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Direct Phenol Synthesis by Selective Oxidation of Benzene with Molecular Oxygen on an Interstitial-N/Re Cluster/Zeolite Catalyst[**]

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Phenol is one of the most important chemicals in industry, and the world production exceeds 7.2 megatons per year. Industrially, phenol has been produced from benzene by the three-step cumene process, which is not only energy consuming but also less efficient. The process is known for its very low yields (≈5% based on the amount of benzene initially used) and for the large amounts of by-products such as acetone and α-methylstyrene. Direct phenol synthesis from benzene is an alternative way to overcome these problems, and O_2,[1–4] H_2O_2,[5,6] N_2O,[7–14] H_2+O_2,[15,16] air/CO,[17] and O_2/H_2O[18] have been used as oxidants. The liquid-phase oxidation reactions of benzene with molecular oxygen in batch closed reactors have been reported to proceed over an iron–heteropolyacid catalyst in the presence of excess catalyst and over a CuO/Al_2O_3 catalyst with ascorbic acid as a reducing agent; however, the yield of phenol is very low.[1,2] A Cu/ZSM-5 catalyst showed a maximum phenol selectivity of 60% with a yield of 1.2% at 673 K.[3] Despite good performances with N_2O and H_2O_2 as oxidants, no economically and environmentally favorable catalytic systems for the selective oxidation of benzene with O_2 to give phenol have been discovered to date because of the difficulties associated with the activation of molecular oxygen. The direct synthesis of phenol with molecular oxygen is thus still regarded as one of the 10 most difficult challenges for catalysis,[19–21] and the development of highly selective catalysts for this reaction is of great interest. Rhenium, which can adopt several oxidation states, provides unique catalytic performances in re-forming of petroleum feedstocks, alkene metathesis, selective oxidation of methanol to formaldehyde, and ammoxidation of

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propene.[22–27] Recently we found that a Re/HZSM-5 catalyst was active in direct phenol synthesis,[4] but the selectivities to date have not exceeded 60%. Herein we report the highly selective oxidation of benzene with O_2 over a new Re cluster/HZSM-5 catalyst in the presence of NH_3. The selectivity for phenol is as high as 88% in the steady-state reaction and 94% in the pulse reaction.

Zeolite-supported Re catalysts were prepared by chemical vapor deposition (CVD) of methyl trioxorhenium (MTO; CH_3ReO_3) and impregnation of ammonium perrhenate (NH_4ReO_4) with several zeolites such as HZSM-5, H-Beta, H-USY, and H-Mordenite. All catalysts were pretreated at 673 K in a He flow before use. Table 1 shows the performances of the Re/zeolite catalysts for the selective oxidation of benzene with O_2. A Re-CVD/HZSM-5 catalyst (SiO_2/Al_2O_3 19:1) preferentially produced phenol with 88% selectivity in the presence of NH_3 (Table 1). No other liquid products were detected and the only by-product was gaseous CO_2. The activity and selectivity of the Re-CVD/HZSM-5 catalyst did not decrease over a period of at least 6 h under steady-state conditions (Supporting Information). Notably, the coexistence of NH_3 is indispensable for the selective oxidation: neither oxidation nor combustion proceed in the absence of NH_3. The addition of H_2O and N_2O gave no positive effects on the catalytic performance. The phenol formation rate and selectivity increased with increasing NH_3 pressure because the coexisting NH_3 produces active Re clusters as described below, and reached maxima at partial pressure of NH_3 of about 35–42 kPa (Figure 1). Excess ammonia leads to lower phenol formation rates and selectivities owing to competitive adsorption (with respect to benzene) and undesirable catalyst poisoning. Pretreatment of the catalyst with NH_3 for longer than 1 h is necessary for selective catalysis, thus indicating the formation of the active structure in situ under the reaction conditions in the presence of NH_3.

