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Direct synthesis of benzene to phenol with molecular oxygen on rhenium/zeolite catalysts

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Introduction

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, H_2O_2, N_2O, NO and H_2+O_2 as oxidants. No selective catalyst with good performance in the economically and environmentally favorable benzene-O_2 system has been discovered to date. 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. Only a preceding 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.

Results and discussion

The supported rhenium catalysts were prepared by chemical vapor deposition (CVD) method using methyltrioxorhenium (CH_3ReO_3: MTO). 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 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. XAFS spectra for the supported rhenium catalysts were measured at BL7C, 9A or 12C stations in a transmission mode.

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[1]. 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 x 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 x 10^{-7} mol g_{Re}^{-1} s^{-1} and a selectivity of 40 %. The CVD catalyst is 16-39 times more active than the impregnation catalyst.

Table 1. 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

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 1). 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 Re^{6+} species.

Reference

[1] T. Kusakari et al., Chem. Commun., 992 (2004).

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