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New direct hydroxylation of benzene with oxygen in the presence of hydrogen over bifunctional ion-exchange resins

Wilhelm Laufer and Wolfgang F. Hoelderich*

Department of Chemical Technology and Heterogeneous Catalysis, University of Technology RWTH Aachen, Worringerweg 1, 52074 Aachen, Germany. E-mail: Hoelderich@rwth-aachen.de; Fax: +49-(0)241-8022291; Tel: +49-(0)241-8026560

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Benzene was hydroxylated directly to phenol with oxygen in the presence of hydrogen over Pt/Pd containing acid resins such as Amberlyst and Nafion/silica composites; over the latter materials the best results were obtained.

The conventional industrial process for the production of the important intermediate phenol, the 3 step Hock process, suffers from many disadvantages as the formation of acetone as an inevitable couple product, the production of 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.

One route is the direct gas phase oxidation with O_2 or air; unfortunately this process leads to low selectivities because of the formation of maleic acid and the oxidation to CO_2. The oxidation over Cu or Cu/Pd catalysts in an acidic medium resulted in low conversions, and the catalysts had to be regenerated under H_2.[1] Better results were obtained using O_2 over palladium and heteropolyacids.[2] An alternative is the use of N_2O over H-[Fe]-MFI or steamed H-[Al]-MFI zeolites. The surface α-oxygen, formed upon decomposition of N_2O, reacts with benzene to phenol, obtaining conversions of *ca.* 30% and selectivities of over 95%.[3,4] The activity seems to be related to the Lewis acidity. These catalysts deactivate rapidly due to strong coking.[4] Sasaki *et al.*[5] and Miyake *et al.*[6] used Pd/SiO_2, Pd or $Pt/V_2O_5/SiO_2$ based systems in acetic acid, and Tatsumi *et al.*[7] investigated the use of Pd containing TS-1 in strong acids such as HCl in the direct oxidation with O_2 and H_2, forming H_2O_2 *in situ*. With these systems only low phenol yields were obtained.

Here the use of Pd and Pt containing acid resins such as Amberlyst 15 and Nafion-silica composites for the direct hydroxylation of benzene with an O_2–H_2 gas mixture was investigated. Nafion is an ionomer with an inert polymeric backbone and highly acidic sulfonic groups, and has hydrophobic ($-CF_2CF_2-$) and hydrophilic ($-SO_3H$) regions. Nafion silica nanocomposites, produced by the entrapment of Nafion particles in a porous silica network, seem promising replacements for hazardous conventional strong homogeneous acids.[8,9] The choice of the type and the amounts of metal was based on previous experiments on the direct epoxidation of propylene with H_2–O_2 over Pd/Pt/TS-1 type materials.[10,11]

2 g of Nafion-silica composites with various Nafion contents (*e.g.* SAC 13 contained 13 wt% Nafion), kindly provided by Du Pont de Nemours & Company, Wilmington and Amberlyst 15 (Aldrich) were suspended for 24 h at 80 °C in 20 g of an aqueous $[Pd(NH_3)_4](NO_3)_2$ and $[Pt(NH_3)_4]Cl_2$ solution. The materials were reduced at 150 °C (heating rate 1 °C min^{-1}) under H_2, 5 vol% H_2 in N_2, or N_2 and characterized by ICP AES (Spectroflame D) and nitrogen sorption (Micromeretics ASAP 2010).

0.2 g of catalyst, 20 g solvent containing 0.5 mmol l^{-1} NaBr and 2 g benzene were charged into a 200 ml autoclave. For batch experiments the autoclave was subsequently pressurized (700–3000 kPa) with O_2, H_2 and N_2 with MFC's. For semi-continuous experiments O_2, H_2 and N_2 were added continuously, maintaining a constant pressure with an overflow valve. The slurry was heated to 43 °C while stirring. After 3 h the reactor was cooled down to 15 °C. Samples were analyzed with HPLC (Merck/Hitachi L-6200A equipped with a L-4500 Diode Array Detector) using MeOH–H_2O mixtures as the eluent.

The best results were obtained over the Nafion based material SAC 13, with a maximum benzene conversion of 4.25% (see Table 1 and Fig. 1; over metal free SAC 13 no conversion could be found). As side products, resulting from the oxidation of phenol, hydroquinone, quinone and catechol were found. Over the strong acid resin Amberlyst there was some phenol formation. The conversion to phenol was also found to be dependent on the amounts of palladium and platinum.

