Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 99 (2005) 193–198

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Hydroxylation of benzene with oxygen and hydrogen over catalysts containing Group VIII metals and heteropoly compounds

N.I. Kuznetsova[a,*], L.I. Kuznetsova[a], V.A. Likholobov[b], G.P. Pez[c]

[a]*Boreskov Institute of Catalysis, Prosp. Lavrentieva, 5, Novosibirsk 630090, Russia*
[b]*Institute of Hydrocarbon Processing, Neftezavodskaya St., 54, Omsk 644040, Russia*
[c]*Air Products and Chemicals, Inc., Corporate Science and Technology Center, 7201 Hamilton Blvd., Allentown, PA 18195-1501, USA*

Abstract

The vapor phase hydroxylation of benzene to phenol with a mixture of oxygen and hydrogen over silica supported bi-component catalysts containing Group VIII metals (M) and heteropoly compounds (HPC) was investigated. The productivity of the catalysts was ascertained for various metal and HPC combinations and a range of reaction conditions. The Pt–PMo_{12}/SiO_2 and Pd–PMo_{12}/SiO_2 catalysts of optimal composition provide up to 380 mol phenol/g-atom Pt or Pd/h. The observed catalysis appears to be associated with an interface between metal particles and those of the heteropoly compound, as illustrated by an HREM image of a Pt–PMo_{12}/SiO_2 sample.

Keywords: Oxidation; Benzene; Platinum; Palladium; Oxygen; Hydrogen

1. Introduction

The industrial production of phenol is, in general, based on three multistep processes: (1) an alkylation of benzene to cumene and its transformation to phenol and acetone; (2) a two-stage oxidation of toluene; (3) the least suitable synthesis—a chlorination of benzene and hydrolysis of the chlorobenzene to phenol.

The more reagent efficient direct reaction of benzene with molecular oxygen requires the presence of radical initiators [1] or transition metal oxide or phosphate catalysts [2]. At the high temperatures required for the gas-phase hydroxylation there is a significant oxidation of benzene to carbon oxides, the resulting selectivity to phenol as seen in laboratory experiments is no more than 60 mol% at about 10% conversion of benzene.

In general, lowering the temperature tends to improve the selectivity. For instance, over V-containing oxides the selectivity of benzene conversion into phenol reaches 90% at 180–240 °C [3]. However, the lower temperature leads to a lower productivity, down to several grams of phenol per kg of catalyst per hour, and also an intensive deactivation of the catalysts resulting from a reduction of the oxides.

In the presence of Pt^{II} and Pd^{II} compounds oxidation of benzene in liquid-phase media proceeds at temperatures of 180–200 °C at elevated pressures [4]. The low productivity of the systems (several grams of phenol per g-atom of the metal for 1 h) along with the requirement of acetic acid as a solvent renders the liquid-phase systems unattractive.

One-oxygen atom donors, such as nitrous oxide [5], hydrogen peroxide and other peroxides [6,7], permit a conversion of benzene into phenol in the presence of appropriate catalysts at low to moderate temperatures. Generally a more selective hydroxylation is achieved than with molecular oxygen, along with a minimum degradation of the benzene ring. For example, a conversion of benzene with hydrogen peroxide in the presence of a P–Mo heteropoly acid can produce phenol with total selectivity [8]. However, molecular oxygen is clearly an economically more desirable oxidant.

As has been recently shown, active peroxide-type species can be obtained by an in situ reductive activation of molecular oxygen when a catalytic oxidation of hydrocarbons is conducted in the presence of co-reductants. These can be Fe or Zn in an acidic medium [9], ascorbic acid [10], iso- or

---

* Corresponding author. Fax: +7 383 2355756.
E-mail address: kuznina@catalysis.nsk.su (N.I. Kuznetsova).

