

# Direct Phenol Synthesis from Benzene with Molecular Oxygen on a Novel N-interstitial Re Cluster/Zeolite Catalyst

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## Introduction

Phenol is one of the most important chemicals in industry and it is industrially produced from benzene with three steps (cumene process), which is not only energy consuming but also less efficient, producing lots of by-products. Direct phenol synthesis from benzene is an alternative way to overcome these problems. However, any economically and environmentally favorable benzene-O<sub>2</sub> catalytic systems with high selectivity for phenol synthesis have not been discovered to date because molecular oxygen is hard activated to selectively proceed the benzene oxidation to phenol. Recently we found that a Re/HZSM-5 catalyst was active for the direct phenol synthesis. Here we report the highly selective oxidation of benzene with O<sub>2</sub> on a new Re cluster/HZSM-5 catalyst under co-existing NH<sub>3</sub>. The phenol selectivity is tremendously high as 88% in the steady-state reaction and 94% in the pulse reaction.<sup>[1]</sup> The formation of the active Re clusters, their structural change, and the role of NH<sub>3</sub> which are relevant to the selective oxidation are also discussed.

## Methods

Zeolite-supported Re catalysts were prepared by chemical vapor deposition (CVD) of CH<sub>3</sub>ReO<sub>3</sub> or conventional impregnation of NH<sub>4</sub>ReO<sub>4</sub> with several zeolites such as HZSM-5, H-Beta, H-USY, and H-Mordenite. The selective oxidation was conducted in a fixed bed down flow reactor, and the products were analyzed by GC. Pulse experiments were carried out after the treatment of NH<sub>3</sub> for 2 h. The Re/HZSM-5 catalyst was characterized by XRD, XRF, XPS, SS-NMR, XAFS, and DFT calculations.

## Results and Discussion

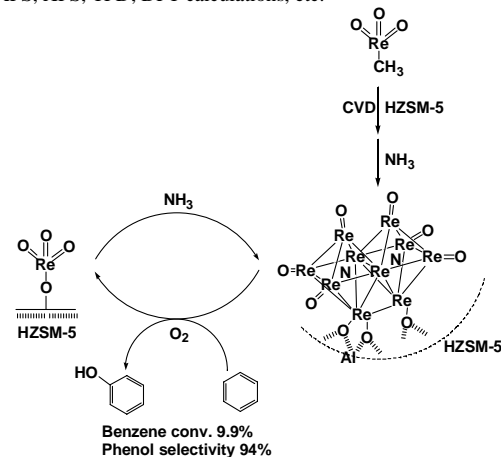
A Re-CVD/HZSM-5 catalyst (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 19) preferentially produced phenol with 87.7% selectivity in the presence of NH<sub>3</sub>. No other liquid products were detected and only a by-product was gaseous CO<sub>2</sub>. The activity and selectivity of the Re-CVD/HZSM-5 catalyst did not decrease for at least 6 h under the steady-state conditions. It is to be noted that the coexistence of NH<sub>3</sub> is indispensable for the selective oxidation. Other basic compounds such as pyridine and isopropyl amine did not proceed the phenol formation at all. Neither benzene oxidation nor combustion proceeded in the absence of NH<sub>3</sub>. The addition of H<sub>2</sub>O and N<sub>2</sub>O gave no positive effects on the catalytic performance. The impregnated catalyst was much less active and much less selective compared to the Re-CVD catalysts. The catalytic performances depended on the kind of zeolites and also on SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios. The decrease in the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio caused large increases in the catalytic activity and the phenol selectivity. The rate of phenol formation decreased in the order; HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 19) > HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 23.8) > HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 39.4) >> H-Mordenite > H-beta > H-USY. Thus HZSM-5

(SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 19) among the employed zeolites is the most favorable support for the Re species. Benzene was converted to phenol by a pulse of a mixture of benzene and O<sub>2</sub> on an NH<sub>3</sub>-pretreated catalyst. It is to be noted that the selective benzene oxidation with molecular oxygen on the active Re<sub>10</sub> clusters proceeds without ammonia. The pulse reaction showed a maximum selectivity of 94%.

The NH<sub>3</sub> treatment caused a drastic transformation of Re species to novel N-interstitial Re<sub>10</sub>O<sub>x</sub> clusters with Re-Re bonds at 0.275 nm determined by Re L<sub>3</sub>-edge EXAFS. The NH<sub>3</sub>-treated Re catalyst released N<sub>2</sub> at 685 K in TPD. The number of encapsulated nitrogen atoms was 0.12 N<sub>2</sub>/Re, which corresponds to be one nitrogen atom per a Re<sub>6</sub> octahedron. DFT calculations showed that the Re clusters possess two octahedral Re<sub>6</sub>-N frameworks edge-shared to each other illustrated in Figure 1. It is to be noted that the interstitial nitrogen atoms are the key element to stabilize the Re<sub>10</sub> clusters. The Re<sub>10</sub> clusters were oxidized with O<sub>2</sub> and decomposed to inactive ReO<sub>4</sub> monomers with Re<sup>7+</sup>, while NH<sub>3</sub> reduced Re<sup>7+</sup> monomers to the lower valence clusters as suggested by XANES and XPS. Although the NH<sub>3</sub>-pretreated catalyst did not produce phenol when benzene only was pulsed, the pulse of benzene and O<sub>2</sub> on the NH<sub>3</sub>-pretreated Re<sub>10</sub> cluster produced phenol effectively, which demonstrates that the N-interstitial Re<sub>10</sub> clusters are active species and molecular oxygen contributes to the selective phenol formation on the Re-CVD/HZSM-5 catalyst.

## Significance

we have found the novel HZSM-5-supported N-interstitial Re-cluster prepared by the CVD of CH<sub>3</sub>ReO<sub>3</sub>, which is active for the selective catalytic oxidation of benzene to phenol with molecular oxygen in the presence of ammonia. The selectivities are as tremendously high as 87.7-93.9% at 553 K. The active Re species is a new kind of Re cluster, which was characterized by XAFS, XPS, TPD, DFT calculations, etc.



**Figure 1.** Preparation steps of active N-interstitial Re cluster and its structural change relevant to the mechanism for selective oxidation catalysis for phenol synthesis.