Low-temperature PROX (preferential oxidation) on novel CeO_2-supported Cu-cluster catalysts under fuel-cell operating conditions†

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Cu^{1+}-clusters on a CeO_2 support, which were prepared by hydrothermal synthesis using cetyltrimethylammonium bromide (CTAB), were found to be highly active and selective for preferential oxidation (PROX) of CO in excess H_2 with H_2O and CO_2 under practical fuel-cell operating conditions.

Hydrogen as the most efficient and cleanest energy source for fuel-cell power is produced by partial oxidation followed by water gas-shift reaction and reforming of hydrocarbons or methanol.[1] A small amount of CO (0.3–1%) present in the produced H_2 must be selectively removed because CO is highly poisonous to electrocatalysts in proton-exchange-membrane (PEM) fuel cells.[2] PROX of CO in excess H_2 is a key reaction in the practical use of H_2 in PEM fuel-cell systems.

The most important requirement for PROX catalysts is high CO oxidation activity accompanied by prohibition of undesirable H_2 oxidation. Various precious metal catalysts such as Pt,[3,4] Au,[4a,5–7] Rh,[4b] Ru,[4b,8] Pt–Sn,[4c,d] Pt–Fe,[4e] *etc.* with good PROX activities have been utilized as candidates for PROX catalysts. However, there are few non-precious metal catalysts which possess sufficient PROX activities at low temperatures. CuO/CeO_2 was reported to be an active catalyst at temperatures >150 °C,[4a,9] but non-precious metals rarely show good CO conversions at lower temperatures, $\leqslant$120 °C, under the practical PEM fuel-cell operating conditions. We have succeeded in preparing novel CeO_2-supported Cu^{1+}-cluster catalysts which are highly active and selective for the PROX reaction.

The supported Cu/CeO_2 catalyst (denoted as Cu/Ce–CTAB) was hydrothermally prepared using Ce and Cu nitrates as precursors with a surfactant CTAB in a manner similar to that we reported for preparation of metallic Cu clusters on MoO_2 (Cu/Mo–CTAB).[10] In a typical synthesis method, 5 g of $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in 8 ml of hot distilled water, to which 0.61 g of $Cu(NO_3)_2{\cdot}3H_2O$ in H_2O (2 ml) was added dropwise. Then, 0.54 g of CTAB was dissolved in a mixture of H_2O (5 ml) and ethanol (2 ml), and the obtained solution was added to the Cu + Ce solution. A typical molar composition is Cu/CTAB/H_2O = 1.0/0.55/325. The homogeneous slurry mixture was hydrothermally treated at 175 °C for 24 h in a Teflon-lined autoclave vessel under an autogeneous pressure. The product was washed with distilled H_2O and EtOH, and dried at ambient temperature for 10 h and then at 100 °C for 8 h, followed by heating at 500 °C for 6 h under a He flow (30 ml min^{-1}). The Cu content of the final catalyst was determined by XRF. The metallic Cu clusters on MoO_2 were completely inactive for CO PROX at 90 °C as shown in Table 1. Metallic Cu clusters on ZnO (Cu/Zn–CTAB) and SiO_2 (Cu/Si–CTAB) were also inactive (Table 1). Similarly prepared Cu/Zr–CTAB, Cu/Fe–CTAB, and Cu/Al–CTAB catalysts were also inactive. It was, however, found that the

Table 1 Catalytic performances of Cu and Ce catalysts for the PROX of CO in excess H_2 at 90 °C[a]

