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Selective oxidation of benzene to phenol with molecular oxygen on rhenium/zeolite catalysts†

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Zeolite-supported rhenium catalysts are active for selective oxidation of benzene with molecular oxygen, where coexisting ammonia is prerequisite to the direct phenol synthesis.

Phenol which is one of the most important basic chemicals has been produced industrially by the cumene process composed of three steps. However, the process has intrinsic problems such as by-product formation, low energy efficiency, *etc.* Direct phenol synthesis from benzene as an alternative way to overcome the problems has been extensively studied by using molecular oxygen,[1–3] H_2O_2,[4,5] N_2O,[6,7] NO[8] and $H_2 + O_2$[9] as oxidants. No selective catalyst with a good performance in an economically and environmentally favorable benzene–O_2 system has been discovered to date.

Rhenium has a similar redox property to molybdenum and vanadium which show selective oxidation catalysis, but its catalytic application has been limited to the reactions in reductive conditions such as rheniforming and olefin metathesis because Re_2O_7 formed under oxidative conditions is easily sublimed. Here we report the first ReO_x catalyst selective for the phenol synthesis from benzene with O_2 under coexisting NH_3. The presence of spectator NH_3 is indispensable to the genesis of the selective benzene oxidation catalysis. The only example similar to this phenomenon is the selective oxidation of propene to acrolein on Re/zeolites, where active $[Re_6O_{17}]$ clusters are formed by the added NH_3.[10]

The supported rhenium catalysts were prepared by two methods; one is a conventional impregnation method using ammonium perrhenate (NH_4ReO_4) and the other is a chemical vapor deposition (CVD) method using methyltrioxorhenium (CH_3ReO_3: MTO). After impregnation, the sample was dried at 373 K for 12 h. In the CVD procedure ZSM-5, Beta, USY and Mordenite were pressed and sieved to 355–710 μm granules, and calcined at 873 K for 2 h, then the zeolite and MTO were placed in a glass apparatus, where only the zeolite was further treated at 673 K for 0.5 h under vacuum. Next, heating the whole apparatus at 333 K, the zeolite was exposed to the MTO vapor for 14 h. The impregnation and CVD catalysts were pretreated in a helium flow (22.4 $cm^3\ min^{-1}$) at 673 K for 1 h and cooled to a given reaction temperature in a helium flow. The selective catalytic reactions were conducted in a fixed bed flow reactor. A typical composition of reaction gases was He:O_2:NH_3:benzene = 72.6:10.4:10.4:6.6 (mol%) and W/F was typically 6.7 $g_{cat}\ h\ mol^{-1}$. The products were analyzed by two on-line gas chromatographs with a FID detector using a NEUTRABOND-1 column for hydrocarbons and with a TCD detector using a Unibeads C column for inorganic materials.

Table 1 shows the performances of the ReO_x/zeolite catalysts for the selective oxidation of benzene with O_2, $PhH + 1/2\ O_2 \rightarrow PhOH$. No phenol was produced on the zeolites and ReO_x/zeolites. No positive effect of H_2O addition on the selective oxidation was observed. Further, N_2O as oxidant never improved the performance unlike a Fe-containing zeolite catalyst.[11] It was found that the coexistence of NH_3 dramatically activated the ReO_x/zeolite catalysts for the direct phenol synthesis. The impregnated ReO_x/H-ZSM-5 catalyst showed a rate of 1.8×10^{-8} mol $g_{Re}^{-1}\ s^{-1}$ and a selectivity of 20% in the presence of NH_3. The NH_3 effect was observed more dramatically with the CVD ReO_x/H-ZSM-5 catalyst which exhibited a rate of 7.1×10^{-7} mol $g_{Re}^{-1}\ s^{-1}$ and a selectivity of 40% (Table 1). The CVD catalyst is 16–39 times more

Table 1 Catalytic phenol synthesis from benzene and molecular oxygen on supported rhenium catalysts at 573 K[a]

