

One-step synthesis of phenol by O^- and OH^- emission material†

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A novel approach to the direct synthesis of phenol from benzene was obtained with high benzene conversion (30%) and phenol selectivity (~90%) by using a microporous material $[Ca_{24}Al_{28}O_{64}]^{4+}\cdot 4O^-$ (C12A7- O^-) as catalyst with oxygen and water; active O^- and OH^- anions are proposed to play important roles in the formation of phenol by hydroxylating the aromatic ring of benzene.

Phenol is one of the most important chemical products (about 7.2 megatons in 2003) and is widely used to produce other chemical products such as dyes and medicines. Currently, phenol is mainly produced industrially by the multi-stage cumene process which consists of three reactions: alkylation of benzene, oxidation of cumene and decomposition of cumene hydroperoxide.¹ However, some drawbacks of the cumene process are the co-production of acetone and the formation of small amounts of by-products which interfere in the separation steps (*e.g.*, *n*-propylbenzene and diisopropylbenzene). Therefore, the direct synthesis of phenol from benzene, even now, is still a fascinating topic.

The most promising results in the direct hydroxylation of benzene have been explored with N_2O as oxidant with various metal oxides,² and so far, with ZSM-5 zeolites or different ZSM-5 modifications as catalysts.³ The generally accepted mechanism of the formation of phenol is the reaction of benzene with the active monoatomic oxygen species by the decomposition of nitrous oxide.³ The synthesis of phenol in the above process takes advantage of the by-product N_2O from the adipic acid process. Also, some interesting results have been obtained by direct synthesis of phenol from benzene with H_2O_2 using modified zeolites as catalysts,⁴ *e.g.*, titanium-silicate (TS-1) zeolites.⁵ More recently, direct hydroxylation of benzene with oxygen and hydrogen catalyzed by the palladium membrane has been shown as an attractive process.⁶

Active anion species, such as O^- and OH^- , are key intermediates in anion chemistry,^{7–13} particularly in the low-temperature oxidation of hydrocarbons.^{10–12} For example, there are many reports about methane coupling on alkaline earth oxide surfaces, where the active oxygen species play a key role in the processes.^{14,15} Conventionally, anions are generated in a complex and costly process such as plasma, or other energetic irradiations. Recently, a special characteristic of the microporous crystal C12A7- O^- , storing and emitting O^- anion radicals, has been revealed in our previous work.¹⁶ Here, we show an approach to

the synthesis of phenol by using the O^- and OH^- anions to directly hydroxylate the aromatic ring of benzene.

The C12A7- O^- sample was prepared by a solid-state reaction at a high temperature. Powders of $CaCO_3$ and $\gamma-Al_2O_3$ were mixed and ground at a molar ratio of $CaCO_3 : \gamma-Al_2O_3 = 12 : 7$. The powder mixture was pressed to a pellet with a diameter of 15 mm and a thickness of 1.5 mm. Then it was sintered at 1573 K for 18 hours and cooled to room temperature under a flowing dry oxygen atmosphere. Afterwards the sintered pellets were ground into powder (250–350 μm), which was used as a catalyst for benzene conversion. Direct synthesis of phenol from benzene was performed in a double-tube type reactor, operating in continuous flow conditions at 1 atm (see ESI†). Normally, the reactor, containing 3 g of the C12A7- O^- sample on the surface of an inner quartz tube (16 mm od), was connected to an ice-cooled condenser. Benzene bubbled by argon gas or other mixed gas was fed to the sample between the inner and outer tubes (the gap: 2.5 mm). In order to continuously form O^- and OH^- , $Ar-O_2$ or $Ar-O_2-H_2O$ together with electrons (supplied by a negative dc power source with a current of 0.3–0.4 mA) were fed to the sample. The reactants and products were analyzed by two gas chromatograms. To clarify the optimum synthesis conditions, we carried out the experiments under three different reaction systems from 523 K to 973 K with air flow rate of 63 ml min^{-1} : (1) $C_6H_6-Ar-C12A7-O^-$, (2) $C_6H_6-O_2-Ar-C12A7-O^-$, and (3) $C_6H_6-O_2-H_2O-Ar-C12A7-O^-$.