Table 1: Catalytic performances for the direct synthesis of phenol on Re/zeolite catalysts at 553 K.[a]

Catalyst	SiO_2/Al_2O_3	Method	Re [wt%]	TOF [10^{-5} s^{-1}][b]	Selectivity [%][c]
HZSM-5	19:1	–	–	trace	0
Re/HZSM-5[d]	19:1	CVD	0.58	trace	0
Re/HZSM-5	19:1	CVD	0.58	66	88
Re/HZSM-5[e]	19:1	CVD	0.58	52	86
Re/HZSM-5[f]	19:1	CVD	2.2	84	82
Re/HZSM-5[g]	19:1	CVD	0.58	75	94
Re/HZM-5[h]	19:1	CVD	0.58	86	91
Re/HZSM-5	19:1	Imp.	0.6	12	28
Re/HZSM-5	19:1	Phys.[i]	0.6	trace	0
Re/HZSM-5[d]	24:1	CVD	0.58	trace	0
Re/HZSM-5	24:1	CVD	0.58	36	68
Re/HZSM-5	24:1	Imp.	1.2	19	15
Re/HZSM-5[d]	39:1	CVD	0.59	trace	0
Re/HZSM-5	39:1	CVD	0.59	31	48
Re/HZSM-5[j]	39:1	CVD	0.40	47	46
Re/HZSM-5	39:1	Imp.	1.2	16	14
Re/H-Beta	37:1	CVD	0.53	19	12
Re/H-USY	29:1	CVD	0.60	trace	0
Re/H-Mordenite	220:1	CVD	0.55	26	23
SiO_2–Al_2O_3	19:1	–	0	0	0
Re/SiO_2–Al_2O_3	19:1	Imp.	1.2	trace	0

[a] Catalyst = 0.20 g; W/F = 6.7 g_{cat} h mol^{-1}; He/O_2/NH_3/benzene = 46:12:35:7 (mol%). The detailed carbon mass balance and material balance were examined in most of the experimental runs and values between 97 and 99% were found. [b] Consumed benzene/Re (s^{-1}). [c] Selectivity for phenol (carbon%). [d] In the absence of NH_3. [e] W/F = 5.2 g_{cat} h mol^{-1}. [f] W/F = 10.9 g_{cat} h mol^{-1}; He/O_2/NH_3/benzene = 46:12:35:7 (mol%). [g] Pulse reaction on the NH_3-pretreated catalyst (0.1 g); 1 pulse of benzene + O_2 (He/O_2/benzene = 81:12:7 (mol%)). [h] Pulse reaction on the NH_3-pretreated catalyst (1.0 g); 1 pulse of benzene + O_2 (He/O_2/benzene = 81:12:7 (mol%)). [i] Physical mixing of MTO. [j] Reference [4]; He/O_2/NH_3/benzene = 55:7:31:7 (mol%). CVD = chemical vapor deposition, Imp. = impregnation, W/F = weight of catalyst/feed rate.

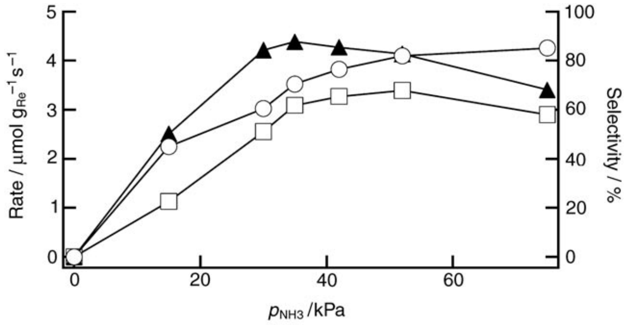


Figure 1. Dependence of the catalytic activity and selectivity on NH_3 pressure in the selective benzene oxidation over the Re/HZSM-5 catalyst (Re: 0.58 wt%, CVD, SiO_2/Al_2O_3 19:1) at 553 K. ○: benzene consumption rate, □: phenol formation rate, ▲: phenol selectivity.

Lower activities and selectivities were attained through impregnation and physical mixing of the catalysts (Table 1, Supporting Information). The CVD catalyst was almost 18 times more active than the impregnation catalyst. Physical mixing and impregnation of results in the transformation of the Re^{7+} catalyst precursors into partly aggregated and ill-defined Re species, unlike the active Re clusters formed in the CVD catalyst (see below). The selectivity for phenol is highly dependent on the structure, acid strength, and SiO_2/Al_2O_3 ratio of the zeolites (Table 1). Lower SiO_2/Al_2O_3 ratios led to large increases in the catalytic activity (TOF: 31.0×10^{-5} s^{-1} to 65.6×10^{-5} s^{-1}) and selectivity (48 to 88%). The rate of phenol formation decreased in the following order: HZSM-5 (SiO_2/Al_2O_3 19:1) > HZSM-5 (SiO_2/Al_2O_3 24:1) > HZSM-5 (SiO_2/Al_2O_3 39:1) ≫ H-Mordenite > H-beta > H-USY. Thus HZSM-5 (SiO_2/Al_2O_3 19:1) is the most favorable support among the employed zeolites for the Re species. The results also suggest that Al-OH in the HZSM-5 framework is a bonding site for active Re species. The selectivity decreased slightly from 88 to 82% by increasing the Re loading (0.58→2.2 wt%) and W/F (6.7→10.9 g_{cat} h mol^{-1}), whereas the conversion increased from 0.8% (TOF: 65.6×10^{-5} s^{-1}) to 6% (TOF: 83.8×10^{-5} s^{-1}) as shown in Table 1.