Catalyst	SiO_2/ Al_2O_3	Method	Amine	Re loading/%	TOF/ $10^{-5}\ s^{-1}$ [b]	PhOH sel./% [c]	$Rate_{PhOH}$/ μmol $g_{Re}^{-1}\ s^{-1}$
H-ZSM-5	39.4	—	NH_3	0.0	0.0	—	0.0
Re/H-ZSM-5	39.4	impregnation	none	2.5	0.0	—	0.0
Re/H-ZSM-5	39.4	impregnation	NH_3	0.5	1.7	20	0.018
Re/H-ZSM-5	39.4	impregnation	NH_3	2.5	4.0	21	0.045
Re/H-ZSM-5	39.4	CVD	none	0.40	0.0	—	0.0
Re/H-ZSM-5	39.4	CVD	Pyridine	0.40	trace	0	0.0
Re/H-ZSM-5	39.4	CVD	$(CH_3)_2CHNH_2$	0.40	trace	0	0.0
Re/H-ZSM-5	39.4	CVD	NH_3	0.40	33.0	40	0.71
Re/H-ZSM-5[d]	39.4	CVD	NH_3	0.40	47.2	46	1.17
Re/H-ZSM-5[e]	39.4	CVD	NH_3	0.40	74.4	41	1.64
Re/H-ZSM-5	193	CVD	NH_3	0.40	44.3	7	0.17
Re/H-Beta	37.1	CVD	NH_3	0.53	58.0	5	0.16
Re/H-USY	29.0	CVD	NH_3	0.60	trace	0	0.0
Re/H-Mordenite	220	impregnation	NH_3	1.0	7.63	8	0.033
Re/H-Mordenite	220	CVD	none	0.55	0.0	—	0.0
Re/H-Mordenite	220	CVD	NH_3	0.55	86.7	15	0.70
Re/γ-Al_2O_3	—	impregnation	NH_3	2.5	0.0	—	0.0
Re/α-Fe_2O_3	—	impregnation	NH_3	1.0	0.0	—	0.0

[a] Catalyst, 0.50 g; W/F = 6.7 $g_{cat}\ h\ mol^{-1}$; He:O_2:NH_3 (amine):benzene = 72.6:10.4:10.4:6.6 (mol%). [b] Amount of consumed benzene/Re/s. [c] Phenol selectivity in the carbon%. [d] Catalyst, 0.50 g; W/F = 6.7 $g_{cat}\ h\ mol^{-1}$; He:O_2:NH_3:benzene = 55.3:6.9:31.2:6.6 (mol%). [e] Catalyst, 0.50 g; W/F = 6.7 $g_{cat}\ h\ mol^{-1}$; He:O_2:NH_3:benzene = 31.0:10.4:52.0:6.6 (mol%).

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† Electronic supplementary information (ESI) available: Fourier transformed EXAFS functions at Re L_{III}-edge. See http://www.rsc.org/suppdata/cc/b4/b401373e/

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active than the impregnation catalyst. The catalytic performance depended on the kind of zeolites as support for Re species; the rate of phenol production decreased in the order, H-ZSM-5 (SiO_2/Al_2O_3 = 39.4) ≥ H-Mordenite > H-ZSM-5 (SiO_2/Al_2O_3 = 193) ~ H-Beta > H-USY, and the selectivity decreased in the order, H-ZSM-5 (SiO_2/Al_2O_3 = 39.4) > H-Mordenite ~ H-ZSM-5 (SiO_2/Al_2O_3 = 193) > H-Beta > H-USY. Thus H-ZSM-5 (SiO_2/Al_2O_3 = 39.4) among the employed zeolites is the most favorable support for Re species. Re/γ-Al_2O_3 and Re/α-Fe_2O_3 were inactive for the selective oxidation of benzene with O_2, which is contrasted to the good performances of these catalysts for the selective oxidation of methanol to methylal.[12] To our knowledge the H-ZSM-5 (SiO_2/Al_2O_3 = 39.4) catalyst shows the highest selectivity for the direct synthesis from benzene with O_2. The activity and selectivity of the H-ZSM-5 (SiO_2/Al_2O_3 = 39.4) catalyst did not decrease for at least 6 h.

Fig. 1 shows the dependencies of phenol formation rate and selectivity on the partial pressures of ammonia (a) and oxygen (b). The activity increased with increasing ammonia and oxygen pressures and reached the saturated values. The maximum selectivity was 46% at 1.17×10^{-6} mol g_{Re}^{-1} s^{-1} and 45 % at 1.36×10^{-6} mol g_{Re}^{-1} s^{-1} (Fig. 1). Ammonia is indispensable to the phenol production on the ReO_x/zeolite catalysts. However, excess ammonia decreased it by poisoning. Excess oxygen did not increase the complete oxidation of benzene to CO_2 so much, which may be an advantage with this catalyst.

