents. With these increasing phenol yields the solvents were more protic, which again is an indication that strong acid sites are needed for this hydroxylation. While using water hydroquinone was formed in high quantities as well. Without a solvent (essentially using the apolar and aprotic substrate benzene as the solvent) only very low yields could be obtained. A 3:1 water/methanol mixture was found to result in the highest phenol selectivities.

The pressure was most likely also an important parameter as the solubility of the gases is a function of the pressure. Therefore, besides the batchwise experiments done up to here, semi-batch experiments were done, in which a constant pressure was maintained,

Table 3. Influence of the oxidation procedure on the catalytic performance. Conditions: batchwise, 1000 kPa O_2, 1000 kPa H_2, 1000 kPa N_2, semi-continuous: 1.3 L/h H_2, 1.3 L/h O_2, 1.4 L/h N_2 at 700 or 1400 kPa. Catalyst: Pd/Pt/SAC 13, 0.5 wt. % Pd + 0.5 wt. % Pt, reduced with 5 vol. % H_2.

procedure	phenol yield [%]	phenol selectivity[a] [%]	HQ selectivity [%]	CAT selectivity [%]	Q selectivity [%]
Batch, 3000 kPa	4.2	40	52	5	2.5
Semi-continuous, 700 kPa	3.2	63	26	10	0.5
Semi-continuous, 1400 kPa	5.6	45	49	5	0.1

[a] Based on products in the liquid phase, HQ = hydroquinone, CAT = catechol, Q = quinone.

Table 4. Influence of the reduction atmosphere on the catalytic performance. Conditions: semi-continuous, 1.3 L/h H_2, 1.3 L/h O_2, 1.4 L/h N_2, 1400 kPa. Catalyst: Pd/Pt/SAC 13, 0.5 wt. % Pd + 0.5 wt. % Pt, heating rate 1 °C/min to 150 °C.

reduction method	phenol yield [%]	phenol selectivity[a] [%]	HQ selectivity [%]	CAT selectivity [%]	Q selectivity [%]
unreduced	0.2	100	–	–	–
N_2	6.9	59	31	9	–
5 vol. % H_2 in N_2	7.6	56	36	8	–
H_2	7.5	57	31	11	0.1

[a] Based on products in the liquid phase, HQ = hydroquinone, CAT = catechol, Q = quinone.

flowing the gases through the reactor. A low constant pressure of 700 or 1400 kPa with O_2:H_2 ratios of 1:1 up to 2:1 in such a semi-continuous mode was found to result in a decrease in the formation of higher oxidised side products. Starting with a high pressure of 3000 kPa in a batch mode resulted in an increased side product formation (see Table 3), which was probably due to the higher oxygen and hydrogen starting concentrations. While keeping the gas concentrations low there was already phenol formation, with less formation of the deeper oxidised consecutive products as hydroquinone, catechol and quinone.

Prior to the reaction the noble metal catalysts were reduced. As the reduction method and temperature are known to influence, e.g., the particle size, or the metal distribution in bimetallic systems, several different reduction methods were compared. In earlier investigations on the direct oxidation of propene to propylene oxide a reduction temperature of 150 °C under nitrogen (i.e., an autoreduction) was found to result in the most active catalysts.[17–19] Combined with the fact that Nafion is destroyed at temperatures of only 250 °C a similar reduction temperature was used for the Nafion based catalysts investigated here, as at 150 °C the Pd- and Pt-tetramine complexes are already partially decomposed. The influence of the reduction atmosphere was investigated; the catalysts were calcined under pure flowing hydrogen, under a 5% H_2 in N_2 mixture, and under flowing nitrogen (see Table 4). In the latter method the noble metals were autoreduced by the ammonia resulting from the decomposition of the tetramine complexes. Although the catalysts have to be reduced in order to obtain an active material (over the unreduced material only traces of phenol were found), there was only little influence of the different reduction methods on the catalytic performance. The yields over the under hydrogen reduced materials (both under pure hydrogen and under the 5% hydrogen) were slightly higher than that over the autoreduced material, which might be due to a less complete decomposition of the amines at 150 °C. However, the selectivities to phenol and the side products hydroquinone, catechol and quinone are comparable.