The Re L_I- and L_{III}-edge EXAFS analysis revealed significant changes in the structure of supported Re species on HZSM-5 (Table 2 and Supporting Information). Table 2 shows the structural parameters of the active Re-CVD/HZSM-5 catalyst determined by curve-fitting of the Re L_{III}-

Table 2: Curve-fitting results of the Re L_{III}-edge EXAFS data measured at 15 K for the Re/HZSM-5 catalyst.[a]

Sample	Shell	C.N.[b]	Bond length [nm]	σ^2 [10^{-5} nm^2]	ΔE_0
He-treated	Re=O	2.5 ± 0.3	0.173 ± 0.001	1.5 ± 0.6	R_f = 2.1 %
	Re−O	1.2 ± 0.5	0.206 ± 0.001	2.9 ± 2.8	
	Re−Re	1.2 ± 0.6	0.275 ± 0.001	5.0 ± 1.5	
NH_3-treated	Re=O	0.3 ± 0.2	0.172 ± 0.001	2.3 ± 2.4	R_f = 0.5 %
	Re−N	2.8 ± 0.3	0.204 ± 0.001	5.8 ± 0.9	
	Re−Re	5.2 ± 0.3	0.276 ± 0.002	5.2 ± 0.2	
After reaction	Re=O	3.7 ± 0.2	0.173 ± 0.001	1.4 ± 0.3	R_f = 1.3 %
	Re−O	1.3 ± 0.7	0.213 ± 0.003	9.1 ± 7.7	

[a] Catalyst: Re: 0.58 wt %, CVD, SiO_2/Al_2O_3 = 19:1. Fourier-transform spectra (k = 30–160 nm^{-1} and fitted in R space of R = 0.10–0.32 nm). [b] C.N. = coordination number. EXAFS = extended X-ray absorption fine-structure.

edge EXAFS data measured at 15 K.[28] After the CVD of MTO to HZSM-5 followed by treatment with He at 673 K, two different Re−O bonds were observed at 0.173 ± 0.001 nm (C.N. (coordination number) = 2.5 ± 0.3) and 0.206 ± 0.001 nm (C.N. = 1.2 ± 0.5), which are attributed to Re=O and $Re{-}O_{bridge}$ and/or $Re{-}O_{lattice}$, respectively. A Re−Re contribution was observed at 0.275 ± 0.001 nm with a C.N. of 1.2 ± 0.6, which indicates that MTO was probably transformed into the Re dimer species in the pore of HZSM-5. The Re dimer is completely inactive in the selective benzene oxidation (Figure 2). The pulses of benzene, a mixture of benzene and O_2, and a mixture of benzene and NH_3 on the Re dimer did not produce phenol at all.

