could be further diminished by using shorter electrical pulses and reducing the backgound luminescence from the sample.

As for the prospects of realizing a single-photon–emitting diode for practical applications, the emission wavelength of the quantum dots chosen for study here is dictated by the spectral response of the Si single-photon detectors used in the experiments. However, InAs self-organized quantum dots can be tailored to emit at the wavelength used for long-distance fiber optic communications, around 1.3 μm (*24*). Furthermore, these longer wavelength quantum dots have much deeper carrier confinement potentials and thus emit efficiently at higher temperatures. In addition, the collection efficiency from the dot can be enhanced by means of an integrated cavity structure (*25*). Quantum dot light-emitting diodes may therefore provide an attractive source of either single photons or photon pairs for applications in quantum information technology and experiments in quantum optics.

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A One-Step Conversion of Benzene to Phenol with a Palladium Membrane

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Existing phenol production processes tend to be energy-consuming and produce unwanted by-products. We report an efficient process using a shell-and-tube reactor, in which a gaseous mixture of benzene and oxygen is fed into a porous alumina tube coated with a palladium thin layer and hydrogen is fed into the shell. Hydrogen dissociated on the palladium layer surface permeates onto the back and reacts with oxygen to give active oxygen species, which attack benzene to produce phenol. This one-step process attained phenol formation selectivities of 80 to 97% at benzene conversions of 2 to 16% below 250°C (phenol yield: 1.5 kilograms per kilogram of catalyst per hour at 150°C).

Phenol is an important commodity chemical in industry: World production exceeded 6.6 megatons in 2000. Industrially, phenol has mainly been produced from benzene via cumene to cumene hydroperoxide (the so-called cumene process), but this three-step process (*1*) not only has a low phenol yield but is also highly energy-consuming. Furthermore, problems arise in treating its by-products, such as acetone and α-methylstyrene. Recently, direct oxidation of benzene to phenol by nitrous oxide (*2–4*) has been commercialized, but it is cost-effective only if nitrous oxide can be obtained cheaply as a by-product (*5*). Here we report an efficient one-step oxidation of benzene to phenol through direct hydroxylation of an aromatic ring in gas phase with oxygen activated by dissociated hydrogen obtained from a palladium membrane.

All direct hydroxylations (*6–16*) of aromatic nuclei with oxygen and hydrogen that have been reported so far have been done by simultaneously mixing an aromatic compound, oxygen, and hydrogen in liquid phase, using a very complicated system containing a multicomponent catalyst, a solvent, and some additives. Besides the possibility of an explosive gas reaction, these hydroxylations give only very low aromatic alcohol yields of 0.0014 to 0.69% (based on the amount of aromatic hydrocarbon initially used). We developed the direct hydroxylation of aromatic nuclei through a system in which hydrogen and oxygen are separately supplied or in which hydrogen is fed into a mixed gas stream of a substrate and oxygen through a metallic thin layer. This system is quite simple and appears to be practical when compared with other direct hydroxylations (*17–25*) reported recently.

The membranes were prepared by coating a porous α-alumina tube (NOK Corporation; α-Al$_2$O$_3$, 99.99%; outer diameter, 2.0 mm; inner diameter, 1.6 mm; void fraction, 0.43; average pore size, 0.15 μm) with a palladium thin layer (thickness, 1 μm; length, 100 mm) by means of a metallorganic chemical vapor deposition technique (*26*), using palladium(II) acetate (reagent grade) as the palladium source. At 300°C, the hydrogen and nitrogen permeation rates of the membranes prepared were 1.0 to 3.0 × 10^{-3} mol m^{-2} s^{-1} Pa$^{-0.5}$ and 0.1 to 1.0 × 10^{-10} mol m^{-2} s^{-1} Pa^{-1}, respectively.

A shell-and-tube reactor was set up with this membrane (Fig. 1) and used for the hydroxylation of aromatics. An aromatic hydrocarbon was fed into the membrane tube together with a mixed gas of oxygen and helium by bubbling it into the hydrocarbon liquid, and a pressurized mixture of hydrogen and helium (about 2 kg/cm^2) was flowed into the shell (outside of the tube). In some cases, the feeding of the gas mixtures was carried out in reverse; that is, hydrogen was fed inside of the tube and a hydrocarbon and oxygen were outside. The gaseous mixture coming out of the reactor was analyzed by an online gas chromatograph equipped with a capillary column (diameter, 0.25 mm; length, 25 m; packing reagent, PEG-20 M wide bore).