It was found that phenol selectivity could reach nearly 100% when benzene and Ar were supplied onto the catalyst. This indicates that benzene could be directly hydroxylated by the active O^- species on the C12A7- O^- surface. However, the benzene conversion was very low ($\leq 0.3\%$) and quickly decreased with increasing reaction time. As shown in Fig. 1(a), with increasing concentration of O_2 , the conversion of benzene rapidly increased

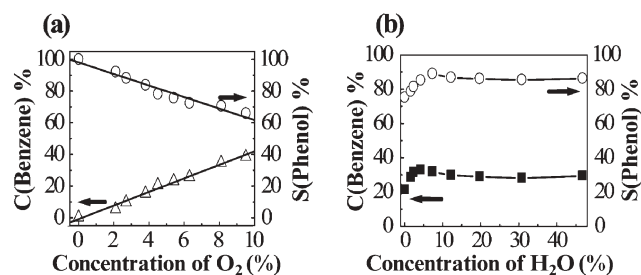


Fig. 1 (a) Effect of the oxygen concentration ($C_6H_6 : Ar = 0.094 : 0.916$) and (b) effect of the water concentration ($C_6H_6 : O_2 : Ar = 0.095 : 0.045 : 0.86$) with air-flow rate: 63 ml min^{-1} , pressure: 1 atm, reaction temperature: 838 K, implantation current: 0.35 mA, and C12A7- O^- : 3 g.

† Electronic Supplementary Information (ESI) available: the setup of TOF measurements and the emission features of C12A7- O^- ; the setup of the double-tube type reactor used for phenol synthesis. See <http://www.rsc.org/suppdata/cc/b4/b419206k/>

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along with a decrease in phenol selectivity. When oxygen concentration changed from 1% to 9.5%, the benzene conversion increased from 3.5% to 38%, but phenol selectivity decreased from 94% to 66%. CO and CO₂ were the major by-products and increased with increasing the oxygen concentration. A trace amount of aromatic by-products (diphenols and benzoquinone) and acids (maleic and fumaric acids) were detectable only at a high oxygen concentration (>5%). The formation of CO and CO₂ may arise from the pyrolysis process of phenol and benzene. Thus, the oxygen concentration should be controlled in order to depress further oxidation or hydroxylation of formed phenol.

Fig. 1(b) shows the dependence of the benzene conversion and the phenol selectivity on water concentration in the flowing gas mixture. The results indicate that the presence of water also plays an important role for the phenol synthesis. For example, the phenol selectivity increased from 75% to near 90% on increasing the concentration of water from 0 to 12% at a given O₂ concentration of 4.5% at 838 K. When the concentration of water was over 12%, no obvious changes of benzene conversion and phenol selectivity were observed. This result may imply that the conversion of benzene is controlled by the initial oxidation of benzene with the active O⁻ radicals, as discussed below. The role of water in the reaction system may enhance hydroxylation of benzene by increasing OH⁻ concentration, and inhibit the consecutive oxidation of phenol to form CO and CO₂.

Fig. 2(a) shows the effects of reaction temperature on benzene conversion and phenol selectivity with the optimum mixture. No benzene conversion was observed at temperatures lower than 523 K. When the reaction temperature was increased from 551 K to 980 K, the benzene conversion yield increased from 2.7% to 46%, but phenol selectivity decreased from about 90% to 78%. Moreover, the major by-products, CO and CO₂, also increased with increasing reaction temperature, resulting in a decrease in the phenol selectivity at a higher temperature. According to our previous work, it has been identified that when temperature rises from 773 K to 1073 K, the emitted O⁻ current density increases more than three orders of magnitude¹⁶ (from nA cm⁻² level to μA cm⁻² level). Accordingly, the concentration of O⁻ anions on the C12A7 surface should increase with the increasing temperature, which may lead to an increase in the catalytic activities for benzene conversion.

Fig. 2(b) shows the changes of the catalyst activity in the tested interval. The conversion of benzene and the phenol selectivity were close to 32% and 88% with a gas mixture of

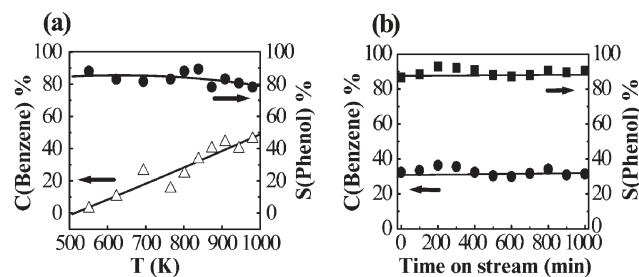


Fig. 2 (a) Effect of reaction temperature, and (b) stability of the catalyst with reactant mixture: C₆H₆ : O₂ : H₂O : Ar = 0.08 : 0.04 : 0.19 : 0.69, air-flow rate: 63 ml min⁻¹, pressure: 1 atm, implantation current: 0.35 mA, and C12A7-O⁻: 3 g.