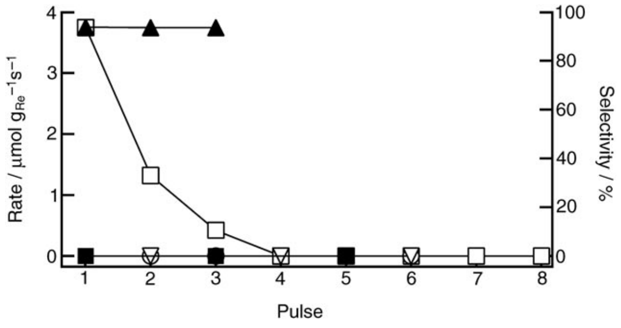
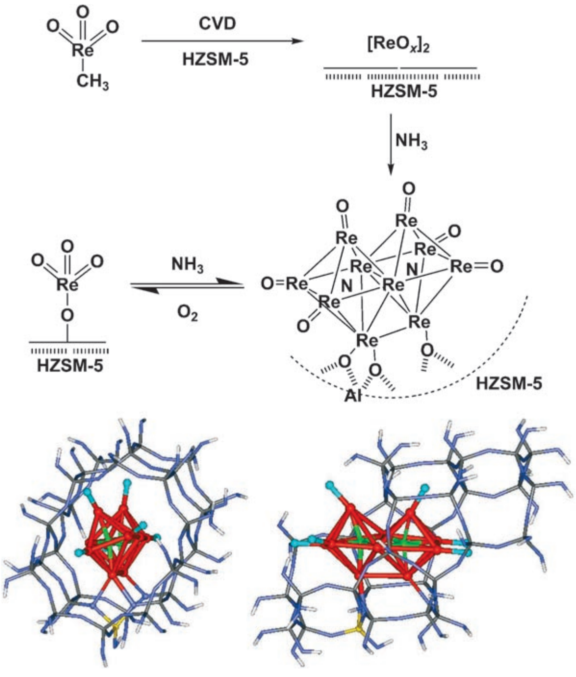


Figure 2. Pulse reactions for selective benzene oxidation at 553 K over the Re/HZSM-5 catalyst (Re: 0.58 wt %, CVD, SiO_2/Al_2O_3 19:1) after pretreatment with NH_3 at 553 K for 2 h. 1 pulse: He/O_2/benzene = 81:12:7; W/F = 6.7 g_{cat} h mol^{-1}; catalyst = 0.10 g. □: phenol formation rate, ▲: phenol selectivity. ■: phenol formation rate in the absence of O_2. ▽ and ○: phenol formation rates on the Re dimer and ReO_4 monomer, respectively, both in the presence and absence of O_2.

Treatment of the inactive Re dimer with ammonia at the reaction temperature brought about catalytic activity for phenol synthesis. The phenol formation rate increased with increasing periods of treatment with NH_3 (75 kPa) at 553 K and reached a saturated value of 3.8 µmol g_{cat}^{-1} s^{-1} after treatment with NH_3 for 2 h, which indicates that the structural transformation to the active Re species is completed after exposure to NH_3 for 2 h.

Indeed, the L_{III}-edge EXAFS data dramatically changed with the NH_3 treatment (Supporting Information). The C.N. of Re−Re bonds (Table 2) increased from 1.2 ± 0.5 with the Re dimer to 5.2 ± 0.3 at 0.276 ± 0.002 nm, demonstrating the formation of Re clusters. If we assume that the Re_6 octahedron is a cluster unit,[27] the C.N. of the Re−Re bonds indicates Re_{10} clusters edge shared with two Re_6 octahedra. Furthermore, it was found that the NH_3-treated Re cluster catalyst released N_2 molecules at 685 K (Temperature programmed desorption (TPD) spectra; Supporting Information). The number of encapsulated nitrogen atoms was 0.12 N_2/Re, which corresponds to one nitrogen atom per Re_6 octahedron. An NH_3-treated HZSM-5 without Re showed no N_2 desorption in TPD. The Re−N(O) bonds in the NH_3-treated Re-CVD/HZSM-5 catalyst were observed at 0.204 ± 0.001 nm (C.N. = 2.8 ± 0.3) by EXAFS (Table 2). Re=O double bonds at 0.172 ± 0.001 nm (C.N. = 0.3 ± 0.2) were also observed. The XPS Re 4f binding energy was 43.8 eV, which indicates a Re^{3+} state.

We have simulated the structure of the active Re clusters in the pore of HZSM-5 by density functional theory (DFT) calculations (Scheme 1). These revealed that a nitrogen atom is located at the interstitial position of each Re_6 octahedral framework of the Re_{10} clusters and is attached to the wall of a zeolite pore through Re−O bonds.[29] Notably, the interstitial nitrogen atoms are key to the stabilization of the Re_{10} clusters. Neither the hollow-site nitrogen atom (Re_3–N), nor the bridged nitrogen atom (Re–N–Re), nor bridged NH species (Re–NH–Re) stabilize the cluster framework with Re−Re



Scheme 1. Proposed structures of the supported Re clusters on HZSM-5 and the modeling of an active interstitial-N/Re_{10}-cluster inside the pore of HZSM-5 by DFT.

bonds at 0.276 ± 0.002 nm determined by EXAFS. We have also simulated many Re clusters coordinated with oxygen atoms. However, the clusters were destabilized by oxygen coordination, and more oxygen decomposed the Re_{10} framework. The stable interstitial-N/Re_{10} cluster presented in Scheme 1 was modeled as a unique solution in the DFT calculations.

