Resolving structures of atomically dispersed M-N-C catalysts

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Single-atom-catalyst (SAC), which is defined as all the metal species in a supported metal catalyst are dispersed as single atoms,[1,2] has emerged as a new frontier in heterogeneous catalysis, and shown distinctive performances in a series of oxidation and hydrogenation reactions. In this presentation, we will show several examples of SACs, and put focus on the atomic characterizations of SACs by using aberration-corrected HAADF-STEM, in situ EXAFS and DFT calculations.

The first example is the FeOx-supported Pt single atoms, which have shown exceptionally high activity and chemoselectivity for nitroarenes hydrogenation.[3,4] HAADF-STEM and in situ EXAFS revealed that Pt could be exclusively dispersed as single atoms when its mass loading was controlled at a pretty low value (< 0.5 wt%) and the catalyst was reduced at milder conditions (e.g., 200 ^{o}C for 1 h). Alkali metal cations (Na^{+}, K^{+}, etc.) could promote the dispersion of Pt, which provided a new opportunity to increase the density of single metal atoms. Moreover, the Pt single atoms are positively charged by strongly interacting with the underlying FeOx support. These positively charged and isolated Pt sites are favorable to the adsorption of nitro group towards the chemoselective reduction.

The second example is the atomically dispersed M-N-C catalysts, which have shown promising performance in a variety of reactions, including hydrogenation of nitroarenes, selective oxidation of C-H bond, and electrochemical reduction of oxygen (ORR). By using XANES, Mössbauer spectroscopy, and DFT calculations, we could identify, without much ambiguity, the structures of M-N-C catalysts. For the atomic dispersed Co-N-C catalyst, the exact structure is identified to be CoN_4C_8-1-$2O_2$, where Co center atom is coordinated with four pyridinic N atoms in the graphitic layer while two oxygen molecules are weakly adsorbed on Co atoms in perpendicular to the Co-N_4 plane.[5] However, for the atomically dispersed Fe-N-C catalyst, there are four types of different FeNx (x = 4, 5, 6) structures and the relative concentration is critically dependent on the pyrolysis temperature. The most active structure is FeN_5, unfortunately, it has the lowest numbers in the total Fe species.

References

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