The performance of the Pd/Pt/Nafion-silica catalyst was probably a result from the strong acidic properties, combined with the hydrophobic/hydrophilic properties. The SAC 13 based catalyst was superior compared to the other composite materials (see Fig. 1). Its higher activity could not be explained with a higher surface area or a larger cumulative pore volume, as the BET surface area ranged from 15 $m^2 g^{-1}$ for SAC 80 to 158 $m^2 g^{-1}$ for SAC 15 (pore volume 36 $cm^3 g^{-1}$), 92 $m^2 g^{-1}$ for SAC 13 (pore volume 21 $cm^3 g^{-1}$), up to 270 $m^2 g^{-1}$ for SAC 5. The better performance of the SAC 13 based catalyst was possibly caused by a higher dispersion of the Nafion resin over the silica matrix, resulting in an optimal distribution of the sulfonic acid groups over the catalyst.

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^{-1} NaBr resulted in yields of up to 4.2%. This was probably a result of a promoting or stabilizing effect of the bromide on the H_2O_2 formation.[12]

Table 1 Catalyst compositions and results of the hydroxylation of benzene with O_2 and H_2. Conditions: solvent water, 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%]	Phenol [mmol]
$Nafion/SiO_2$ SAC 13	0.6% Pd + 0.6% Pt	1.0881
Amberlyst 15	1.0% Pd + 0.01% Pt	0.0619
Amberlyst 15	2.5% Pd + 1.2% Pt	0.2274

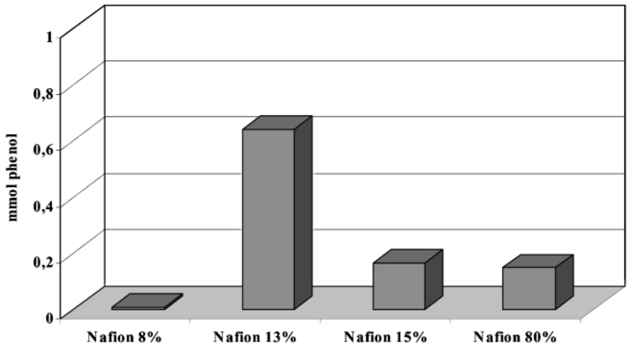

Fig. 1 Influence of the Nafion content in the composite on phenol formation. Conditions: solvent 15 g methanol + 5 g H_2O, batchwise, 1000 kPa O_2, 1000 kPa H_2, 1000 kPa N_2. Catalyst: $Pd/Pt/Nafion/SiO_2$, 0.5 wt% Pd + 0.5 wt% Pt, reduced under 5 vol% H_2.

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The addition of higher amounts of NaBr resulted in a strong decrease of the yield: upon addition of 60 mmol l^{-1} NaBr the yield dropped to only 0.2%, which was probably due to a decrease of the number of acid sites by the ion-exchange with sodium.

The reaction parameters were optimized for an SAC 13 based catalyst containing 0.5 wt% Pd and 0.5 wt% Pt, reduced under 5 vol% H_2. The highest amounts of phenol were formed between 30–40 °C, with increasing amounts of higher oxidized compounds, especially hydroquinone, at increasing temperatures (see Fig. 2). At temperatures below 20 °C only very low phenol yields were found.

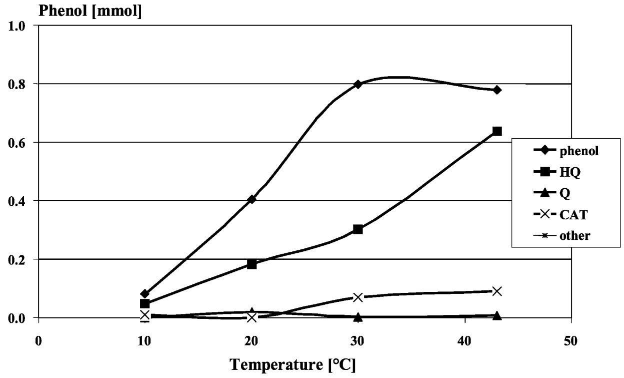

Fig. 2 Influence of the reaction temperature on the catalytic performance; HQ: hydroquinone, Q: quinone, CAT: catechol. Conditions: semi-continuous, 1.3 l h^{-1} H_2, 1.3 l h^{-1} O_2, 1.4 l h^{-1} N_2, 700 kPa.

The phenol yield increased with the polarity of the solvents in the order acetone < 2-propanol < ethanol < methanol < water, which was somewhat surprising as the solubility of benzene decreases in these solvents (see Table 2). With these increasing phenol yields the solvents were more protic. This 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 only very low yields could be obtained. A 3 : 1 water/methanol mixture was found to result in the highest phenol selectivities.