The Re_{10} clusters with interstitial nitrogen atoms were highly selective in the catalytic phenol synthesis (Table 1 and Figure 2). Benzene was converted into phenol by a pulse of a mixture of benzene and O_2 on 0.1 g of the NH_3-pretreated catalyst (Figure 2). Notably, the selective oxidation with molecular oxygen on the active Re_{10} clusters proceeds without ammonia. Repetition of the pulse caused a large decrease in the catalytic activity, and formation of phenol stopped after the admission of three pulses of the feed (Figure 2). The selectivity was constant (94 %) during the reaction of the three pulses. These results demonstrate that the active Re_{10} clusters were converted into inactive Re species without significant formation of unselective Re species on the way. In the absence of O_2, the Re clusters did not produce phenol, suggesting that the oxygen of the active Re cluster framework is not active in the selective oxidation. In the pulse reaction on 1.0 g of the NH_3-pretreated catalyst the conversion of benzene into phenol increased to 10 % (TOF (turnover frequency): $86.1 \times 10^{-5}\,s^{-1}$), while keeping a high phenol selectivity of 91 % (Table 1).

After the pulse reactions with a mixture of benzene and O_2, the Re species showed no Re–Re bond, whereas Re=O and Re–O bonds were observed at 0.173 ± 0.001 nm (C.N. = 3.7 ± 0.2) and at 0.213 ± 0.003 nm (C.N. = 1.3 ± 0.7) as shown in Table 2 (Supporting Information). The XPS Re 4f peak was observed at 48.5 eV. These results demonstrate that the Re_{10} clusters were oxidized with O_2 and decomposed to inactive ReO_4 monomers with Re^{7+} (Scheme 1).

The Re_{10} clusters are not stable under O_2 in the absence of NH_3. Oxygen not only produces phenol but also converts the active Re_{10} clusters into the inactive ReO_4 monomers competitively. The amount of phenol molecules produced in the pulse reactions was 3.2 % of the amount of the Re_{10} clusters. Under the steady-state conditions in the presence of NH_3, the population of the active Re_{10} clusters in the Re species is 3.7 %. A mechanism for the oxidation may involve oxygen-free radical formation on the Re_{10} clusters. Alternatively, molecular oxygen associatively adsorbed on the partially reduced Re_{10} clusters may be the active oxygen species. In the latter case, the theoretical maximum phenol selectivity would be 94 %.

In conclusion, we have found that the novel HZSM-5-supported interstitial-N/Re-clusters prepared by the CVD of CH_3ReO_3 are active for the selective catalytic oxidation of benzene to phenol with molecular oxygen in the presence of ammonia. The impressive selectivities are as high as 94 % at 553 K.

Experimental Section

HZSM-5 (SiO_2/Al_2O_3 19:1) was synthesized by a procedure similar to that described in the literature.[30] Other zeolites were purchased from TOSOH, Japan. The supported Re catalysts were prepared by two methods: 1) conventional impregnation by using NH_4ReO_4 and 2) CVD by using CH_3ReO_3. In the CVD procedure, ZSM-5, Beta, USY, Mordenite were pressed and sieved to 355–710 µm granules and calcined at 873 K for 2 h. The zeolites were then treated further at 673 K for 0.5 h under vacuum. The whole apparatus was heated at 333 K, and the zeolites were exposed to MTO vapor for 14 h. The catalysts were pretreated under a helium flow at 673 K for 1 h and cooled in a He flow. The selective catalytic reactions were conducted in a fixed-bed down-flow reactor by charging 0.2 g of the catalyst. A typical composition of the reaction gases was $He/O_2/NH_3$/benzene = 46:12:35:7 and W/F was typically $6.7\,g_{cat}\,h\,mol^{-1}$. The products were analyzed by two online GCs with an FID detector by using a NEUTRABOND-1 Column for hydrocarbons and with a TCD detector by using a Unibeeds C column for inorganic materials. Pulse experiments were carried out with 0.1 g of catalyst, and the volume of each pulse was 0.42 mL.

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