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.09.040

Table 1
Literature described catalytic systems for hydroxylation of benzene with O_2 and H_2

Catalyst	Conditions	Productivity (mol phenol/ (1 g-atom Pt or Pd) h	Conversion of benzene (%)	References
Liquid-phase oxidation				
Pd–Cu/SiO_2	25 °C	4	0.02	[14]
Pt–V_2O_5	HOAc, 60 °C	67	0.07	[15]
Pd, Pt–V_2O_5/SiO_2	HOAc, 60 °C	46	0.14	[16]
Pt/ZrO_2 + V(acac)$_3$	HOAc, 60 °C	400	0.45	[17]
Pt, Rh, Ir, Pd or Ru + V_2O_5, Y_2O_3, Nb_2O_5, WO_3, La_2O_3 or MoO_3/SiO_2	HOAc, 60 °C	264	0.6	[18]
Pd/Ti-silicalite	H_2O + HCl, 25 °C	13	0.36	[19]
Pd/Al_2O_3 + V(acac)$_3$ or $FeCl_2$	HOAc, 65 °C	50	2.3	[20]
Gas-phase oxidation				
Pd–Cu/SiO_2	200 °C	80	0.9	[21]
Pt/VO_x/SiO_2 or Pd/VO_x/SiO_2	150–200 °C	60	0.68–0.97	[22]
Pd membrane	150–200 °C		3–13%	[23]

allyl alcohols [11]; and in the gas phase, ethylene [12], carbon monoxide [13], and hydrogen [14–22]. Studies based on the use of hydrogen as the co-reductant are the most numerous and, have been mostly directed at achieving a selective hydroxylation of benzene. A number of catalyst systems consisting of Pt or Pd and transition metal oxides for effecting an oxidation of benzene with a mixture of O_2 with H_2 in the liquid phase have been described (cf. summary in Table 1), which possess substantial productivity referred to the metal, and provide over 90% selectivity at a 0.1–0.6% conversion of benzene to phenol. The utilized polar and acidic solvents are, seemingly critical for providing the observed catalysis, since the catalyst productivity is much less for similar catalysts when the reaction is conducted in the gas phase (Table 1 and Refs. [21,22]). However the same high selectivity is apparently achievable in the two media. The conversion of benzene is typically close to 1%, and is much higher (3–13%) in the work using a Pd membrane reactor at an over-stoichiometric ratio of O_2 and H_2 [23].

In practice, an oxygen and hydrogen reagent mixture (well outside the explosive regime!) offers obvious advantages over conventional oxidants, in raw material costs and as potentially, a source of a one-oxygen atom oxidant, enabling a more selective conversion of benzene to phenol. Our attempts therefore concentrated on investigating the use of O_2/H_2 mixtures for a direct catalytic hydroxylation of benzene.

Our previous studies on liquid oxidation systems resulted in the identification of catalysts consisting of combinations of Pt, Pd and heteropoly compounds [24,25]. In the present work catalytic systems of similar composition were adapted for an oxidation of benzene in the vapor phase [26,27] in the presence of O_2 and H_2.

2. Experimental

2.1. Preparation of catalysts

Bi-component metal–HPC samples were prepared from a combination of one of a number of heteropoly acids $H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}$, $H_5PMo_{10}V_2O_{40}$, $H_6PMo_9V_3O_{40}$, $H_3PMo_6W_6O_{40}$, $H_3PW_{12}O_{40}$, $H_4PW_{11}VO_{40}$, $H_6PW_9V_3O_{40}$, $H_5PW_{11}ZrO_{40}$ and VIII group metal chlorides: H_2PtCl_6, $PdCl_2$, H_3IrCl_6, $K_2Ru(OH)Cl_5$, $H_3[RhCl_3(OH)_3]$, $CoCl_2$, $NiCl_2$. The active components were dispersed on silica supports of specific surface area ranging from 13 to 400 m^2/g and particle size 0.2–0.5 mm. Typically, the samples contained 5–60 wt.% of the HPC and 0.1–2.0 wt.% of the VIII group metal.

The M–HPC/SiO_2 samples were normally prepared by an impregnation of the support with a solution of the metal chloride and HPC followed by drying at 100 °C in air, calcination at 450 °C and finally H_2 reduction in a temperature programmed regime to 300 °C. In another procedure the silica was first impregnated with the HPC solution, then, after drying and calcination at 450 °C, it was imbibed to incipient wetness with a solution of H_2PtCL_6, then dried, calcined and activated as above.