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

Solvent	Yield [%]	Selectivity [%]
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
Isopropanol	<0.1	100
Acetone	—	—

Using a low constant pressure of 700 or 1400 kPa with $O_2 : H_2$ ratios of 1 : 1 up to 2 : 1 in a semi continuous mode less higher oxidized side products were formed. Starting with a 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 O_2 and H_2 starting concentrations. When keeping the gas concentrations low there was less side product formation.

Table 3 Influence of the oxidation procedure on the catalytic performance. Conditions: batch wise, 1000 kPa O_2, 1000 kPa H_2, 1000 kPa N_2, semi-continuous: 1.3 l h^{-1} H_2, 1.3 l h^{-1} O_2, 1.4 l h^{-1} N_2 at 700 or 1400 kPa

Procedure	Phenol yield [%]	Phenol sel. [%]	HQ sel. [%]	CAT sel. [%]	Q sel. [%]
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

Table 4 Influence of the reduction atmosphere on the catalytic performance. Conditions: semi-continuous, 1.3 l h^{-1} H_2, 1.3 l h^{-1} O_2, 1.4 l h^{-1} N_2, 1400 kPa

Reduction method	Phenol yield [%]	Phenol sel. [%]	HQ sel. [%]	CAT sel. [%]	Q sel. [%]
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

Prior to the reaction the noble metal catalysts were reduced. In earlier investigations on the direct epoxidation of propene an autoreduction at 150 °C under nitrogen resulted in the most active catalysts.[10,11,13] As Nafion is destroyed at *ca.* 250 °C a similar reduction temperature was used, 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 H_2, a 5% H_2 in N_2 mixture, and N_2. In the latter method the 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 little influence of the different reduction methods on the catalytic performance (see Table 4). The yields over the under H_2 reduced materials were somewhat higher than that over the autoreduced material, which might be due to an incomplete decomposition of the amines. The selectivities to phenol and the side products hydroquinone, catechol and quinone were comparable. After regenerating the spent catalyst with a methanol wash the materials regained their activity for at least two recycles, although the yield dropped to *ca.* 3% with comparable selectivities.

Benzene could be hydroxylated directly to phenol over Pt/Pd impregnated acid resins like Amberlyst or Nafion/silica composites with oxygen in the presence of hydrogen. The best results were obtained over a Nafion/silica composite containing 13% Nafion between 30–40 °C in a 3 : 1 water/methanol mixture. The catalyst had to be reduced at 150 °C; however, the reduction atmosphere had little influence on the performance. A semi-continuous reactor system keeping the O_2 and H_2 concentration constant at 700–1400 kPa resulted in higher phenol yields than when using a batch reactor.

Notes and references

1 A. Kunai, T. Kitano, Y. Kuroda, J. LiFen and K. Sasaki, *Catal. Lett.*, 1990, **4**, 139.
2 L. C. Passoni, F. J. Luna, M. Wallau, R. Buffon and U. Schuchardt, *J. Mol. Catal.*, 1998, **134**, 129.
3 G. I. Panov, A. K. Uriarte, M. A. Rodkin and V. I. Sobolev, *Catal. Today*, 1998, **41**, 365.
4 J. L. Motz, H. Heinichen and W. F. Hölderich, *J. Mol. Catal.*, 1998, **136**, 175.
5 K. Sasaki, A. Kunai, S. Ito, F. Iwasaki and M. Hamada (Tosoh Corp.), JP 02138233, 1990.
6 T. Miyake, M. Hamada, Y. Sasaki and K. Sekizawa (Tosoh Corp.), JP 03178946, 1991.
7 T. Tatsumi, K. Yuasa and H. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1992, 1446.
8 F. J. Waller and R. W. van Scoyoc, *Chemtech.*, 1987, **17**, 438.
9 M. A. Harmer, Q. Sun, A. J. Vega, W. E. Farneth, A. Heidekum and W. F. Hölderich, *Green Chem.*, 2000, **2**, 7.
10 W. Laufer, R. Meiers and W. F. Hölderich, in *Proc. 12th Int. Zeolite Conf.*, July 1998, eds. M. M. J. Treacy, B. K. Marcus, M. E. Bisher and J. B. Higgins, Material Research Society, Warrendale, Pennsylvania, 1999, 1351.
11 W. Laufer and W. F. Hölderich, *Appl. Catal. A: General*, 2001, **213**, 163.
12 L. W. Gosser (E.I. Du Pont de Nemours Co.), EP 0342047, 1989.
13 R. Meiers, U. Dingerdissen and W. F. Hölderich, *J. Catal.*, 1998, **176**, 376.