Structure and catalytic behaviors of distinct Cu active sites over ceria surface

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Abstract: Cu/CeO_2 composites are the bench mark catalysts for water-gas-shift and CO_2 to methanol conversion. On the surface of ceria, at least three distinct Cu actives sites are formed. They are Cu^{2+} single site, Cu-O-Cu dimers, and CuO clusters. Here we identify and quantify those species by *operando* EPR, XRD and EXAFS. Cu^{2+} single site dominates at the loading below 1wt% and is the most active species for CO oxidation. CuO clusters are formed above 5wt% and will transform in to Cu nanoparticles, which are the only active site for water-gas-shift. H_2O activation over Cu surface is the rate limiting step.

Keywords: Cu actives sites, *Operando* spectroscopy, CO oxidation and WGS.

1. Introduction

Copper and its oxides, CuO and Cu_2O, offer redox reactions involving three valence states at relatively low temperatures. These can serve as catalytically active components in water gas shift and methanol synthesis catalysts. The combination of ceria and copper establishes a unique system with rich redox properties and attractive oxygen storage capacities. It represents the benchmark catalyst for the water gas shift reaction, the preferential CO oxidation, and, recently, also the methanol synthesis. The identification and understanding of Cu active species over ceria is the key step towards the design of more efficient and selective catalysts in those reactions. Here we use a bottom up synthetic approach to obtain three Cu active sites across a wide range of Cu^{2+} loadings. The presence and quantities of those sites are studied via *operando* EPR, XRD and EXAFS. Cu^{2+} single site dominates at the loading below 1wt% and is the most active species for CO oxidation.[1] CuO clusters are formed above 5wt% and will transform in to Cu nanoparticles, which are the only active site for water-gas-shift. H_2O activation over Cu surface is found to be the rate limiting step. Our study unveils the active site structure for those reactions.

2. Experimental

CuO/CeO_2 composites at different Cu loading were prepared via flame spray methods. The Cu/Ce-precursor solutions with different Cu:Ce ratio were prepared by mixing appropriate amounts of cerium-acetylacetonate with copper-2-ethylhexanoate in a solution of acetic acid, methanol and xylene. The resulting total metal concentration was 0.1 mol/L. These precursor solutions were sprayed at 2 ml/min, dispersed with 8 L/min O_2, and ignited by a premixed CH_4/O_2 ring-shaped flamelet. The resulting flame-made materials were collected from the filter and were not subject of additional temperature treatment.

The catalytic activity for CO oxidation and water gas shift were measured in a conventional fixed bed reactor in a reactive gas mixture. The catalysts were initially activated *in situ* at 573 K in a sequence of synthetic air (20 vol.% O_2 / 80 vol.% N_2, Air Liquide) for 60 min, 20 vol.% H_2 in N_2 for 40 min, and again synthetic air for 60 min. The concentrations of CO and CO_2 were analyzed with nondispersive infrared spectroscopy, and O_2 was analyzed with a paramagnetic analyzer at the outlet of the reactor using URAS 3E analyzers. At each temperature measured, the reaction was performed for 30 min in order to reach a steady-state condition.

3. Results and discussion

The Cu/CeO_2 catalyst has high specific surface area, evenly distributed Cu sites and high thermal stability. When the loading of Cu is below 1wt%, only monomeric Cu site present on the CeO_2 surface. As showed in Figure 1a, the catalytic activity presents an upward trend with the increase of Cu content. The activation energies E_a at the same Cu weight hour space velocity are uniformly around 66 kJ/mol for all Cu loadings. The catalytic activities at each loading are very similar to each other, as indicated in Figure 1b that the intercept at Y axis of all lines are close to each other. This suggests the presence of only one type of active site. HAADF-STEM images of the catalysts show clear CeO_2 lattice fringes with small particle sizes (Figure 1c,d).