The utilized catalysts are specified in terms of weight percent of metal, HPC, and with respect to the surface area of the silica support (m^2/g, in brackets), for example: 1% Pt–20% PMo_{12}/SiO_2 (200). The HREM image of the catalyst was recorded with a JEOL 2010 instrument providing a lattice resolution of 1.4 Å with an accelerating voltage of 200 kV.

2.2. Catalytic experiments

The hydroxylation of benzene was performed in a fixed-bed flow reactor (glass tube of 15 mm in diameter) at ambient pressure. Oxygen, hydrogen and nitrogen rates were controlled by mass-flow controllers, the benzene liquid was introduced by a syringe pump which provided a measured volume rate. The pre-mixed at 150 °C vapor/gas-phase reagents were passed through the catalyst bed. The reactor was supplied with an on-line GC for an analysis of O_2, H_2, CO (NaX molecular sieves), CO_2 (Hausep C + 4.5% KOH) and phenol (0.4% 1-nitroanilinoanthraquinone on carbon black) in the outlet gas, which was then passed through a trap at −10 °C, the condensed organic liquid from which was subsequently analyzed by GC using a capillary column (DB-1701 30 m × 0.00055 m).

In a typical experiment, the catalyst loaded reactor was heated to the appropriate temperature. Then the mixture of gases, $N_2/O_2/H_2/C_6H_6$ was passed through the catalyst bed for 1 h in order to attain a steady-state concentration of O_2, H_2 and phenol in the outlet gas, as determined by the GC analysis. In the next hour, the outlet gas was now passed through the cold trap, and the organic products in the thus collected liquid were analyzed.

3. Results

As an initial survey, a number of silica supported M–HPC catalysts prepared by a single impregnation with a solution containing both, H_2PtCl_6 and HPC were evaluated for the desired hydroxylation of benzene. In the experiments for which data is presented in Figs. 1 and 2, phenol amounted to over 90% of the total collected liquid products of benzene conversion. Other identified products were cyclohexanol, biphenyl as well as CO and CO_2 in the effluent gases. There were also depending on conditions, varying amounts of unidentified tarry products collected in the cold trap. The amount of phenol produced in 1 h (mmol/h) and the productivity of the catalysts (mol phenol/g-atom M h) as based on the phenol content of the product liquid are as expected highly dependent on the composition of the respective catalyst.

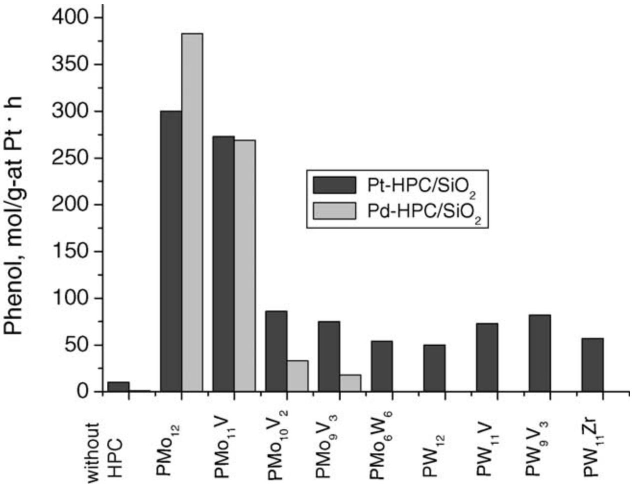


Fig. 1. Productivity of the 0.2% Pt–20% HPC/SiO_2 (400) and 0.1% Pd–20% HPC/SiO_2 (400) catalysts. Conditions: 0.1 g of catalyst, composition of gas O_2:H_2:C_6H_6:N_2 = 5.5:5.5:33:57, flow rate 160 ml/min, T 200 °C.

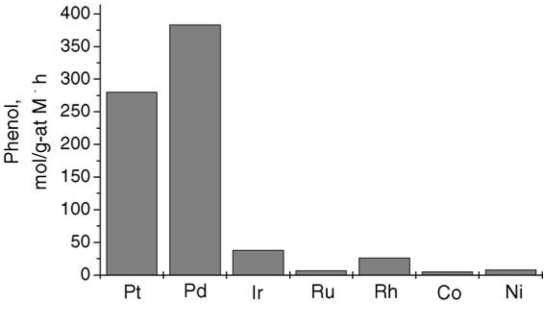


Fig. 2. Productivity of the M–20% HPC/SiO_2 (400) catalysts containing Group VIII metals M: 0.2% Pt, 0.1% Pd, 0.2% Ir, 0.1% Ru, 0.1% Rh, 0.2% Co, 0.2% Ni. Conditions: 0.1 g of catalyst, composition of gas O_2:H_2:C_6H_6:N_2 = 5.5:5.5:33:57, flow rate 160 ml/min, T 200 °C.

