Selective Oxidation of Benzene to phenol by Single Alkali and Alkaline-Earth Metal/Zeolite Catalysts

Shilpi Ghosh,[a] **Shankha S. Acharyya,**[a] **Yusuke Yoshida,**[a] **Kotaro Higashi,**[a] **Takuma Kaneko,**[a] **Takehiko Sasaki,**[b] **Yasuhiro Iwasawa**[a,]*

[a]*Innovation Research Center for Fuel Cells, The University of Electro-Communications,Chofu,Tokyo182-8585, Japan*

[b]*Graduate School of Frontier Sciences, The University of Tokyo, Kashiwa, Chiba 277-8561, Japan*

**Corresponding author: +81-(0)42-443-5483, iwasawa@pc.uec.ac.jp*

Abstract: In general, selective oxidation reactions proceed on metal and metal oxide catalysts with redox property, whereas they are not promoted significantly by acid-base catalysts without redox functions. We have found the unprecedented and novel aspects of the selective oxidation catalysis for benzene hydroxylation with O_2 and N_2O as oxidant by single alkali and alkaline-earth metal sites confined in zeolite pores.

Keywords: Selective Oxidation, Phenol Synthesis, Single alkali and alkaline-earth metal site, Zeolite.

1. Introduction

The selective oxidation of ubiquitous but inert C-H bonds of benzene phenol still remains to be a major challenge [1]. Phenol is an important chemical intermediate in industry owing to its widespread use. Industrially, phenol is produced by the cumene process, which is a multi-step process, and involves an explosive cumene hydroperoxide intermediate, utilizes sulfuric acid and also suffers from low yield. Although there have been lots of reports using different oxidizing agents such as O_2, N_2O, H_2O_2, NH_3+O_2 etc. over redox transition metal catalysts, a gas-phase single-path selective phenol synthesis process with good conversion and selectivity has not been achieved to date [2, 3]. In general, the gas-phase selective oxidation proceeds on metal and metal oxide catalysts with redox property, but acid-base catalysts without redox functions do not promote the selective oxidation significantly. We have found the unprecedented and novel aspects and mechanism of the selective oxidation catalysis for phenol production from benzene with high selectivity (with N_2O and NH_3+O_2 as oxidants) by single alkali and alkaline-earth metal sites in zeolite pores.

2. Experimental

Alkali metal and alkaline earth metal (M)/zeolite catalysts (M= Na, K, Rb, Cs, Mg, Ca, etc.) were prepared by an ion-exchange method using a given amount of M precursors. A given amount of the obtained M/ß sample was charged in a continuous down-flow fixed-bed glass reactor. The reaction products were analyzed by two on-line FID and TCD gas chromatographs. The catalysts were characterized by XRD, XRF, TEM/STEM/EDS, XPS, XAFS, DFT calculations, TPD, etc.

3. Results and discussion

The performances of typical alkali and alkaline-earth metal/zeolite catalysts for single-path gas-phase benzene hydroxylation reactions are listed in Table 1. We have found that alkali and alkaline-earth metal ions such as Cs^+, Rb^+, Mg^{2+}, etc. incorporated into the zeolite pores are active for the direct phenol synthesis, and typically Cs/β affords phenol from benzene using O_2 and NH_3 with very high phenol selectivity (96%) and without significant NH_3 consumption with ~7% yield. This is the unprecedented selective phenol synthesis on acid-base catalysts. We have also found that these catalysts are active and selective in the hydroxylation of benzene to phenol using N_2O as oxidant. Cs/β and Rb/β zeolite catalysts showed better benzene conversion of ~16-19% and phenol selectivity ~ 99.9% among several catalylsts tested, while N_2O consumption was nearly stoichiometric (produced phenol/consumed N_2O=1.0). It is notable that phenol is the sole product detected by the gas chromatographs. The TOFs for Cs/β and Rb/β were larger than that of a transition metal Ni/β catalyst. The inactivity of M/amorphous SiO_2-Al_2O_3 catalysts towards the phenol synthesis indicates the confinement effect of the zeolite pore structures.

