XAS study of Cu species loaded on Bi_2O_3 hierarchical photocatalysts

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Abstract: Pristine Bi_2O_3 is known to possess a poor photocatalytic activity due to its low conduction band potential. Herein, we introduce an attempt to enhance the photocatalytic activity of Bi_2O_3 by loading Cu species through an impregnation method. Based on XANES and EXAFS analysis, we suggest that Cu species exists in +2 oxidation state, coordinated with four O atoms with bond lengths of ~1.93 Å in the form of amorphous nanoclusters.

Keywords: Photocatalyst, Bismuth Oxide, Copper loading.

1. Introduction

For practical and commercial applications, searching and optimizing visible light active photocatalysts with high performance is of great importance since visible light accounts for about 44% of the total radiation emitted by the sun [1]. In this context, Bi_2O_3 seems to be a suitable material as it possesses a small band gap of ~2.7 eV [2] and thus is able to harvest visible light. However, Bi_2O_3 was found not to be as good as expected [2]. This is due to its low conduction band (CB) potential (+0.32 V *vs.* NHE) which cannot make one-electron transfer reaction through the reduction of O_2 to $\bullet O_2^-$ ($E°(O_2/\bullet O_2^-)$ = -0.33 V *vs.* NHE) thermodynamically favorable. Having these in mind, we herein perform an in-depth investigation into structural properties of Cu species loaded on Bi_2O_3. Cu loading is aimed to enable the multi electron transfer reaction for improvement of charge carrier separation

2. Experimental

Pristine Bi_2O_3 was synthesized through a sol-gel method. The loading of Cu on Bi_2O_3 was done through impregnation of an aqueous solution of $CuCl_2$. The aqueous Bi_2O_3 suspension containing Cu was then heated at 90 °C under continuous stirring. After 1 h, the solid product was collected through centrifugation, washed with copious amounts of DI water, dried at 100 °C for 24 h and denoted as x% Cu, where x represents Cu loading (0.1, 0.2, 0.4, 0.6, and 0.8 wt%). The obtained samples were characterized by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at BL8 of the Synchrotron Light Research Institute (Public Organization), Thailand. The XANES and EXAFS spectra were recorded at ambient temperature in fluorescence mode due to low concentrations of Cu. The analysis of XANES and EXAFS spectra was done using Athena and Artemis software packages, respectively.

3. Results and discussion

Fig. 1(a) shows the XANES spectra of standard compounds. In CuO and $Cu(OH)_2$, we observe weak pre-edge absorption at 8975 eV due to a dipole-forbidden 1s → 3d transition of unoccupied 3d orbital in Cu(II) [3]. Such a pre-edge feature is not observed in Cu_2O since the 1s → 3d transition does not occur for the fully occupied d orbitals. We also see weak absorption at 8986 eV due to a dipole-allowed 1s → 4p transition in Cu(II), and rather strong absorption at 8981 and 8982 eV due to 1s → 4p transition for Cu(0) and Cu(I), respectively [4]. Characteristic white lines positioned at 8997 for $Cu(OH)_2$ and 8998 eV for CuO are also identified in the samples with Cu(II). Then, as shown Fig. 2(b), their spectra display well-defined pre-edge absorptions at 8975 eV, characteristic shoulders at about 8986 eV and sharp white lines at around 8998 eV, which are ascribed to the $1s \rightarrow 3d$, $1s \rightarrow 4p_z$ (shakedown) and 1s → 4p (continuum) features for Cu(II), respectively [3]. As clearly seen, the features of Cu(0) and Cu(I) are absent in all the samples. Based on these results, the oxidation state of Cu species is identified to be +2. Moreover, the overall shape and features of XANES spectra of all the Cu-loaded samples are similar to those of $Cu(OH)_2$, rather than those of CuO, Cu_2O or Cu metal. Therefore, the local structure of Cu(II) species loaded on Bi_2O_3 must be similar to that in $Cu(OH)_2$.