Transmission electron micrographs (a typical example is presented in Figure 3) showed a homogeneous distribution of the noble metal clusters over the carrier, which were spherically shaped with a diameter of 2–10 nm. Unfortunately, from EDX analysis it did not become clear whether the noble metal clusters were present on the silica matrix or on the Nafion resin particles. The noble metal particles were probably equally distributed over both the SiO_2 as well as over the Nafion. The palladium was mostly present as completely reduced Pd(0), but could also be partially present as unreduced Pd(II) bonded to the Nafion HSO_3 groups. The presence of these unreduced species could be explained by the relatively low reduction temperature (higher reduction temperatures could not be used because of the temperature sensitivity of the Nafion), resulting in an incomplete decomposition of the tetramine complexes. This species could be the explanation for the small Pd signal next to the sulphur signal in the EDX spectrum (see Figure 3).

Unfortunately, the catalyst was found to deactivate: after several hours reaction time no more conversion of benzene could be observed. This deactivation could be due to the formation of heavies, which might be formed by a decomposition of the products. Therefore, some

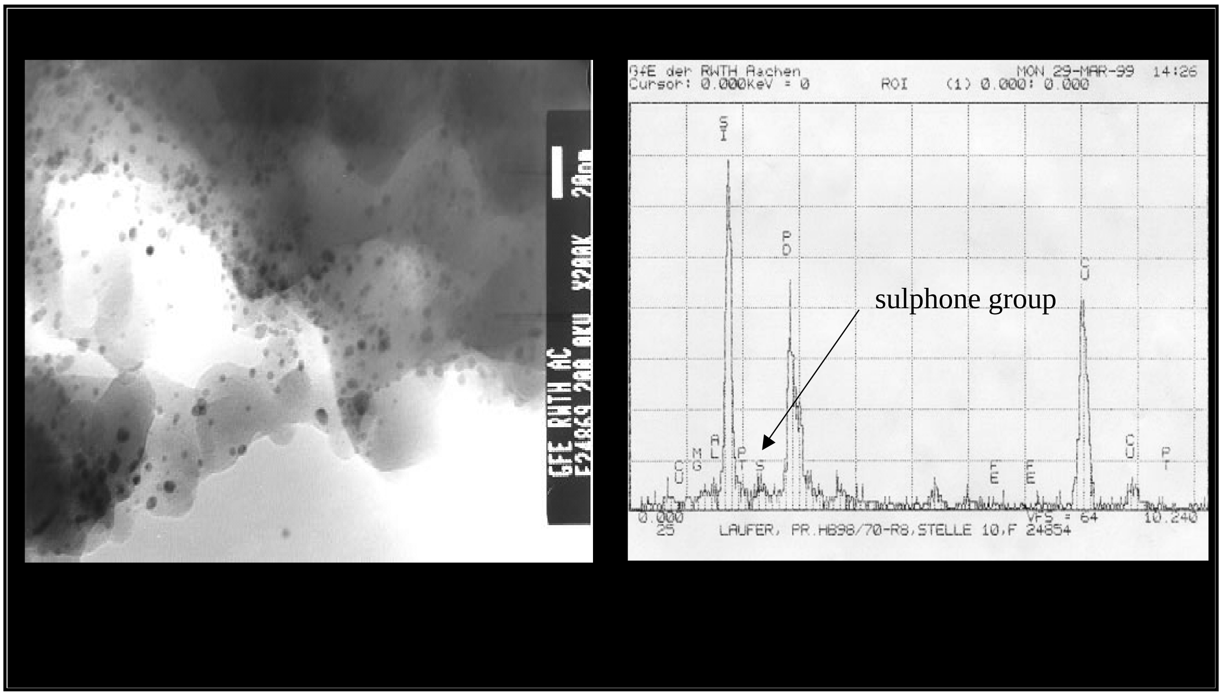

Figure 3. TEM image of 0.5 wt. % Pd + 0.5 wt. % Pt on SAC 13 (autoreduction at 150 °C under pure N_2).

preliminary experiments on the regeneration behaviour of the Pd/Pt/SAC 13 catalyst were done. After recovery of the catalyst it was washed with methanol and subsequently reduced under 5% H_2 in N_2. Unfortunately, the original activity could not yet be restored completely: the phenol yield dropped from 7.6% to 3.0%, with comparable selectivities. If the catalyst was only washed with methanol, and not reduced, the yield in the second reaction cycle dropped to only 2.6.