Catalyst	Cu wt%	CO conv.%	O_2 selec.%	Specific rate/μmol_{CO} g_{Cu}^{-1} s^{-1}
CeO_2	0	0	—	0
Ce_2O_3	0	0	—	0
Ce–CTAB	0	0	—	0
Cu–CTAB	100	0	—	0
Cu/Ce_2O_3 (impreg.)[b]	10	8.9	100	1.1
Cu/Ce_2O_3 (impreg.)[b,c]	10	12.8	100	1.6
Cu/CeO_2 (impreg.)[b]	10	7.2	100	0.9
Cu/CeO_2 (post-impreg. with CTAB)[b]	7.5	0	—	0
$CuBr/CeO_2$ (impreg.)	7.5	0	—	0
$CuBr_2/CeO_2$ (impreg.)	7.5	0	—	0
Cu–Ce (co-precip.)[d]	10	5.6	100	0.7
Cu–Ce (co-precip.)[c,d]	10	7.3	100	0.9
Cu/Ce–noCTAB[e]	9.6	10.2	100	1.3
Cu/Ce–noCTAB[c,e]	9.6	15.9	100	2.1
Cu/Ce–CTAB	7.5	91.9	99.8	15.2
Cu/Ce–CTAB[f]	7.5	72.1	100	23.8
Cu/Ce–CTAB[f]	4.5	32.0	100	17.6
Cu/Ce–CTAB[f]	15	53.9	100	8.9
Pt–Cu/Ce–CTAB[f,g]	7.5	16.5	100	5.4
Pd–Cu/Ce–CTAB[f,g]	7.5	14.8	100	4.9
Au–Cu/Ce–CTAB[f,g]	7.5	58.4	100	19.3
In–Cu/Ce–CTAB[f,g]	7.5	4.2	100	1.4
Cu/Ce–Pluorunic®[h]	7.5	0	—	0
Cu/Ce–dodecyl sulfate[i]	7.5	0	—	0
Cu/Zr–CTAB[j]	10	0	—	0
Cu/Fe–CTAB[k]	10	0	—	0
Cu/Mo–CTAB[l]	7.8	0	—	0
Cu/Zn–CTAB[m]	3.7	0	—	0
Cu/Al–CTAB[n]	5.3	0	—	0
Cu/Si–CTAB[o]	8.9	0	—	0

[a] Catalyst: 0.4 g, time on stream: 2 h, W/F = 2.24 g_{cat} h mol^{-1}, $CO/O_2/H_2/He$ = 1/1/50/48 (mol%). [b] Impregnation of Cu nitrate. [c] Reduced with H_2 (15% in He) at 500 °C. [d] Co-precipitation. [e] Hydrothermal synthesis without CTAB. [f] Catalyst: 0.2 g, W/F = 1.12 g_{cat} h mol^{-1}, 80 °C. [g] An additional metal was impregnated on Cu/Ce–CTAB. [h] Pluorunic® was used as a neutral surfactant. [i] Dodecyl sulfate was used as an anionic surfactant. [j] Prepared with Zr nitrate. [k] Prepared with Fe nitrate. [l] Prepared with $(NH_4)_6Mo_7O_{24}$. [m] Prepared with Zn nitrate. [n] Prepared with $Al_2(SO_4)_3$. [o] Prepared with $Si(OC_2H_5)_4$.

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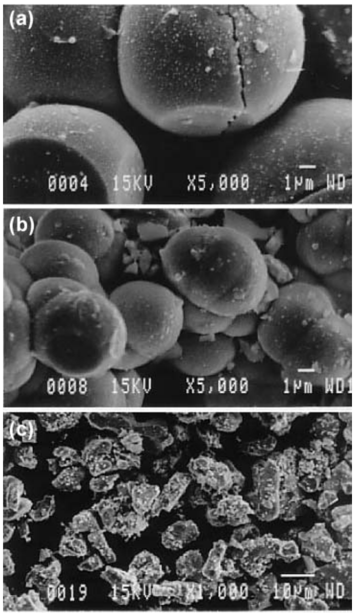

Fig. 1 SEM photographs of Cu/Ce catalysts. (a) Fresh Cu/Ce–CTAB (7.5 Cu wt%), (b) after the PROX reaction in the presence of H_2O, (c) impregnated Cu/Ce_2O_3 (10 Cu wt%).

new Cu/Ce–CTAB catalyst exhibited high activities with the feed of $CO/O_2/H_2/He$ = 1/1/50/48 (mol%) (Table 1), which are contrasted to the much lower performances of conventional impregnated Cu/Ce-oxide catalysts and co-precipitated Cu–Ce catalysts as shown in Table 1.