C₆H₆ : O₂ : H₂O : Ar = 0.08 : 0.04 : 0.19 : 0.69 over the catalyst at 838 K, respectively. The phenol yield was about 1.26 ± 0.16 mmol g_{cat}⁻¹ h⁻¹, and remained nearly constant within the tested interval of 1000 min. It has been demonstrated that C12A7-O⁻ has an air-stable positively charged lattice framework structure even at a high temperature of 1073 K and exhibits excellent O⁻ emission properties.¹⁶ The stable performance for the catalytic conversion from benzene to phenol with C12A7-O⁻ catalyst may be attributed to the structural stability of C12A7-O⁻ and the sustainable formation of active O⁻ and OH⁻ anion species.

In order to reveal the reaction mechanism, the intermediates in the formation of phenol were measured using a TOF (time of flight) spectrometer. The experimental apparatus is described in the ESI.† The anionic intermediates in the above reaction systems were investigated under low-pressure conditions (C₆H₆ ≈ 3 × 10⁻⁴ torr). When only benzene was fed to the C12A7-O⁻ surface by a nozzle, the desorbed anionic species such as O⁻, OH⁻, C₆H₅⁻ and C₆H₅OH⁻ were clearly identified by their TOF spectra (Fig. 3(a)). As oxygen or oxygen–water mixtures together with electrons were supplied onto C12A7-O⁻, both OH⁻ and C₆H₅OH⁻ intensity increased (Fig. 3(a)). Weak anionic signals such as CO⁻, CO₂⁻, H₂O⁻, C₆H₄⁻, C₆H₅O⁻ and other anionic hydrocarbon species were also observed. The intensity of O⁻, OH⁻ and C₆H₅OH⁻ increased with increasing the surface temperature of C12A7-O⁻ in our investigated range (823–1003 K).

It was noted that the atomic oxygen radical anion (O⁻) has an extremely high oxidation power and high reactivity, and it has been reported that O⁻ can react with methane on MgO even at 130 K.¹⁷ The reaction of benzene with the active monoatomic oxygen species was also suggested to play a key role in the formation of phenol with N₂O as oxidant over various metal oxides or ZSM-5 zeolites.^{2,3} According to our investigations mentioned above, the formation of phenol should be correlated with the active species on the C12A7-O⁻ surface (e.g., O⁻ (s) and OH⁻ (s)). As schematically described in Fig. 3(b), O⁻ (s) was suggested as an active species in initiating the benzene conversion process *via* hydrogen abstraction reaction (C₆H₆ (s) + O⁻ (s) → C₆H₅ (s) + OH⁻ (s)). Then, the intermediate species C₆H₅OH⁻ (s) was formed from the reaction of phenyl radical C₆H₅ (s) with OH⁻ (s), leading to the formation of phenol by a detachment process: C₆H₅OH⁻ (s) → C₆H₅OH (g) ↑ + e⁻ (s). The above approaches were supported by the following facts: (1) O⁻ (s) and

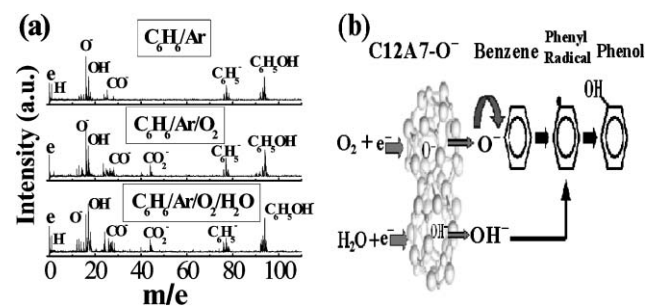


Fig. 3 (a) TOF spectra for three reaction systems: C₆H₆-Ar-C12A7-O⁻, C₆H₆-O₂-Ar-C12A7-O⁻, and C₆H₆-O₂-H₂O-Ar-C12A7-O⁻. C₆H₆: 3 × 10⁻⁴ torr; T: 923 K; Ar, O₂-Ar (0.5 : 0.95), and O₂-H₂O-Ar (0.05 : 0.20 : 0.75) were supplied on the back side of C12A7-O⁻, respectively. (b) The schematic pathway of phenol synthesis by directly hydroxylating the aromatic ring of benzene with O⁻ and OH⁻.

