

Preparation of Single-Site Co Catalyst from Co(salen) Complex and Carbon Materials

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Catalytically active metal species exhibit unique properties depending on their size, morphology, and structure. In particular, the size of the metal species, such as single-site, metal nanoparticles (NPs), or bulk state, directly affects on the catalytic activity. Recently, some researchers pay attention to the organometallic compounds with complicated structures to achieve both high activities and recyclability. Such complexes show higher thermal stability than simple metal salts and their decomposition occur gradually upon increasing the thermal treatment temperature. Considering these properties, recently, organometallic compounds are heat treated with carbon materials to prepare Co-N-C single-site structure, which shows different catalytic activities from the common metal NPs. However, these reports focused only on the single-site metal species and their catalytic performances. Despite fundamental industrial and academic interest, systematic control of the active species from single-site to NPs by using simple heat treatment as well as the study of their structure-activity relationship have not been investigated.

In this study, we successfully monitored the structural transformation of the active center during heat treatment and the corresponding catalysis by using the Co(salen) complex as a metal precursor on a carbon support. The obtained structures were characterized using techniques such as XRD, in-situ XAFS, and TEM. From these characterizations, the first decomposition of the deposited Co(salen) complex is initiated by the dissociation of the

Co-O-C moiety at around 250 °C without the destruction of the Co-N-C moiety. This Co-N-C bonding is maintained up to 450 °C and acts as an anchor to fix the Co species onto the carbon support to maintain the single-site structure. Moreover, the single-site Co species are confirmed to be in an electron-deficient oxidation state compared to the original one by the interaction between Co species and the carbon support. Heat treatment at around 500 °C triggers dissociation of the Co-N-C bond and the formation of the Co nanocluster, which finally transforms into Co NPs by grain growth during heat treatment above 500 °C (Fig. 1).

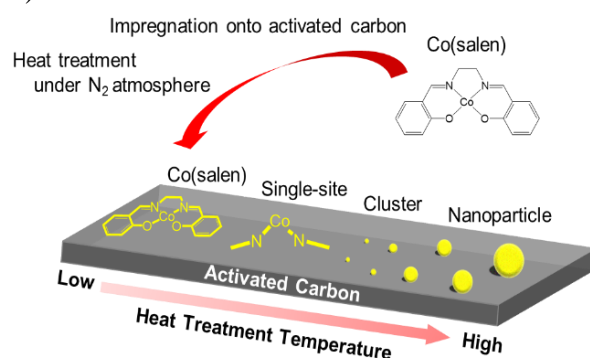


Fig. 1 Structural change of the Cobalt during the heat treatment.

In order to investigate the effects of the different structures of the Co sites on the catalytic performance, the oxidation of ethylbenzene using TBHP was carried out. Co/AC-salen-300 and -400 showed higher catalytic performances with increasing of the heat treatment temperature with respect to both conversion and selectivity in comparison with the original Co(salen) complex. Co/AC-salen-400 exhibited the highest activity among those investigated, with a conversion and selectivity of 47.9% and 83.5%, respectively. The creation of highly dispersed Co species with a single-site structure was the main reason for the improvement of catalytic performance in the oxidation of ethylbenzene.

REFERENCES

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