The Cu/Ce–CTAB catalyst hydrothermally prepared in the presence of the CTAB surfactant showed a single-phase morphology reflecting an assembly effect of the surfactant as imaged by SEM in Fig. 1(a), which was completely different from the inhomogeneous disordered morphology of a conventional Cu/Ce-oxide catalyst as shown in Fig. 1(c). The SEM image did not change after the PROX reaction (Fig. 1(b)), which indicates a high stability under the PROX conditions.

XRD showed the formation of fluorite CeO_2, while no XRD peaks attributed to Cu metal or oxides were observed (ESI† 1), indicating that Cu species were dispersed as small units on the CeO_2 surfaces. XPS Cu $2p_{3/2}$ binding energy of 932.4 eV (referred to C 1s of 284.6 eV) suggested that the Cu^{2+} precursor was reduced to Cu^0 or Cu^{1+} under the hydrothermal conditions. The reduction of the Cu^{2+}-nitrate precursor similarly occurred on other oxide surfaces such as MoO_2, ZnO, and SiO_2 reported previously.[10] In contrast to these previous supports, however, the Cu^{2+} precursor along with the Ce-nitrate precursor was not fully reduced to metallic Cu^0 under the hydrothermal synthesis conditions. The Cu atoms of Cu/Ce–CTAB were bonded to oxygen atoms making Cu–O at 0.194 nm besides Cu–Cu bonding at 0.256 nm as proved by Cu K-edge EXAFS (ESI† 2). The XRD, XPS, and XAFS data reveal the formation of Cu^{1+} clusters rather than Cu^0 metallic clusters on CeO_2 prepared from the Ce-nitrate precursor.

The detailed mechanism for the formation of reduced Cu^{1+} species under the hydrothermal synthesis conditions in the presence of CTAB without any additional reducing reagent is not clear at present, but the degree of the reduction of the Cu-precursor and oxide-precursor may depend on the oxophilicity of the metal oxides: Cu oxide (most reducible) < Mo oxide < Zn oxide < Si oxide < Al oxide ∼ Zr oxide ∼ Ce oxide (hard to reduce). Further, chemical interaction of the Cu^{1+} clusters with CeO_2 surfaces may also be the key to stabilize the clusters on the support.

Table 1 shows the catalytic performances of various Cu and Ce catalysts for CO PROX reactions in excess H_2 at 90 °C. Ce oxides, Ce–CTAB, and Cu–CTAB were completely inactive for CO oxidation at 90 °C. On the other hand, the hydrothermally-prepared Cu/Ce–CTAB catalyst (7.5 Cu wt%) exhibited good catalytic performances for the CO PROX with 91.9–96.1% CO conversion and 99.4–99.8% O_2 selectivity at 90 °C in a feed of $CO/O_2/H_2$ = 1/1/50 (Table 1). The performances of the Cu/Ce–CTAB catalyst under the various reaction conditions at different W/F, reaction temperatures, and feed compositions are summarized in Table 2. It is to be noted that high CO conversions and O_2 selectivities were also achieved in the reactant feeds containing substantial amounts of H_2O and CO_2. The CO conversions and O_2 selectivities at W/F = 2.24 g_{cat} h mol^{-1} and 90 °C were 85.7% and 98.7%, respectively when H_2O (10%) existed, and 81.4% and 98.2%, respectively when H_2O (10%) and CO_2 (20%) co-existed. The CO conversion increased significantly with an increase in W/F, while the O_2 selectivity decreased a little from 100%. The catalytic performances of the Cu/Ce–CTAB catalyst (Cu 7.5 wt%) were examined more systematically at W/F = 1.12 g_{cat} h mol^{-1}. The conversion increased with increasing temperature from 80 to 120 °C, while keeping good selectivities (96.9–100%); for example, the conversions (selectivities) at 90 °C were 82.5% (100%), 75.3% (100%), and 62.9% (100%) for the feeds of $CO/O_2/H_2$ (1/1/50), $CO/O_2/H_2/H_2O$ (1/1/50/10), and $CO/O_2/H_2/H_2O/CO_2$ (1/1/50/10/20), respectively, and at 120 °C the performances increased respectively to 100% (99.2%), 100% (97.1%), and 97.3% (96.9%) (Table 2). Au/Fe_2O_3 catalysts are highly active for CO oxidation at 80 °C, but O_2 selectivity is as low as 51%[5a] (<60%)[4a,5c] in the presence of H_2O and CO_2. A conventional CuO/CeO_2 catalyst is more selective, but high temperature (>150 °C) is required for sufficient CO conversion (90%).[4a,9a,9b] Pt/Al_2O_3[3b,3d,4a] exhibits average performances. The Cu/Ce–CTAB catalyst is the first example with remarkable performances in both activity and selectivity for the CO PROX with H_2O and CO_2 at low temperatures (⩽120 °C).