Conclusions

Benzene could be hydroxylated directly to phenol over Pt/Pd impregnated acid carriers such as zeolites (BEA, MOR, FER, MFI), resins like Amberlyst, or Nafion/silica composites, using oxygen in the presence of hydrogen as the oxidant. The best results were obtained over a strong acidic Nafion/silica composite carrier with 13% Nafion containing 0.5 wt. % Pd and 0.5 wt. % Pt, at temperatures between 30 – 40 °C, using a water/methanol mixture as the solvent. Besides the higher yields a major advantage of this catalyst in comparison with the catalytic systems developed by Miyake et al.[11,12,14] and Tatsumi et al.[13] is that no homogeneous acids are used, thus preventing associated problems such as their neutralisation and resulting salt formation. It was found to be necessary to reduce the catalyst at 150 °C; however, the reduction atmosphere did not have any influence on the catalytic performance. A semi-continuous reactor system in which the hydrogen and oxygen concentration is kept at a constant pressure of 700 – 1400 kPa resulted in higher phenol yields than when using a batch reactor, starting at high pressures of 3000 kPa, letting the pressure drop over the reaction time. Although the catalyst could be recycled with a methanol wash followed by a reduction, the original activity could not yet be restored completely.

Experimental Section

Catalyst Preparation and Characterisation

Nafion-silica composites with various Nafion contents (for example, SAC 13 contained 13 wt. % Nafion), kindly provided by Du Pont de Nemours & Company, Wilmington, the acid ion-exchange resin Amberlyst 15 (Aldrich), and aluminium containing FER, MOR, BEA and MFI type zeolites were used as carriers for bifunctional oxidation catalysts. For the impregnation with palladium and platinum 2 g of the carrier were suspended in 20 g of water, after which the required amounts of $[Pd(NH_3)_4](NO_3)_2$ and $[Pt(NH_3)_4]Cl_2$ were added. The suspension was heated to 80 °C and stirred for 24 h, after which the catalyst was filtered off, washed and dried at 110 °C under air. The thus obtained materials were subsequently reduced at 150 °C (heating rate 1 °C/min) under H_2, 5 vol % H_2 in N_2, or autoreduced under N_2.

The materials were characterised with transmission electron microscopy (TEM; Jeol JEM-2000 FX, acceleration voltage 200 kV) for which the samples were dispersed on a carbon coated copper grid, energy dispersive analysis of X-rays (EDX), inductive coupled plasma atomic emission spectroscopy (ICP AES; Spectroflame D) and nitrogen sorption (Micromeretics ASAP 2010; prior to the measurement the samples were outgassed at 100 °C).

Benzene Hydroxylation

As the reactant mixture was within the explosion limits (1/3 N_2, 1/3 O_2, 1/3 H_2) the reactor system was controlled remotely in an explosion safe bunker. The reactor, a 200-mL stainless steel autoclave, was equipped with two inlets, an outlet with an overflow valve, temperature and pressure indicators and a magnetic stirrer. The temperature was controlled with an outer water jacket. The gases were added using Brooks Mass Flow Controllers.

0.2 g of catalyst, 20 g solvent containing 0.5 mmol/L NaBr and 2 g benzene were charged into the autoclave. For batch experiments the autoclave was subsequently pressurised (700 – 3000 Pa) with hydrogen, nitrogen and oxygen using the mass flow controllers, assuming an ideal gas behaviour. For semi-continuous experiments O_2, H_2 and N_2 were added during the reaction with mass flow controllers, maintaining a constant pressure with the overflow valve. The slurry was heated to 43 °C while stirring vigorously, this temperature was maintained for 3 h. Subsequently, the reactor was cooled down to 15 °C. Samples were analysed with HPLC (Merck/Hitachi L-6200A equipped with an L-4500 diode array detector), using MeOH/H_2O mixtures as the eluent.