The active species and structures in the zeolite pores were characterized by XAFS, XPS, Raman, STEM-EDS, XRD, XRF, DFT calculations, etc. The XAFS analysis revealed a single alkali metal site structure. XPS spectra for Cs/β indicated Cs^+ valence with a different coordination structure from that of Cs_2CO_3. From the DFT calculations, it is noted that the first step is associated with benzene adsorption on Cs ion through σ bond in a monodentate fashion. Interestingly, the DFT calculations indicate that N_2O adsorbs molecularly, which is rather contrasted to the typical redox catalysis.

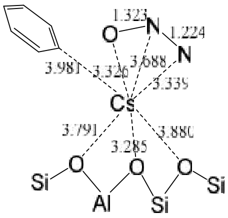

Figure 1. Adsorbed coordination structure on Cs/β for phenol synthesis.

Table 1. Catalytic performances of single alkali/alkaline-earth metal/β catalysts for the synthesis of phenol from benzene/N_2O [a].

Entry	Catalyst	Temp(K)	Benzene reaction rate [mmol $h^{-1}g_{cat}^{-1}$]	Benzene Conversion [%]	TOF [h^{-1}]	Phenol Selectivity [%]	$[N_2O]_{reacted}$/ $[Phenol]_{produced}$
1.	Mg /β	573	0.47	14.06	10.11	99.9	1.16
2.	Ca /β	573	0.63	18.9	13.59	99.9	2.05
3.	K /β	573	0.36	10.88	7.8	99.9	1.57
4.	Rb /β	573	0.63	18.86	13.56	99.9	1.00
5.	Cs/β	573	0.54	16.1	11.57	99.9	1.11
6.	Cs/$SiO_2Al_2O_3$	573	-	0.0	-	-	-
7.	Cs/Mordenite	573	0.01	0.53	0.38	99.9	5.60
8.	Ni/β	573	0.39	11.6	8.3	99.9	1.23
9.	Cs/β [b]	593	0.14	5.89	1.39	83.4	1.10 [c]
10.	Cs/β [b]	623	0.15	6.84	1.62	77.5	2.25 [c]

[a] Reaction Conditions: catalyst amount: 0.4 g; time=30-150 min; Bz/N_2O/CH_4/He =0.5/3.0/5.0/20 mL/min; loading of metal = 1.0 wt%. Methane was used as an internal standard. TOF is defined as reacted benzene/total metal per hour. [b] Reaction Conditions: catalyst amount: 0.6 g; time=30-150 min; Benzene/ O_2/ NH_3/ He = 0.5/1.8/4.0 mL/min. The catalysts were pretreated with benzene/O_2/NH_3/He 400 °C for 0.5h; loading of metal = 2.0 wt%. [c] [NH_3] reacted/[Phenol] formed.

4. Conclusions

We found the selective alkali metal and alkaline-earth metal/ß catalysts for the steady-state direct phenol synthesis from benzene with N_2O as oxidant, where N_2O reacted nearly stoichiometrically with benzene to phenol formation. The stoichiometric consumption of N_2O is highly desirable from the commercial point of view. The active structure constitutes single metal-ion sites with large radii in the zeolite pores as suggested by XAFS, XPS and DFT calculations. The present finding is entirely different from the prediction of the conventional principle for acid-base and redox catalyses.

References

1. R. Bal, M. Tada, T. Sasaki, Y. Iwasawa, Angew. Chem. Int. Ed. 45 (2006) 4487) 456.
2. L. Wang, S. Yamamoto, S. Malwadkar, S. Nagamatsu,T. Sasaki, K. Hayashizaki, M. Tada, Y. Iwasawa, ChemCatChem. 5 (2013) 2203.
3. L. Wang, S. Yamamoto, K. Hayashizaki, S. Nagamatsu, S. Malwadkar, T. Sasaki, Y. Iwasawa, ChemCatChem. 7 (2015) 3248.