Table 2 PROX performances (conv.% and O_2 selec.%) of the Cu/Ce–CTAB catalyst (Cu 7.5 wt%) at different W/F (g_{cat} h mol^{-1}), reaction temperature, and reactant composition

W/F	Temp./ °C	CO/O_2 (1/1) conv.	$CO/O_2/H_2$ (1/1/50) conv. (selec.)	$CO/O_2/H_2/H_2O$ (1/1/50/10) conv. (selec.)	$CO/O_2/H_2/H_2O/CO_2$ (1/1/50/10/20) conv. (selec.)
0.56	80	76.8	64.5 (100)	54.1 (100)	
	90	82.4	71.9 (100)	66.7 (100)	
	100	94.0	87.5 (100)	82.3 (100)	
1.12	80	83.4	72.1 (100)	64.8 (100)	55.3 (100)
	90	91.2	82.5 (100)	75.3 (100)	62.9 (100)
	100	99.2	93.2 (100)	88.2 (100)	83.9 (99.4)
	110	100	96.3 (100)	93.8 (99.2)	89.3 (98.9)
	120	100	100 (99.2)	100 (97.1)	97.3 (96.9)
2.24	80	87.9	75.8 (100)	64.9 (100)	
	90	97.8	91.9 (99.8)	85.7 (98.7)	81.4 (98.2)
	100	100	98.5 (99.8)	91.5 (96.5)	
3.36	80	89.2	77.9 (99.5)	67.2 (98.5)	
	90	100	96.1 (99.4)	88.4 (95.1)	
	100	100	100 (98.2)	93.7 (90.2)	

Cu/Ce–noCTAB hydrothermally prepared in the absence of CTAB was much less active (10.2–15.9% CO conv.), similar to conventional impregnated and co-precipitated catalysts as shown in Table 1. The reduction of these catalysts with hydrogen did not efficiently improve their catalytic activities. The high PROX activity was characteristic of the hydrothermal synthesis, which *in-situ* produced reductive Cu species dispersed on CeO_2. The conventional impregnated Cu/CeO_2 catalyst was post-impregnated with CTAB, but no activity appeared at 90 °C as shown in Table 1. Other surfactants, neutral Pluorunic® and anionic dodecyl sulfate, did not produce any catalytically active Cu species by the hydrothermal procedure (Table 1). Additional metals (Pt, Pd, Au, or In) supported on the Cu/Ce–CTAB catalyst inhibited the PROX activity more or less as shown in Table 1. Only the Cu/Ce–CTAB among the examined catalysts exhibited such good PROX performances at $\leqslant 120$ °C. The catalytic performances were maintained for at least 10 h in the presence of H_2O and CO_2.