OH^- (s) exist on the C12A7-O^- surface (see ESI†); (2) $\text{C}_6\text{H}_5\text{OH}^-$, phenol and OH^- were observed in the $\text{Ar-C}_6\text{H}_6\text{-C12A7-O}^-$ system; (3) on increasing the amount of OH^- (by implanting water and electrons onto the C12A7-O^- surface), $\text{C}_6\text{H}_5\text{OH}^-$ and phenol yield increased. On the other hand, the phenol produced by the gas-phase reactions among O^- (g), OH^- (g), and C_6H_6 (g) was found to be negligible under our investigated conditions. Thus, the phenol is mainly produced by the reactions on the C12A7-O^- surface. To achieve a clearer description of the reaction mechanism of the benzene conversion to phenol, we still need to do lots of work such as neutral radical measurements and catalyst characterization. Work towards this goal is in progress.

In summary, we present a new method for one-step synthesis of phenol by hydroxylation of benzene over the C12A7-O^- catalyst with oxygen and water. C12A7-O^- material appears to possess a high catalytic activity and stability. The active anions of O^- and OH^- should play a key role in the phenol synthesis process. The present approach might be useful and extend to other processes such as methane conversion to methanol and material synthesis or modification.

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Notes and references

- 1 R. A. Sheldon and R. A. van Santen, *Catalytic Oxidation, Principles and Applications*, World Scientific, Singapore, 1995.
- 2 M. Iwamoto, J. Hirata, K. Matsukami and S. Kagawa, *J. Phys. Chem.*, 1983, **87**, 903.
- 3 (a) A. Reitzmann, E. Klemm and G. Emig, *Chem. Eng. J.*, 2002, **90**, 149; (b) G. I. Panov, A. K. Uriarte, M. A. Rodkin and V. I. Sobolev, *Catal. Today*, 1998, **41**, 365; (c) G. I. Panov, *CATTECH*, 2000, **4**, 1, 18.
- 4 (a) C. W. Lee, W. J. Lee, Y. K. Park and S. E. Park, *Catal. Today*, 2000, **61**, 137; (b) K. Fujishima, A. Fukuoka, A. Yamagishi, S. Inagak, Y. Fukushima and M. Ichikawa, *J. Mol. Catal. A*, 2001, **166**, 211; (c) V. I. Parvulescu, D. Dimitriu and G. Poncelet, *J. Mol. Catal.*, 1999, **140**, 91.
- 5 A. Thangaraj, R. Kumar and P. Ratnasamy, *Appl. Catal.*, 1990, **57**, L1.
- 6 S. I. Niwa, M. Eswaremoorthy, J. Nair, A. Raj, N. Itoh, H. Shoji, T. Namba and F. Mizukami, *Science*, 2002, **295**, 105.
- 7 D. V. Deubel and G. Frenking, *J. Am. Chem. Soc.*, 1999, **121**, 2021.
- 8 R. W. Fessenden and D. Meisel, *J. Am. Chem. Soc.*, 2000, **122**, 3773.
- 9 J. Lee and J. J. Grabowski, *Chem. Rev.*, 1992, **92**, 1611.
- 10 M. Born, S. Ingemann and N. M. M. Nibbering, *Mass Spectrom. Rev.*, 1997, **16**, 181.
- 11 T. Tashiro, T. Watanabe, M. Kawasaki and K. Toi, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1263.
- 12 (a) K. I. Aika and J. H. Lunsford, *J. Phys. Chem.*, 1977, **81**, 1393; (b) T. Ito, T. Tashiro, M. Kawasaki, T. Watanabe and K. Toi, *J. Phys. Chem.*, 1991, **95**, 4476.
- 13 S. G. Neophytides, D. Tsiplakides, P. Stonehart, M. M. Jaksic and C. G. Vayenas, *Nature*, 1994, **370**, 45.
- 14 E. P. J. Mallens, J. H. B. J. Hoebink and G. B. Marin, *J. Catal.*, 1996, **160**, 222.
- 15 R. Spinicci, *Mater. Chem. Phys.*, 1997, **49**, 124.
- 16 (a) K. Hayashi, M. Hirano, S. Matsuishi and H. Hosono, *J. Am. Chem. Soc.*, 2002, **124**, 738; (b) Q. X. Li, H. Hosono, M. Hirano, K. Hayashi, M. Nishioka, H. Kashiwagi, Y. Totimoto and M. Sadakata, *Surf. Sci.*, 2003, **527**, 100; (c) Q. X. Li, K. Hayashi, M. Nishioka, H. Kashiwagi, M. Hirano, H. Hosono and M. Sadakata, *Appl. Phys. Lett.*, 2002, **80**, 4259.
- 17 K. Aika and J. H. Lunsford, *J. Phys. Chem.*, 1977, **81**, 1393.