This palladium membrane reactor works well under mild conditions (below 250°C) for the direct hydroxylation of an aromatic nu-

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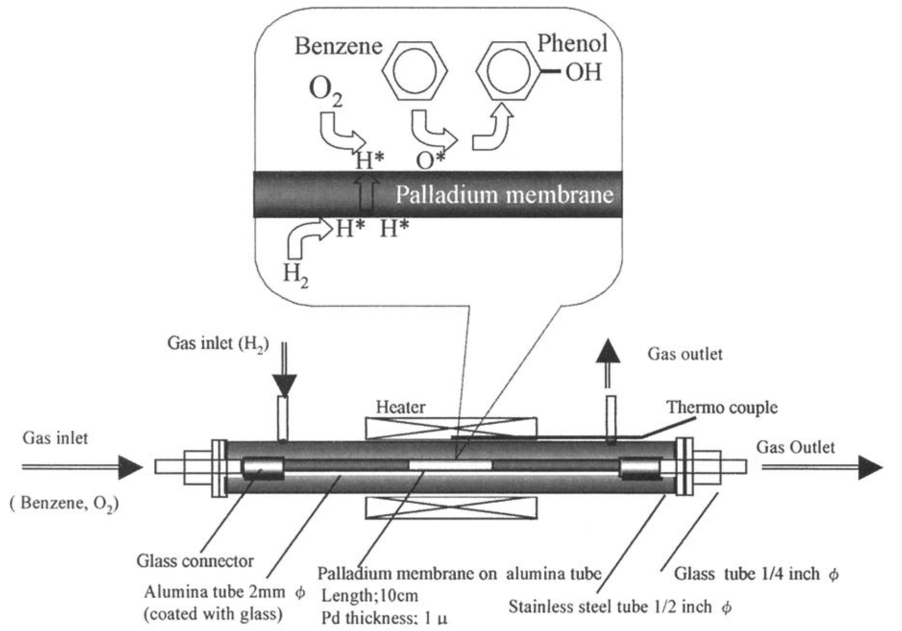

Fig. 1. Apparatus for direct hydroxylation of aromatics and the working principle of the palladium membrane.

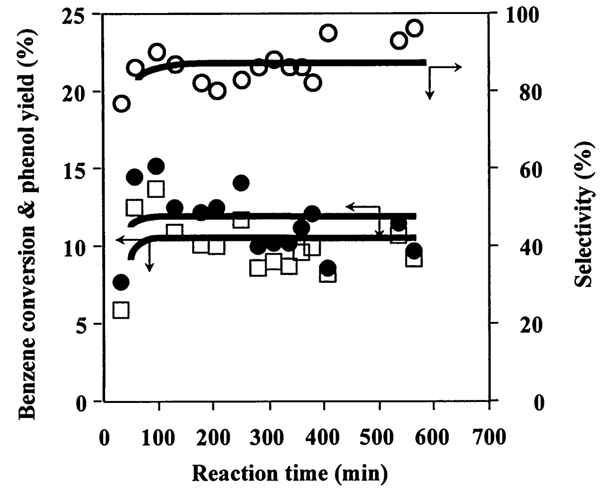

Fig. 2. Oxidation of benzene with oxygen and hydrogen catalyzed by a palladium membrane at 200°C. Flow rates: shell (outside), 25 ml/min (H_2/He = 5.6/20, volume ratio); tube (inside), 25 ml/min (benzene/O_2/He = 0.4/3.8/25, volume ratio). Solid circles, squares, and open circles denote benzene conversions, phenol yields, and phenol selectivities, respectively.

Table 1. Direct hydroxylation of benzene to phenol and toluene to cresol with oxygen and hydrogen catalyzed by a palladium membrane. "Inner" and "outer" mean that a gaseous mixture containing a hydrocarbon was flowed inside or outside of the palladium membrane tube, respectively. Selectivity was based on the amount of benzene or toluene consumed.