Active Cu species in the Cu/Ce–CTAB catalyst could not be imaged by TEM, while the EXAFS analysis (ESI† 2) provided structural parameters (bond distance and coordination number) for Cu–O and Cu–Cu. The small coordination number (0.9) of the Cu–Cu bond together with the small coordination number (2.4) of the Cu–O bond indicates that the hydrothermal synthesis prohibited the growth of Cu species and produced small Cu^{1+}-oxide clusters, which did not significantly change in their sizes after the PROX reaction (ESI† 2). CO of 5.75×10^{-4} mol was adsorbed on 1 g of Cu/Ce–CTAB (0.49 CO/Cu), but no CO_2 formation was observed. The results indicate that neither water-gas shift reaction nor CO oxidation with lattice oxygen proceeded on the Cu/Ce–CTAB catalyst. On the other hand, O_2 of 2.40×10^{-4} mol was adsorbed on 1 g of the fresh Cu/Ce–CTAB catalyst (0.20 O_2/Cu) and the stoichiometric amount of CO_2 (0.39 CO_2 per Cu) was produced when this surface was subsequently exposed to CO, which suggests high oxidation activity of the Cu^{1+}-oxide cluster species on the CeO_2 surface. XRF analysis showed that a small amount of Br (Br/Cu atomic ratio less than 0.26), derived from the surfactant CTAB, remained on the hydrothermally prepared Cu/Ce–CTAB catalysts. However, no Cu–Br contribution was observed by Cu K-edge EXAFS.

LDI-MASS (laser-desorbed-ionization mass spectroscopy) detected typical mass signals of Cu(I)Br as shown in ESI† 3. We measured LDI-MASS using MALDI-MASS equipment for characterization of the supported metal species on solid catalyst surfaces for the first time. The mass signals of Cu clusters were detected in a negative reflectron mode without any matrices for ionization. A UV/VIS spectrum of the Cu/Ce–CTAB catalyst suggested that the N_2 laser of the MALDI-MASS apparatus (337 nm) excited a band around 310 nm of the Cu catalyst. Three distinct components were detected for the hydrothermally-prepared Cu/Ce–CTAB (7.5 Cu wt%) by LDI-MASS (ESI† 3-I (g)), whose mass numbers and patterns implied the atomic compositions of $(CuBr)Br^-$, $(CuBr)_2Br^-$, and $(CuBr)_3Br^-$. These mass numbers were nominally identical masses to the Cu-oxide clusters of $Cu_3O_2^-$, $Cu_5O_3^-$, and $Cu_7O_4^-$, but all the intensity patterns of isotopes were fitted to theoretical patterns of the Cu-bromide anions rather than the Cu-oxide cluster anions. Cu(I)Br gave similar mass patterns with the three components, while those of Cu(II)Br_2 were entirely different from the observed ones. However, impregnated CuBr as well as $CuBr_2$ on CeO_2 had no PROX activity (Table 1). The Cu(I)Br species were also observed after the PROX reaction in excess H_2 at 90 °C as shown in ESI† 3-II (b). When the Cu/Ce–CTAB catalyst was exposed to O_2 at 90 °C, the three patterns of CuBr completely disappeared (ESI† 3-II (d)) and they were reversibly recovered by subsequent reaction with CO at 90 °C (ESI† 3-II (e)). There may be a positive effect of the remaining Cu bromide species on the PROX catalysis of Cu/Ce–CTAB.

In conclusion, we successfully prepared Cu^{1+}-oxide clusters on CeO_2 by the hydrothermal synthesis method using a surfactant, CTAB. These small Cu clusters on CeO_2 exhibited good CO PROX performances under the PEM fuel-cell operating conditions. This is the first report of a non-precious metal catalyst with good performances for the CO PROX in the presence of H_2O and CO_2. The PROX performances of the Cu^{1+}-oxide clusters may be promoted by traces of bromides. We also applied LDI-MASS to characterization of the composition of supported metal species for the first time.

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