Phenol Hydroxylation Catalyzed by the Rare Earth-adulterated Copper-containing Hydrotalcites

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Owing to the fact that the presence of the Cu^+ species in La–Cu–HTLcs/H_2O_2 system is detected by the X-ray photoelectron spectra (XPS), the generation of HO• radicals is deduced to be carried out by the reaction of HO–Cu^+–OH species with H_2O_2.

Since the copper-containing hydrotalcites (Cu–HTLcs) were found to exhibit good catalytic properties in phenol hydroxylation with H_2O_2,[1,2] the researchers have introduced the other transition metal ions (such as Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{2+}, Mn^{2+}, Zn^{2+}, and so on) into Cu–HTLcs materials to form ternary or quarternary oxide system in order to improve their catalytic activities, which was achieved by the synergistic effect of the added transition metal ions with Cu^{2+} ions. However, there still have had no reports about the effect of rare earth adulteration on the catalytic activity of Cu–HTLcs. For the phenol hydroxylation on Cu–HTLcs, it was recognized to be carried out through the free radical reaction of phenol with HO• radicals, which were reckoned to be generated through the oxidation of HO–Cu^{2+}–OH with H_2O_2 to HO–Cu^{3+}–OH,[1,2] however, the generation mechanism of the free radicals was only originated from the theoretical consequence.

Here we prepare the precursors of Cu–HTLcs by co-precipitation from aqueous solutions of metal nitrates: $Cu(NO_3)_2 \cdot 3H_2O$ and $Al(NO_3)_3 \cdot 3H_2O$.[1,3] The mixture of metal nitrates (Cu^{2+}/Al^{3+} molar ratio being 4) and the other solution containing NaOH and Na_2CO_3, are synchronously added dropwise at 70 °C, the pH value is maintained at 9–10. The crystallization of Cu–HTLcs is carried out at 70 °C for 10 min under the microwave irradiation. At the same time, we also investigate the effect of rare earth (RE) adulteration on the catalytic activities of Cu–HTLcs in phenol hydroxylation. The adulteration of RE, such as Ce^{4+}, Y^{3+}, Sm^{3+}, La^{3+}, and so on, is carried out during the preparation of Cu–HTLcs precursors. The adulterated amount is 4 mol % of the total metals, and the RE-adulterated samples are denoted as RE–Cu–HTLcs. The results show that all samples exhibit a pure hydrotalcites-like phase without cocrystallization of any detectable impurity, which is characterized by the X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR), respectively.

Figure 1 illustrates the XPS spectra of copper-containing hydrotalcites samples, and all binding energy values (BE (eV)) are calibrated with respect to the C $1s_{1/2}$ of contaminant carbon at 284.8 eV. It can be observed that all samples give a peak near 934.5 eV along with a satellite peak at 942.1 eV, which are assigned to Cu $2p_{3/2}$ of Cu^{2+} ions according to the literatures.[4] And at the same time, the Cu $2p_{1/2}$ peak near 954.5 eV and its satellite peak at about 962.2 eV, can also be clearly seen in all samples. However, the peaks for both Cu $2p_{3/2}$ and Cu $2p_{1/2}$ exhibit a positive shift as the order of Cu–HTLcs < Ce–Cu–HTLcs < Y–Cu–HTLcs < Sm–Cu–HTLcs < La–Cu–HTLcs, indicating that the HO–Cu^{2+}–OH species in the RE-adulterated copper-containing hydrotalcites will have an increasing electron-withdrawing capacity as the order of Ce < Y < Sm < La.

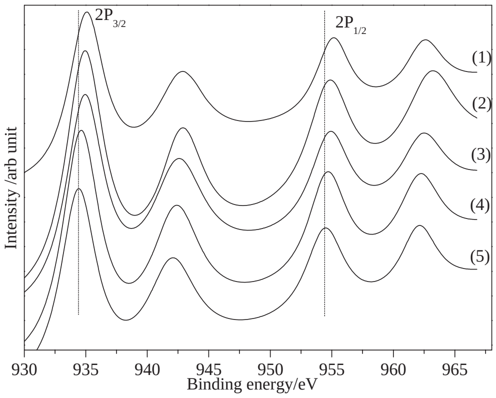

Figure 1. Cu 2p XPS region in the corresponding XPS spectra of (1) La–Cu–HTLcs, (2) Sm–Cu–HTLcs, (3) Y–Cu–HTLcs, (4) Ce–Cu–HTLcs, and (5) Cu–HTLcs.

Figure 2 compares the catalytic properties of catalysts in phenol hydroxylation. It can be observed that the products catechol (CAT), hydroquinone (HQ), and benzoquinone (BQ) exhibit a similar distribution for all catalysts. However, RE–Cu–HTLcs catalysts always give a higher phenol conversion than Cu–HTLcs free of RE. In order to make clear the function of RE elements, we further investigate the catalytic properties of RE-containing HTLcs samples free from Cu^{2+}, and it is found that they almost have no catalytic activities in phenol hydroxylation. It shows that the RE elements in hydrotalcites can't act as the catalytic active centers, and is only beneficial to the improvement on the catalytic activity of Cu–HTLcs. The increase on the catalytic activities of RE–Cu–HTLcs is probably attributed to the synergistic effect of rare earth element with Cu^{2+} species in hydrotalcites. Moreover, from Figure 2, the different RE elements are also observed to exhibit different extents on the improvement of the catalytic activities of RE–Cu–HTLcs. The catalytic activities of RE–Cu–HTLcs are increased as the order of Ce < Y < Sm < La, which is just coincident with the increasing order of their Cu 2p binding energies of Cu^{2+} in RE–Cu–HTLcs. It is estimated that the catalytic activities of RE–Cu–HTLcs are probably related to the electron-withdrawing capacity of Cu^{2+} ions in hydrotalcites. The stronger the electron-withdrawing capacity is, the higher the catalytic activities of RE–Cu–HTLcs. Thus, it can be inferred that the active centers HO–Cu^{2+}–OH species are easy to adsorb electrons to form the transition state HO–Cu^+–OH during the phenol hydroxylation with H_2O_2.