The highest catalyst productivity of 270–380 mol phenol/g-atom metal h was recorded for the M–PMo_{12} and M–$PMo_{11}V$ systems where M = Pt or Pd (Fig. 1). At a benzene conversion of 0.3% selectivity to phenol formation was 95–98%. In this case the only side product was biphenyl, and no carbon oxides were detected by GC in the outlet flow; also no tarry compounds accumulated in the cold trap.

The very significant promotion of benzene hydroxylation by the HPCs is seen by reference to the productivity of a Pt/SiO_2 catalyst which as shown in Fig. 1 is about two orders of magnitude less than for the most active Pt–HPC/SiO_2 composition. Of the surveyed Group VIII metal catalyst components (Fig. 2) Pt and Pd were found to be by far the most active.

The benzene hydroxylation reaction was investigated in the temperature range of 180–250 °C for which data on the amount of phenol produced in the first hour (after steady-state conditions had been reached) is presented in Fig. 3. In order to avoid possible problems with an inadequate desorption of phenol from the catalyst, no runs were made below 180 °C. A maximum production of phenol was seen at 180–200 °C. It dropped steeply at temperatures near 250 °C where a deep oxidation of benzene began to occur as indicated by the now substantial amounts of carbon oxides detected in the outlet gas. Further data was therefore recorded at 200 °C, an apparent optimal reaction temperature.

From here on we surveyed a number of catalyst and further reaction variables. The data in Fig. 4 relates the phenol production rate and catalyst productivity to platinum loadings for Pt–20% PMo_{12}/SiO_2 catalysts prepared using 400 (A) and 200 m^2/g (B) silica supports. The reaction rate shows a clear maximum at 0.5 and 1% Pt, respectively, while the catalyst productivity continually rises with diminishing metal loadings. Generally better results are seen here when using the higher surface area support. In attempts to better

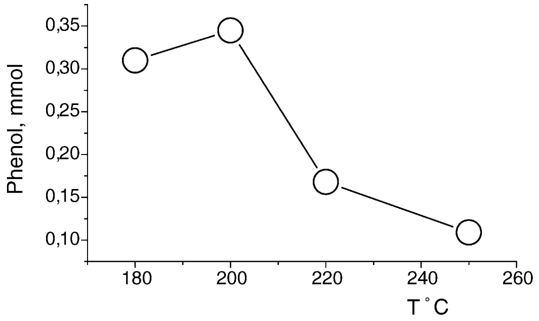


Fig. 3. Effect of temperature on phenol production in 1 h. Catalyst: 0.1% Pd–20% PMo_{12}/SiO_2 (400). The other conditions were as specified for Fig. 1.