Ammonia was replaced by pyridine and isopropylamine to examine the effect of basicity of coexisting gases on the performance. The catalysts were inactive under these basic compounds. Ammonia may reduce the Re species under the reaction conditions, which was indicated by EXAFS. The MTO precursor reacted with OH groups (Brønsted acid site) in the pores of H-ZSM-5 to form CH_4 (evolved in the gas phase) and [$OReO_3$] species. The [$OReO_3$] species was analyzed by EXAFS to have three Re=O bonds at 0.173 nm similar to the MTO and a Re–O bond at 0.209 nm, and a part of the Re species is further coordinated by another oxygen of the pore wall as indicated by the coordination number (CN) of 1.84 for Re–O (Table 2). The CN of Re=O decreased from 2.70 to 2.20 after the catalytic phenol synthesis at 573 K, which indicates the reduction of the Re^{7+} species to probably the Re^{6+} species. The non-selective Re/H-Mordenite catalyst showed about half CN value (1.49) and definite Re–Re bonding at 0.273 nm with 1.65 CN (Table 2 and Supplementary Information†). The results demonstrate the aggregation of reduced Re species in the Mordenite pores. The part of aggregates was dispersed under the reaction conditions (0.51 CN), while the Re species were more reduced compared to the ReO_x species in the H-ZSM-5 pores.

Table 2 Curve-fitting analysis for Re L_{III}-edge EXAFS spectra

Shell	CN	R/10^{-1} nm	DW/10^{-5} nm^2
Re/H-ZSM-5(SiO_2/Al_2O_3 = 39.4)/CVD			
before the reaction			
k-range: 3–16, R-range: 1.0–2.5, ΔE_0: 15.1, R_f: 0.84%			
R=O	2.70	1.73	1.65
R–O	1.84	2.09	9.06
after the reaction			
k-range: 3–16, R-range: 1.0–2.5, ΔE_0: 17.3, R_f: 2.30%			
R=O	2.20	1.73	1.53
R–O	1.56	2.10	1.20
Re/H-Mordenite/CVD			
before the reaction			
k-range: 3–14, R-range: 1.0–3.0, ΔE_0: 13.0, R_f: 0.91%			
R=O	1.49	1.72	1.02
R–O	1.93	2.05	5.73
Re–Re	1.65	2.73	7.18
after the reaction			
k-range: 3–14, R-range: 1.0–3.0, ΔE_0: 11.1, R_f: 1.12%			
R=O	1.36	1.71	1.14
R–O	1.55	2.02	4.92
Re–Re	0.51	2.72	9.83

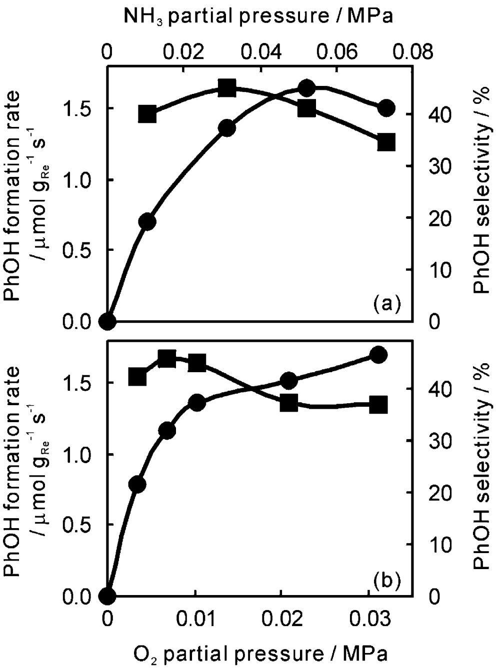

Fig. 1 The dependencies of the phenol formation rate (filled circle) and selectivity (filled square) to phenol on the partial pressures of ammonia and oxygen on the 0.40 wt% ReO_x/H-ZSM-5 (SiO_2/Al_2O_3 = 39.4) CVD catalyst; (a) O_2: 0.10 MPa, (b) NH_3: 0.31 MPa.

In summary we have found that the H-ZSM-5-supported [ReO_4] catalyst prepared by the CVD of CH_3ReO_3 is active for the selective oxidation of benzene with molecular oxygen, where NH_3 is indispensable for reducing and stabilizing the Re species efficiently.

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