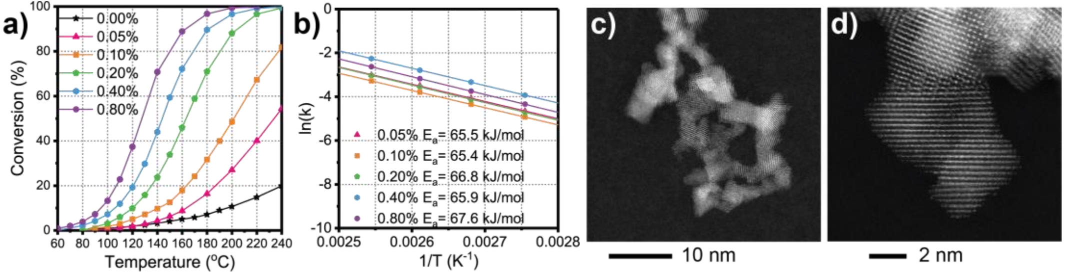

Figure 1. a) Conversion of CO as a function of temperature and Cu content (1% CO + 10% O_2). All the catalysts were tested with same Weight Hourly Space Velocity (WHSV) of 150,000 $mL \cdot h^{-1} \cdot g^{-1}$. **b)** Arrhenius plots (natural logarithm of conversion as a function of reciprocal of temperature) of the Cu/CeO_2 catalyst. The kinetics results were obtained with same Cu WHSV (75,000,000 $mL\ h^{-1}\ g^{-1}Cu$). **c, d)** HAADF-STEM images of 0.80% $CuO\text{-}CeO_2$. These images are obtained through previous TEM session EM16966-1.

EPR identifies the presence of Cu monomer (figure 2a, 2b) and the peak intensity is in nearly linear relationship with Cu loading (Figure 2c, 2d). When the Cu loading exceeding 1wt%, the single site intensity starts to decrease, indicating the formation of dimers and CuO clusters. This also verified by XRD measurement. The activation energy starts to increase from 68 kJ/mol to 100 kJ/mol, indicating a change of reaction active sites.

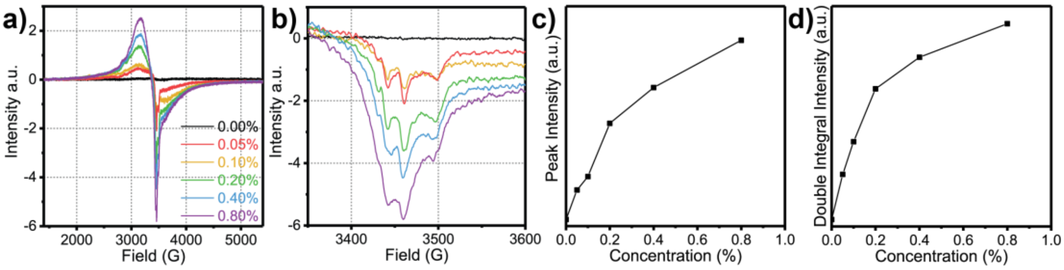

Figure 2. a, b) cw X-band (9.83 GHz) EPR spectra of 0.00 wt% to 0.80 wt% $CuO\text{-}CeO_2$ recorded at 293 K. The spectra in magnetic field range of 3400 to 3500 G shows the monomer Cu(II) EPR signal in all $CuO\text{-}CeO_2$ catalysts. **c)** Plot of peak intensity of EPR spectra as a function of Cu concentration. d) Plot of double integral intensity of EPR spectra as a function of Cu concentration.

The Cu single site is not active for water gas shift reaction. The active of WGS starts at 5wt% Cu loading, suggesting that either CuO clusters or metallic Cu is the active species. The latter is confirmed by *operando* XRD, showing the presence of metallic Cu during the reaction.

4. Conclusions

We have shown that Cu single site, dimers and CuO clusters are presented on the surface of ceria upon different Cu loadings. They are quantified by *operando* EPR, XRD and EXAFS. Cu^{2+} single site dominates at the loading below 1wt% and is the most active species for CO oxidation. CuO clusters are formed above 5wt% and will transform in to Cu nanoparticles, which are the only active site for water-gas-shift. H_2O activation over Cu surface is the rate limiting step.

References

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