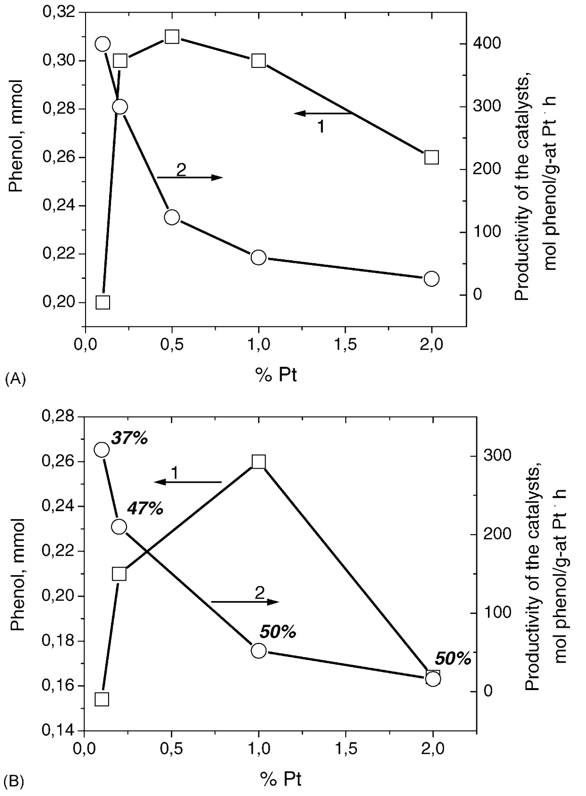


Fig. 4. Effect of Pt loading on phenol production in mmol in 1 h (1) and catalyst productivity in mol/g-atom Pt h (2). Catalysts: (A) Pt–20% PMo_{12}/SiO_2 (400); (B) Pt–20% PMo_{12}/SiO_2 (200); conversion of O_2 is given as percent in discrete points. The other conditions were as specified for Fig. 1.

understand the effect of the support and metal loadings a limited number of experiments were done using a variety of silicas of surface areas ranging from 13 to 400 m^2/g [27]. Also, catalyst samples were prepared using a double impregnation technique with the intent of thus providing a greater dispersion of platinum. The resulting variable phenol production rates however, provided no clear trends in this series of experiments.

By varying the $H_3PMo_{12}O_{40}$ heteropoly acid content in the range of 5–60 wt.%, an optimal value of 20–40% was determined for the Pt–PMo_{12}/SiO_2 (400) samples containing 0.1–0.2% of platinum; both an increase and reduction of HPC loading had a negative effect on phenol production.

The above initial survey experiments were conducted as noted with an equimolar feed of O_2 and H_2 and a maximum 5.5 vol.% O_2, to conservatively be outside the explosive limit for such mixtures. The data in Fig. 5 shows the effect of varying the H_2 content in the feed on the production of phenol, for a 1% Pt-20% PMo_{12}/SiO_2 (200 m^2/g) catalyst. Hydrogen is clearly necessary for a non-trivial formation of phenol and its production rate is almost proportional to the concentration of H_2 in the feed gas. It is seen however, that the reaction is very wasteful in hydrogen, most of which is converted to water. The effect of hydrogen is also seen in the prior Fig. 4B for the same catalyst for a similar O_2:N_2:C_6H_6:N_2 = 5.5:5.5:33:37 feed gas composition but with now a varying Pt content. Here the percent numbers at the discrete data points on the catalyst productivity curve are the O_2 conversion amounts as calculated from the oxygen concentration in the outlet flow. Even at low Pt loadings where the catalyst productivity is the highest only a few percent of the H_2 is used for the hydroxylation. At the 50% value, within the experimental variance, all of it appears to have been converted to water and at these conditions thus limiting a further hydroxylation of benzene.

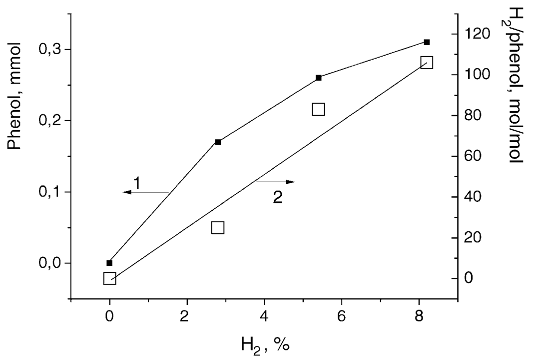


Fig. 5. Effect of hydrogen on phenol production in 1 h, and mol of H_2 consumed for 1 mol of phenol produced. Catalyst: 1% Pt–20% PMo_{12}/SiO_2 (200), 0.1 g. Composition of gas: 5.5% O_2, 33% C_6H_6 and H_2 in N_2, flow rate 160 ml/min, T 200 °C.

It was clear thus far in our work that heteropolymetal compounds (HPCs) can significantly promote or enhance the productivity of Pt/SiO_2 and Pd/SiO_2 catalysts for a hydroxylation of benzene to phenol with N_2-diluted 1:1 O_2:H_2 mixtures at 180–200 °C; by far the most effective HPC precursors being the heteropolyacids, $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$. In these survey experiments the benzene conversion was very low (~0.3%) and attempts were made to improve it.