The yields were calculated relating the molar amount of phenol to the molar amount of benzene. The phenol selectivities were based on the total molar amounts of organic products.

References

[1] W. Jordan, H. van Barneveld, O. Gerlich, M. Kleine-Boymann, J. Ullrich, in *Ullmanns Encyclopedia of Industrial Chemistry*, 6th edn., Electronic Release (Eds.: J. E. Bailey et al.), VCH, Weinheim, **1998**.

[2] A. Kunai, T. Kishihata, S. Ito, K. Sasaki, *Chem. Lett.* **1988**, 1976.

[3] A. Kunai, T. Kitano, Y. Kuroda, J. LiFen, K. Sasaki, *Catal. Lett.* **1990**, *4*, 139.

[4] L. C. Passoni, A. T. Cruz, R. Buffon, U. Schuchardt, *J. Mol. Catal.* **1997**, *120*, 117.

[5] L. C. Passoni, F. J. Luna, M. Wallau, R. Buffon, U. Schuchardt, *J. Mol. Catal.* **1998**, *134*, 129.

[6] G. I. Panov, A. S. Khatitonov, V. I. Sobolev, *Appl. Catal.* **1993**, *93*, 33.

[7] G. I. Panov, A. K. Uriarte, , M. A. Rodkin, V. I. Sobolev, *Catal. Today* **1998**, *41*, 365.

[8] J. L. Motz, H. Heinichen, W. F. Hölderich, *Stud. Surf. Sci. Catal.* **1997**, *105*, 1053.

[9] J. L. Motz, H. Heinichen, W. F. Hölderich, *J. Mol. Catal.* **1998**, *136*, 175.

[10] K. Sasaki, A. Kunai, S. Ito, F. Iwasaki, M. Hamada, (Tosoh Corp.), *JP* 02138233, **1990**.

[11] T. Miyake, M. Hamada, Y. Sasaki, K. Sekizawa, (Tosoh Corp.), *JP* 03178946, **1991**.

[12] T. Miyake, M. Hamada, Y. Sasaki, M. Oguri, *Appl. Catal. A: General* **1995**, *131*, 33.

[13] T. Tatsumi, K. Yuasa, H. Tominaga, *J. Chem. Soc. Chem. Commun.* **1992**, 1446.

[14] T. Miyake, M. Hamada, H. Niwa, M. Nishizuka, M. Oguri, *J. Mol. Catal. A: Chemical* **2002**, *178*, 199.

[15] F. J. Waller, R. W. van Scoyoc, *Chemtech* **1987**, *17*, 438.

[16] M. A. Harmer, Q. Sun, A. J. Vega; W. E. Farneth, A. Heidekum, W. F. Hölderich, *Green Chem.* **2000**, *2*, 7.

[17] R. Meiers, U. Dingerdissen, W. F. Hölderich, *J. Catal.* **1998**, *176*, 376.

[18] W. Laufer, R. Meiers, W. F. Hölderich, in *Proceedings 12th International Zeolite Conference*, July 1998, (Eds.: M. M. J. Treacy et al.), Material Research Society, Warrendale, Pennsylvania, **1999**, p. 1351.

[19] W. Laufer, W. F. Hölderich, *Appl. Catal. A: General* **2001**, *213*, 163.

[20] A. Corma, H. Garcia, *Catal. Today* **1997**, *38*, 257.

[21] A. S. C. Brown, J. S. J. Hargreaves, *Green Chem.* **1999**, *1*, 17.

[22] L. W. Gosser, (E. I. Du Pont de Nemours and Company), *US Patent* 4,681,751, **1987**.

[23] E. I. Du Pont de Nemours and Company, *EP* 0274830, **1988**.

[24] L. W. Gosser, (E. I. Du Pont de Nemours and Company), *EP* 0342047, **1989**.