Catalyst	Reaction temp. (°C)	Reaction system (volume ratio)		Results	
		Aromatic/O_2/He (28 ml/min)	H_2/He (14 ml/min)	Reactant conversion (%)	Product selectivity (%)
		Benzene			
Pd membrane (inner)	150	0.40/1.29/24.6	2.43/20.0	13.25	85.3
Pd membrane (inner)	160	0.45/4.70/29.8	6.72/28.2	1.60	96.3
Pd membrane (inner)	250	1.80/8.51/24.6	10.06/24.9	2.05	92.7
Pd membrane (outer)	150	2.00/1.29/24.6	2.43/20.0	2.11	94.8
Pd membrane (outer)	200	2.00/1.29/24.6	2.43/20.0	3.00	93.3
		Toluene			
Pd membrane (inner)	150	0.40/1.29/24.6	2.43/20.0	34	80

cleus. The hydrogen permeation rate of the membrane markedly increased with feeding of a gaseous mixture of oxygen and a substrate, as compared with the rate without such feeding (the intrinsic hydrogen permeation rate) (*27*). Phenol was produced in a high selectivity over 90% at low benzene conversions (below 3.0%) and over 80% at high conversions (10 to 15%) (Table 1 and Fig. 2). Dihydroxy compounds and quinones were detected in trace amounts only at the high conversions, which suggests that successive oxidations were considerably limited. Under our reaction conditions, hydrogenated compounds such as cyclohexane, cyclohexanol, and cyclohexanone were hardly produced at all. Thus, it is concluded that the hydrogen consumed turns almost completely into water; the molar ratios of water to phenol were 5 to 9 (*28*). However, when the reactions were prolonged, cyclohexanol and cyclohexanone were detected in small amounts, and the deterioration of the membrane was also observed (*29*).

When the substrate was toluene, a mixture of cresols (*o*-:*m*-:*p*-isomer ratio = 3.2:1.0:5.1) was produced in a high selectivity (>80%) even at a high toluene conversion (>34%). Methyl cyclohexane (hydrogenated compound) was hardly produced at all. Aromatic by-products (dihydroxy compounds) were barely detected (<1%), and methyl group–oxygenated compounds such as benzaldehyde and benzyl alcohol were produced in small amounts (<5% in sum of the two). Direct hydroxylations (*12–16*) of toluene reported recently, such as those catalyzed by 0.5 weight % (wt %) Pt/1 wt % V_2O_5/SiO_2 (*12*), $EuCl_3$-Zn-CH_3COOH (*14*), and EuX_3-$TiO(acac)_2$-Pt oxide/SiO_2 (*15*) (acac, 2,4-penntanedionate ion; X = Cl, ClO_4, and $CF_3SO_3^-$), had respective ratios (*12–15*) of ring oxygenation to methyl group oxygenation of 3.7, 2.6, 0.2, 0.6, and 7.0. In the present work, this ratio was more than 8.0.

Generally speaking, the methyl group oxygenation requires abstraction of an H• radical by active oxygen species, whereas ring oxygenation is initiated by the attack of active oxygen species on the ring (*15*). Active oxygen species that are electrophilic tend to prefer the ring to the methyl group, and oxygen species that have a radical character prefer the methyl group to the ring (*15*). Thus, the active oxygen species in the present process appear to be relatively more electrophilic.

Among the various active oxygen species (denoted as O* in Fig. 1) considered {for example, O [atomic oxygen at the ground state: ^3P, oxene (*7*)], HOO•, HO•, O^{2-}, O^-, OH^-, etc.} negatively charged species are unlikely (*7*) to be the active species because they are nucleophilic but not electrophilic. The former three species can act as the electrophile and be produced as follows. Hydrogen is dissociated in permeating through the palladium membrane

(*30–32*), and the dissociated hydrogen (denoted as H* in Fig. 1) appearing on the surface of the opposite side of the membrane immediately reacts with oxygen to give HOO· and H_2O_2. Then H_2O_2 is decomposed to HO·, atomic oxygen, and water. In the direct hydroxylation (*8–12*) of hydrocarbons with oxygen and hydrogen catalyzed by transition metals, it has been considered so far that, at the first step, oxygen and hydrogen react with the catalysis of the metals to give hydrogen peroxide. We also recognized that this membrane reactor can easily produce hydrogen peroxide under the reaction conditions used here without hydrocarbons, and quite recently it was reported (*33*) that a similar palladium membrane works well in water as a reactor for the direct production of hydrogen peroxide from oxygen and hydrogen. Oxene, one of the active oxygen species produced by the decomposition of hydrogen peroxide, has been known to easily add to carbon-carbon double bonds, including conjugated ones such as benzene (*7*, *34*). This type of addition is 10^3 times faster in rate than the hydrogen abstraction from the methyl group (*7*, *35*). Thus, it is not unreasonable to consider that oxene is largely responsible for the hydroxylation in this membrane process.