We then take the first derivative of the XANES spectra to determine the precise position of absorption edge representing the oxidation state of Cu. As shown in Fig. 1(c), more distinct features of XANES spectra at near-edge region are typically seen after taking their first derivatives. We observe absorption edge, defined as the position of the first maximum of the first derivative, at 8979, 8980, 8984, and 8986 eV for Cu foil, Cu_2O, CuO, and $Cu(OH)_2$, respectively. We also notice that the Cu(II) species in an octahedral symmetry, that is Cu(II) in $Cu(OH)_2$, exhibits an edge energy larger than that in a tetragonal symmetry, that is Cu(II) in CuO. We perform a detailed inspection on the derivative spectra of the Cu-loaded samples and see that the edge position of all the samples is almost the same, situated at around 8987 eV (Fig. 4(d)). Taking the edge positions into account, we conclude that the loaded Cu species is in +2 oxidation state and have similar chemical environment with those in $Cu(OH)_2$.

We next employ the EXAFS technique to elucidate the local geometry of Cu species loaded on Bi_2O_3. The EXAFS spectra were Fourier transformed (FT) without phase shift-correction. Therefore, the distances in the spectra are shifted to lower values [5]. The FT spectrum of all the Cu-loaded samples up to R of 2 Å is determined (the data are not shown here). FEFF code in Artemis [6] is then employed for fitting the FT spectra with a k^2 weight over the k range of 3-11 $Å^{-1}$ and R range of 1-2 Å. Based on the fitting analysis, we find that the local structure of Cu(II) atom in the first coordination shell possesses analogous structural parameters with increasing Cu loading. The Cu(II) atom is surrounded by four O atoms with a bond length of ~1.93 Å. The identities of the four-coordinate O species are most likely –O– and –OH. Moreover, we can see that with increasing Cu loading, the length of Cu-O bond increases linearly.

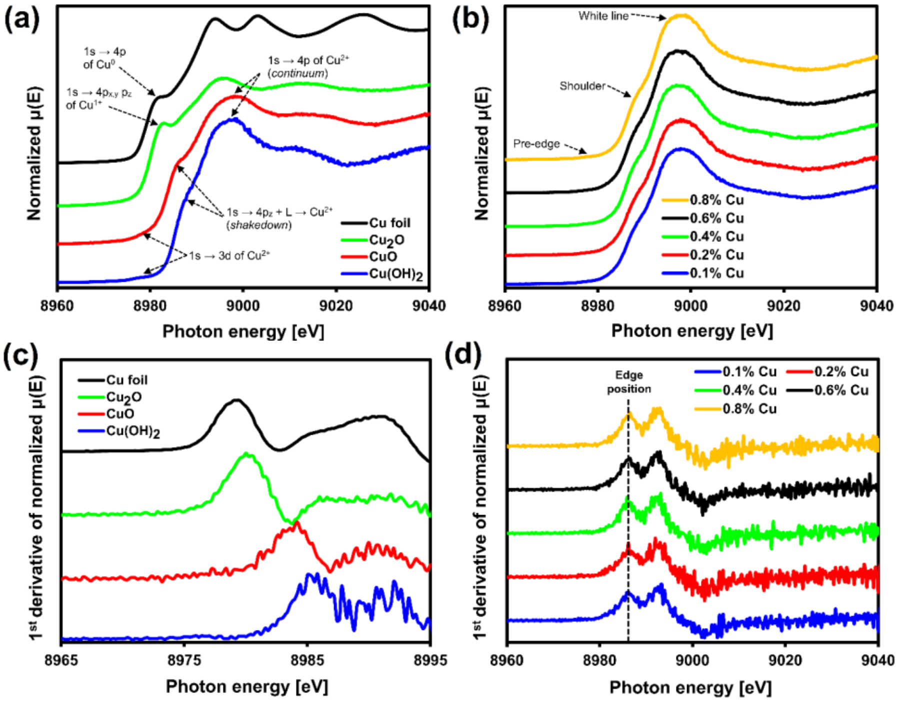

Figure 1. The Cu K-edge spectra of reference compounds (a) and Cu-loaded samples (b). The first derivative of Cu K-edge spectra of reference compounds (c) and Cu-loaded samples (d).

4. Conclusions

Investigation by XANES and EXAFS reveals that the loaded Cu species is solely present as Cu(II), bound to four O atoms with bond lengths of ~1.93 Å. No substitutional doping through replacement of Bi by Cu is indicated.

References

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