It was possible to increase the benzene conversion, from 0.3 to 1.3% with a now lower catalyst productivity by using a larger amount of catalyst and a more dilute (6% versus 33%) benzene feed to the reactor (Entry #1 in Table 2). We observed a surprising and significant increase in benzene conversion without loss in selectivity for phenol by introducing water vapor with the feed gases (cf. #1 and #2 in Table 2). From the further data in this table it is clear that the water co-feed results in an encouragingly higher (up to 4.4%) benzene conversion at a least reasonable (60 mol phenol/g-atom Pt h) catalyst productivity.

A high resolution TEM micrograph (Fig. 6) taken of a 1% Pt–PMo_{12}/SiO_2 sample shows agglomerates of large particles with a high contrast Pt metal lattice. While the HPC is indiscernible on the silica surface it is apparently seen as a light structure next to the edge of the platinum particles. This TEM image represents a general view of the catalyst surface including some platinum/HPC interface regions (pointed to by arrows).

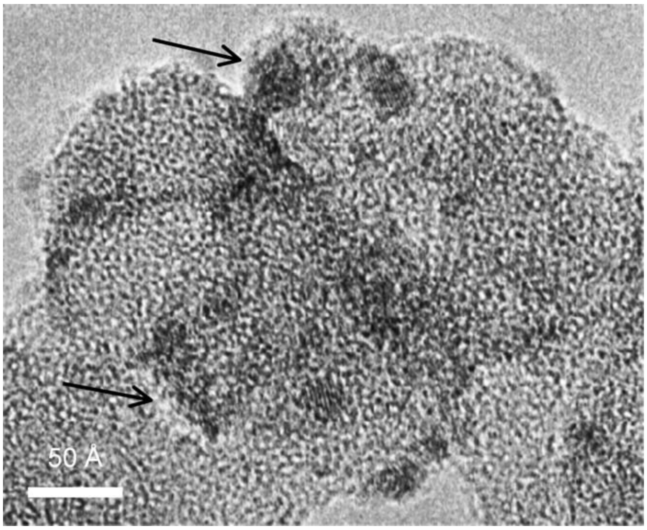


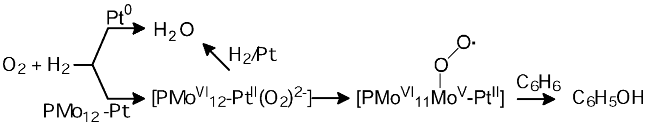
Fig. 6. HREM image of the 1% Pt–20% PMo_{12}/SiO_2 (200) sample prepared by a conventional single impregnation.

4. Discussion

It is clearly evident from the presented experimental data (Figs. 1 and 2) that the examined heteropolycompounds (HPCs), and $H_3PMo_{12}O_{40}$ and $H_3PMo_{11}VO_{40}$ in particular, significantly promote the hydroxylation of benzene by O_2/H_2 to phenol by Pt or Pd/SiO_2 catalyst systems.

The highest catalyst productivity of 360 mol phenol/g-atom metal h is seen for the 0.2% Pd–PMo_{12}/SiO_2 catalyst for which at a benzene conversion of 0.3% a 95–98% selectivity to phenol was realized. With a feed that is more dilute in benzene and contains added water vapor, a 0.2% Pt–PMo_{12}/SiO_2 catalyst productivity of 60 mol PhOH/g-atom h was noted at now a 4.9% conversion of benzene and 97% selectivity to phenol (Table 2). The overall performance of the Pt–HPC/SiO_2 and catalysts here represents a significant improvement over the prior art for benzene hydroxylation by O_2/H_2 which is collected and summarized in Table 1. The higher (up to 13%) benzene conversion made possible by the Pd membrane reactor in Ref. [24] is expected to be associated with a lower catalyst productivity and would clearly benefit from the catalyst promotion effect that we have seen here.