If the HO· radical is the main active species, as has been considered (*12*), benzyl alcohol and benzaldehyde should be produced more in the hydroxylation of toluene, as occurs with EuX_3-$TiO(acac)_2$-Pt oxide/SiO_2 (X = Cl and ClO_4) catalysts (*15*). However, it is difficult to specify the real active species from the three (HOO·, HO·, and oxene) at present, although it seems likely that the active oxygen species is derived from HOO· and H_2O_2.

It should be emphasized that this membrane system could be practical, because it is simple in structure; produces phenol in a yield of 1.5 kg per kilogram of catalyst per hour; and has a low probability of causing a detonating gas reaction, because oxygen and hydrogen are not simultaneously mixed.

References and Notes

1. For example, at the first step for the production of cumene from benzene and propylene with the traditional supported phosphoric acid catalyst (200° to 250°C, 14 to 21 kg/cm^2), the benzene conversion is about 20%, and at the second step for the oxidation of cumene to cumene hydroperoxide with air (80° to 130°C), the conversion is about 25%. At the third step for the decomposition of cumene hydroperoxide to phenol and acetone with sulfuric acid, phenol is produced in a yield over 93%. Accordingly, in this traditional process, the one-pass yield of phenol based on the amount of benzene initially used is less than 5%.
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25. The phenol yields based on the amount of benzene initially used are 2.79% for the hydroxylation with oxygen and carbon monoxide (*17*, *18*), 3.4 to 4.3% for the hydroxylation with oxygen (*20*, *21*), and 0.085 to 18.15% for the hydroxylation with expensive hydrogen peroxide (*11*, *22–24*).
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27. This means that the reaction of oxygen with dissociated hydrogen permeating through the membrane is faster than the recombination between the dissociated hydrogen atoms themselves on the opposite membrane surface. At the same time, this suggests that under our reaction conditions, the rate-limiting step for the conversion of benzene to phenol is the reaction between oxygen and hydrogen rather than the hydrogen permeation, and direct mixing of oxygen and hydrogen in gas phase is very limited (oxygen and hydrogen are well separated except on the membrane interface where both meet).
28. The ratios of water to phenol were changed with the palladium membranes used, because it is impossible to prepare exactly the same membranes. Generally speaking, the ratios were lower with the membranes that showed higher performance for the phenol formation.
29. The deterioration was mainly due to peeling off of the palladium thin layer from the α-alumina tube. This peeling off could be suppressed by coating the thin layer with a certain polymer. The polymer-coated membrane also works well for the hydroxylation.
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Constraints on Melt Movement Beneath the East Pacific Rise From ^{230}Th-^{238}U Disequilibrium

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We report ^{230}Th-^{238}U disequilibrium data on mid-ocean ridge basalts recovered 5 to 40 kilometers off the ridge axis near 9°30′N of the East Pacific Rise. These data indicate near-symmetrical eruptions of normal mid-ocean ridge basalts (NMORBs) and incompatible element–enriched mid-ocean ridge basalts (EMORBs) as far as 20 kilometers off axis. Our results suggest large-scale subsurface lateral transport of NMORB melt at 19 to 21 centimeters per year and also provide constraints on the petrogenesis of EMORBs of off-axis origin.

Lavas that erupt on the seafloor away from the axis of mid-ocean ridges (MORs) contain information about melting, melt movement, and crustal accretion processes associated with MOR spreading centers (*1–3*). For off-axis basalts to be used to develop a better understanding of the process of melt movement, they must be demonstrably distinguished from those originally erupted at the ridge axis. ^{230}Th-^{238}U disequilibrium can provide temporal information crucial to identifying basalts of off-axis origin and has been used to study basalts as far as 4 km away from the ridge axis (*4*). To span a scale of melt movement beneath MORs that may be greater than 4 km, and to avoid large axial eruptions that send lava flows as far as 3.5 km away from the axis (*5*), we measured the ^{230}Th-^{238}U disequilibrium of basalts from 5 to 40 km off-axis.

Our samples were collected during the

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