Dynamic agglomeration and re-dispersion of Cu species in supported catalysts and its influences on their catalytic performances

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Abstract: In this work, using Cu supported on γ-Al_2O_3 as model catalyst, we have performed systematic study on the dynamic structural transformation of Cu species during redox processes. It is found that the dispersion of Cu species has significant influences on their redox property.

Keywords: Copper oxide, dispersion, NO.

1. Introduction (11-point boldface)

Cu (including Cu(0), Cu(I) and Cu(II)), as a one of the components in catalysts for many chemical reactions,[1] can undergo in-situ structural transformations during the catalytic reactions, which have been demonstrated by many works. Corma et al. have shown the migration of Cu species in zeolite crystallites during the NH_3-SCR reaction in their recent work.[2] However, the correlations between the dynamic transformations and their catalytic properties are still not very clear. In this work, using Cu supported on γ-Al_2O_3 as model catalyst, we have performed systematic study on the during redox processes. With different types of spectroscopic techniques, we tried to look into the dynamic structural transformations (including the chemical states and aggregation state of Cu species) under certain redox treatments. The structural characteristics of Cu species were found to have significant influences on their catalytic properties in heterogeneous reactions (NO+CO, NO+O_2 and NH_3-SCR).

2. Experimental

CuO/γ-Al_2O_3 samples were prepared by wet impregnation method, denoted as xCuAl (x represent for the CuO loading), i.e., 01CuAl corresponds to a sample with Cu^{2+} loading amount of 0.1 mmol/100 m^2 γ-Al_2O_3. To investigate the evolution of CuO species under H_2 atmosphere, xCuAl samples were pretreated at 500 ^oC in H_2-Ar mixture stream (denoted as xCuAl-H). Then xCuAl-H were pretreated in N_2-O_2 mixture stream with or without H_2O (denoted as xCuAl-HO and xCuAl-HW, respectively).

3. Results and discussion

According to the characterized results from XRD, EPR, XPS, we tentatively derived the surface CuO into three different species, i.e., highly dispersed CuO, CuO clusters, and metallic Cu particles in fresh and/or pretreated xCuAl samples. After reduced by hydrogen, the agglomeration of the surface copper species can be generated. Followed by the oxidation process, the agglomerate copper species can be re-dispersed with the introduction of H_2O（Figure1a）. As a result, CuO clusters are the main species in xCuAl-HO, when highly dispersed CuO in xCuAl and xCuAl-HW. The catalytic performance of fresh and pretreated xCuAl in NO+CO, NO+O_2 and NH_3-SCR model reactions are shown in Figure 1b. Samples xCuAl-HO have shown obviously higher NO conversion in NO+CO and NO+O_2 reactions, which are in line with previously reported results that CuO clusters have better performance than isolated CuO in NO activation. When it comes to NH_3-SCR model reaction, H_2O, the product of the reaction, may have induced the re-dispersion of CuO clusters. Fresh and pretreated xCuAl may have similar behaviors as a result.

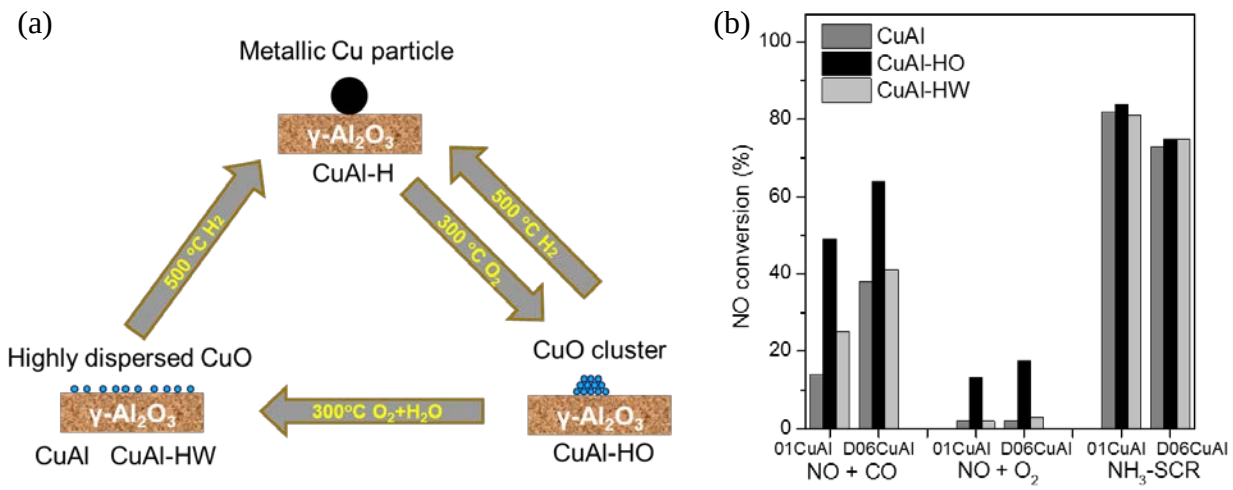

Figure 1 (a) Schematic dynamic structural transformations of Cu species. (b) NO conversion of fresh/pretreated CuAl samples in NO+CO, NO+O_2 and NH_3-SCR model reactions.

4. Conclusions

The structural and chemical environment of CuO are unstable during redox process. Reduction by H_2 can lead to the agglomeration of Cu species. Reversely, oxidation with assist of H_2O can reversely result in re-dispersion of Cu species. Since the catalytic behavior of copper species are significantly related with their structural properties, these findings will be helpful for gaining insights into the applications of copper related catalysts.

References

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