It is known even from previous studies [28] that highly dispersed forms of metallic platinum show only a very low activity in the gas-phase oxidation of benzene with O_2/H_2 mixtures. The herein demonstrated very significant effect of the HPC strongly suggests that the catalysis takes place at the interface or contact point between Pt (or Pd) clusters and particles of the heteropolymetallate species (an illustration of which is provided in Fig. 6) as illustrated by the following scheme:



It is postulated here that there is an initial adsorption of oxygen on Pt as a superoxo or peroxo species, which is then oxidized by the HPC to provide a more electrophilic reactive oxygen, most likely having radical character, which can then selectively react with benzene to produce phenol. There is in parallel an unproductive oxidation of the H_2 to water. This mechanism employing a combination of the catalytic metal and the HPC promoter was also invoked for our clearly related prior work on the hydroxylation of benzene [24] and oxygenation of the other hydrocarbons [25] in liquid media where the same promotion effect by the above cited HPCs is observed. According to the mechanism proposed, the HPC operates as an acceptor of the peroxo species and as a reversible one-electron oxidant. Such a reversible electron transfer step would require access to an optimal redox level of the HPC, as appears to be the case in the corresponding liquid-phase oxidation chemistry where there is a high degree of correlation between the redox potentials in the series of P–Mo and P–Mo–V HPCs and their catalyst promotion activities [25].

The mechanistic scheme, however speculative is nevertheless useful for conceptualizing how one might arrive at an improved catalyst for the process. Clearly needed is a very high Pt dispersion where the metal cluster surface is in maximum contact with the HPC and where this interface is accessible to the feed gases, and permits a facile desorption of (the less volatile) product. Our very limited data (Fig. 4) where there is improved productivity with a higher surface area silica support is at least consistent with this notion.

Table 2
Data on phenol formation (mmol/h), selectivity of hydrogen utilization (mol of H_2 consumed for 1 mol of phenol produced) and benzene conversion (mol%) over Pt–PMo_{12}/SiO_2 catalysts in the presence of water

No.	Catalyst	O_2:H_2:C_6H_6:H_2O (%)	Phenol (mmol/h)	mol H_2/mol phenol	Conv. of benzene (%)	Catalyst productivity[a]
1	1.3 g 1% Pt–20% PMo_{12}/SiO_2 (400)	5.5:5.5:6:0	0.25	70	1.3	4
2	1.3 g 1% Pt–20% PMo_{12}/SiO_2 (400)	5.5:5.5:6:22	0.39	30	2.0	6
3	1.5 g 0.2% Pt–20% PMo_{12}/SiO_2 (100)	5.0:9.0:5:15	0.61	12	2.8	40
4	1.5 g 0.2% Pt–20% PMo_{12}/SiO_2 (100)	14:9.0:5:15	0.65	29	3.0	40
5	1.5 g 0.2% Pt–20% PMo_{12}/SiO_2 (100)	9.0:9.0:5:15	0.96	11	4.4	60

Total flow rate 130 ml/min in Exps. 1 and 2 and 174 ml/min in Exps. 3 and 4, T 200 °C.

As is well evident from the data in Fig. 4 and Table 2 the present process is wasteful in H_2 and there is some indication from the Table 2 data that this situation might be mitigated by (a) reducing the Pt level—thus potentially exposing less metal surface for H_2 combustion and (b) adding water to the feed gas. Water, which is in any case produced in the system, but at lower concentrations, probably functions beneficially by adsorbing on the Pt or perhaps by facilitating the redox chemistry that is occurring at the heteropolymetallate sites. In summary, the challenge lies in tailoring the catalyst so as to achieve an optimal metal–HPC interface that is easily accessible to the organic molecules. And the means to quench as far as possible the combustion of hydrogen, to not only minimize the cost of this co-reagent but also to have sufficient oxygen remaining for an adequate conversion of the benzene to phenol.

Acknowledgment

The authors are grateful to the staff members of BIC: Dr. L.G. Simonova for the samples of silica supports, and Dr. V.I. Zaikovskii for the micrograph.

This study obtained financial support from Russian Foundation of Basic Research, grant 03-03-32787, and President Support of Leading Scientific Schools, grant 2287.2003.3.