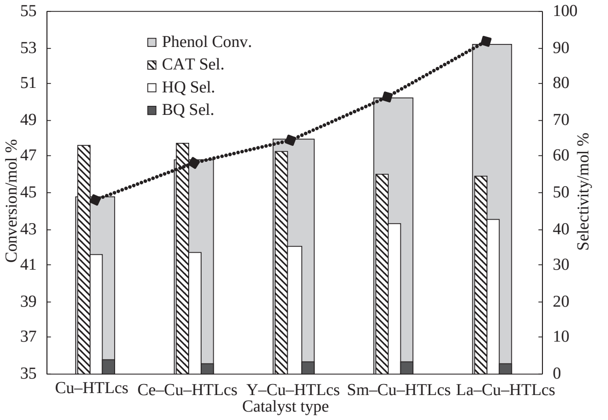

Figure 2. Phenol hydroxylation on Cu–HTLcs adulterated by different rare earth elements. Reaction conditions: 0.5-g phenol, 0.025-g catalyst, a 1 mL 30 wt % H_2O_2 solution, 10-mL distilled water, temperature 70 °C, time 120 min. The products were analyzed by GC on the SC-1001 gas chromatograph (China) fitted with FID detector, PTE™ capillary column (15 m × 0.53 mm × 0.5 µm film thickness, Supelco, U. S. A.)

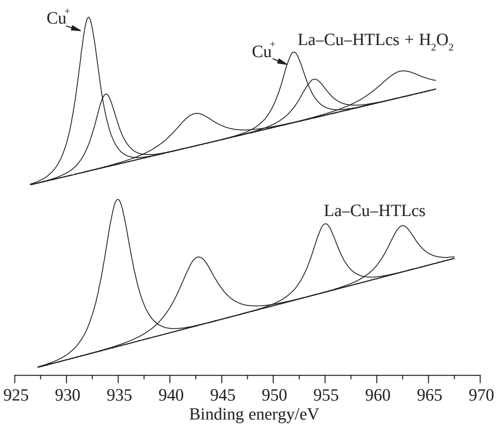

Figure 3. Comparison of Cu 2p XPS spectra of La–Cu–HTLcs and La–Cu–HTLcs/H_2O_2.

For the purpose of proving the above viewpoint, we investigate the valence change of copper for HO–Cu^{2+}–OH species in La–Cu–HTLcs mixed with aqueous H_2O_2 solution by XPS technique, the results are depicted in Figure 3. From it, it can be clearly observed that the fresh La–Cu–HTLcs sample only exhibits four signals, which are attributed to the Cu 2p electron binding energies of Cu^{2+}. However, the La–Cu–HTLcs/H_2O_2 system, resulting from the solid–liquid interaction between La–Cu–HTLcs and H_2O_2, gives two additional strong signals located at the binding energy of 932.1 and 953.9 eV, attributing to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu^+, respectively.[5] The same results are also found in the Cu–HTLcs/H_2O_2 system. Associated with the effect of RE-adulteration on Cu 2p binding energies and catalytic activities of RE–Cu–HTLcs, it can be concluded that the transition state HO–Cu^+–OH species will be produced in the phenol hydroxylation with H_2O_2 catalyzed by copper-containing hydrotalcites. Therefore, the generation of HO• radicals is deduced to be carried out not through the oxidation of HO–Cu^{2+}–OH to HO–Cu^{3+}–OH as previously reported,[2] but through the reduction of HO–Cu^{2+}–OH to HO–Cu^+–OH as depicted in Figure 4.

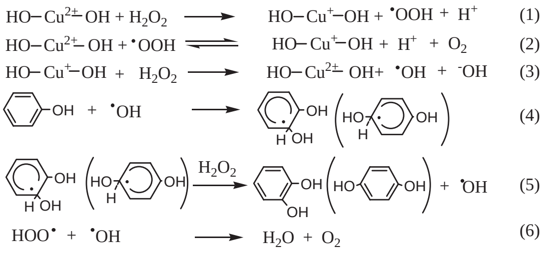

Figure 4. Reaction mechanism for phenol hydroxylation.

The HO• radicals are generated by the redox reaction of H_2O_2 with HO–Cu^{2+}–OH species in hydrotalcites. HO–Cu^{2+}–OH species are firstly reduced by H_2O_2 to HO–Cu^+–OH through the reactions (1) and (2), and then HO–Cu^+–OH species react with H_2O_2 to produce HO• radicals. This path for the generation of HO• radicals can also be supported by the previous reports in literatures.[6] According to the proposed mechanism, reaction (1) is a chain-initiation step, the produced HO• radicals attack phenol to form two kinds of transition complexes (see reaction (4) in Figure 4), which continue to react with H_2O_2 to yield catechol and hydroquinone, respectively, and give rise to the HO• radicals, simultaneously. Thus, reactions (2)–(5) can be considered as the chain-propagation steps. At the same time, the produced HO• radicals can also contact with HOO• radicals to form O_2 as shown in reaction (6), which is regarded as the chain-termination step. If a proper solvent, such as water, is introduced into the reaction system, the mutual collisions of free radicals can be avoided, resulting in the increase of the probability for phenol hydroxylation, which has been proved by the effect of solvent types on phenol hydroxylation in the present work. On the other hand, reactions (2) and (6) give rise to decomposition of H_2O_2, which are the main processes as the side reactions.

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