Preparation and Evaluation of Redox Performance/Catalytic Ammoxidation Performances of Copper and Ruthenium Incorporated Ceria

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We previously reported the incorporation of Cr and Rh ions to the ceria achieved high redox performance below 423 K and exhibited high catalytic activity toward alcohol oxidation.[1] In this study, we report a ceria-based mixed oxide by adjusting the incorporated metal ions to Cu and the trace amount of Ru. The mixed cerium oxide with Cu and Ru was found to exhibit redox performance at low temperature and high catalytic activity and selectivity for the ammoxidation of benzyl alcohol.

Prepared mixed cerium oxide with Cu and Ru incorporation (denoted as $Cu_{0.18}Ru_{0.05}CeO_z$) was characterized by XRD and TEM and it was found that $Cu_{0.18}Ru_{0.05}CeO_z$ had fluorite structure of ceria with dispersed Cu and Ru on the surface. TPR/TPO showed that $Cu_{0.18}Ru_{0.05}CeO_z$ exhibited the reversible redox performance below 423 K. *In situ* XANES measurement during the reduction process demonstrated the three metal species of Cu, Ru and Ce contributed in the redox behavior, and this multi-reduction behavior was elucidated by the reduced Ru at first with subsequently promoted reduction of Cu and Ce species.

$Cu_{0.18}Ru_{0.05}CeO_z$ significantly promoted the conversion of benzyl alcohol (95%) to benzonitrile (90% yield) (conditions: Ru/Cu/benzyl alcohol/NH_3 = 1/3.5/100/191, [benzyl alcohol] = 1.93 mol, NH_3: 0.32 MPa, O_2: 1 MPa, toluene: 1.0 mL, 423 K, 24 h) compared with $Cu_{0.18}CeO_z$ without Ru, $Ru_{0.04}CeO_z$ without Cu, and CeO_2 (Table 1). Several control reaction experiments (N_2 1 MPa instead of O_2, with/without NH_3) suggested that Ru efficiently processed the oxidation of benzyl alcohol to form benzaldehyde and Cu worked as active site for the cyanation of benzaldehyde to benzonitrile. The catalytic performances of the ammoxidation and the role of each metal in the catalyst will be presented.

Table 1. Catalytic Performances of $Cu_{0.18}Ru_{0.05}CeO_z$ for Ammoxidation of Benzyl Alcohol[a]

Entry	Catalyst	Conv. %	Benzonitrile	
			Selec. %	Yield %
1[b]	$Cu_{0.18}Ru_{0.05}CeO_z$	95	95	90
2[c]	$Cu_{0.18}CeO_z$	70	78	55
3[d]	$Ru_{0.04}CeO_z$	91	29	27
4[e]	CeO_2	77	10	8
5	Blank	0	0	0
6[f]	$Cu_{0.18}Ru_{0.05}CeO_z$	20	0	0

[a] Reaction conditions: **Benzyl alcohol (BA)**: 1.93 mmol (1.61 mol L^{-1}), toluene: 1.0 mL, dodecane (internal standard): 0.07 mL (1.98 mmol), NH_3: 0.32 MPa (3.7 mmol), O_2: 1.0 MPa, 423 K, 24 h. [b] $Cu_{0.18}Ru_{0.05}CeO_z$: 74 mg (Ru: 0.019 mmol, Cu 0.068 mmol), Ru/Cu/**BA**/NH_3/dodecane = 1/3.5/100/191/100. [c] $Cu_{0.18}CeO_z$: 77 mg (Cu: 0.068 mmol), Cu/**BA**/NH_3/dodecane = 1/29/58/29, [d] $Ru_{0.04}CeO_z$: 72 mg (Ru: 0.019 mmol), Ru/**BA**/NH_3/dodecane= 1/100/191/100, [e] CeO_2 74 mg, **BA**/NH_3/dodecane= 1/1.91/1, [f] N_2 1.0 MPa (instead of O_2). The major product was *N*-Benzylidenebenzamine (Selec.: >99%, Yield 22%)

[1] Ikemoto, S. *et al. Phys. Chem. Chem. Phys.* 2019, *21*, 20868-20877.