References

[1] O.M. Niazyan, A.A. Mantashuan, A.B. Nalbandyan, Armenian Chem. J. 21 (3) (1968) 266 (in Russian).
[2] S. Umemura, R. Kitoh, T. Uda, Process for preparing phenol, USA Patent 433,871 (1982).
[3] V.A. Durante, T.P. Wijesekera, S. Karmakar, Catalysts for hydroxylation of aromatics using molecular oxygen as the terminal oxidant without coreductant, USA Patent 5,981,421 (1999).
[4] U.F. Schuchardt, L.C. Passoni, Phenol production by direct oxidation of benzene using oxygen in carboxylic acid or anhydride solvent in presence of palladium catalyst, Brazil Patent 9,302,551 (1995).
[5] A.K. Uriarte, M.A. Rodkin, M.J. Gross, A.S. Kharitonov, G.I. Panov, Stud. Surf. Sci. Catal. 110 (1997) 857.
[6] A. Keshavaraja, V. Ramaswamy, H.S. Soni, A.V. Ramaswamy, P. Ratnasamy, J. Catal. 157 (2) (1995) 501.
[7] A. Kumar Jr., S.K. Das, A. Kumar, J. Catal. 166 (1997) 108.
[8] R. Huang, X. Lu, B. Zhang, E. Wang, J. Li, J. Shi, Chin. Chem. Lett. 4 (4) (1993) 319.
[9] A.F. Duprat, P. Capdevielle, M. Maumy, J. Chem. Soc., Chem. Commun. (7) (1991) 464.
[10] T. Ohtani, S. Nishyama, S. Tsuruya, J. Catal. 155 (1) (1995) 158.
[11] L.V. Shibaeva, D.I. Metselitsa, E.T. Denisov, Neftekhimia 10 (5) (1970) 682 (in Russian).
[12] T. Jintoku, K. Takaki, Y. Fujiwara, Y. Fuchita, K. Hiraki, Bull. Chem. Soc. Jpn. 63 (2) (1990) 438.
[13] M. Lin, T.E. Hogan, A. Sen, J. Am. Chem. Soc. 118 (1996) 4574.
[14] A. Kunai, T. Kitano, Y. Kuroda, J. Li-Fen, K. Sasaki, Catal. Lett. 4 (1990) 139.
[15] N. Hideyki, N. Mitiyki, K. Motohiro, A method of hydroxylation of aromatic compounds, Japan Patent 6-256241 (1994).
[16] M. Hamada, Y. Sasaki, T. Mitake, A method for manufacturing a phenol, Japan Patent 5-4935 (1993).
[17] M. Hamada, H. Niwa, M. Oguri, T. Miyake, Process for producing phenols, USA Patent 5,426,245 (1993).
[18] T. Miyake, M. Hamada, Y. Sasaki, M. Oguri, Appl. Catal. A: Gen. 131 (1995) 33.
[19] T. Tatsumi, A method for manufacturing an aromatic hydroxy compound, Japan Patent 5-320082 (1993).
[20] J.E. Remias, T.A. Pavlosky, A. Sen, J. Mol. Catal. A: Chem. 203 (2003) 179.
[21] T. Kitano, T. Nakai, M. Nitta, M. Mori, S. Ito, K. Sasaki, Bull. Chem. Soc. Jpn. 67 (10) (1994) 2850.
[22] H. Ehrich, H. Berndt, M.-M. Pohl, K. Jahnisch, M. Baerns, Appl. Catal. A: Gen. 230 (2) (2002) 271.
[23] S. Niwa, M. Eswaramoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba, F. Mizukami, Science 295 (2002) 105.
[24] N.I. Kuznetsova, L.I. Kuznetsova, L.G. Detusheva, V.A. Likholobov, M.A. Fedotov, S.V. Koscheev, E.B. Burgina, Stud. Surf. Sci. Catal. 110 (1997) 1203.
[25] N.I. Kuznetsova, N.V. Kirillova, L.I. Kuznetsova, V.A. Likholobov, J. Mol. Catal. A: Chem. 204–205 (2003) 591.
[26] N.I. Kuznetsova, L.I. Kuznetsova, V.A. Likholobov, G. Pez, Catalyst and method of synthesis of phenol from benzene, RF Patent 2,205,688 (2003).
[27] N.I. Kuznetsova, L.I. Kuznetsova, V.A. Likholobov, Catal. Ind. 4 (2003) 17 (in Russian).
[28] A.P. Suknev, B.V. Goncharov, V.I. Zaikovskii, A.S. Belyi, N.I. Kuznetsova, V.A. Likholobov, B.S. Bal'zhnimaev, Stud. Surf. Sci. Catal. 130 (2000) 2297.