Atomically dispersed M-N-C catalyst for green organic transformations

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Abstract: Atomically dispersed M-N-C (M refers to Fe, Co, Ni) catalysts were prepared with a template-sacrificial approach, and characterized with a spectra of advanced physico-chemical technologies. The exact structure of the M-N-C catalysts, although M is exclusively single-atom dispersed, varies with the nature of metal. Depending on their structure and electronic properties, the M-N-C catalysts can be used for selective oxidation or hydrogenation reactions towards a sustainable and green chemistry world.

Keywords: single-atom catalyst, M-N-C, selective transformation.

1. Introduction

Single-atom catalysts (SACs), with active metal atomically dispersed on a support, have shown superior performances to the NPs counterparts in a variety of industrially important reactions.[1-2] The extreme dispersion maximizes the utilization efficiency of active metals, which is of paramount importance for reducing the high cost of noble metal catalysts. On the other hand, the unique geometrical (isolation of the active sites) and electronic (positively charged) properties of SACs endow them with distinctive interaction with reactants and intermediates, thus giving rise to promising chemoselectivities in organic transformations. Atomically dispersed M-N-C catalysts can be considered as a new type of SACs if the nitrogen atoms bonding to the central metal are viewed as a robust ligand. In this work, we prepared atomically dispersed Co-N-C, Fe-N-C, and Ni-N-C, and studied the structure-performance relationship in selective hydrogenation and oxidation reactions.

2. Experimental

The atomically dispersed M-N-C (M refers to Co, Fe, Ni) catalysts were prepared by a template-sacrificial approach.[3,4] Briefly, the M(phen)x (phen=1,10-phenanthroline) complex supported on nano-MgO template was pyrolyzed at 600-800 °C under N_2 atmosphere, followed by acid leaching to remove the MgO template. The structures of the M-N-C catalysts were characterized and identified with a spectra of advanced physico-chemical techniques, including aberration-corrected HAADF-STEM, X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and Mössbauer spectroscopy.

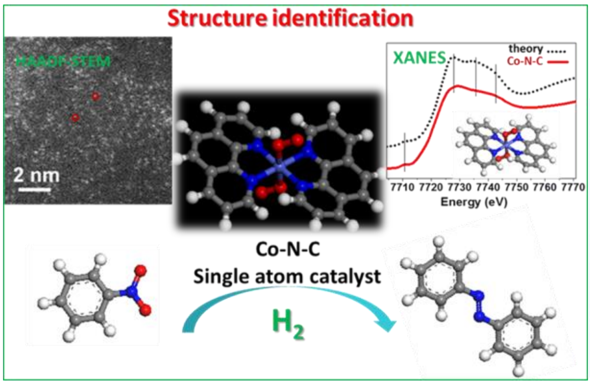
The selective oxidation of C-H bonds was conducted in a flask equipped with a dropwise addition system. Before the reaction test, 10 mg catalyst and substrate (0.5 mmol) were put into the flask. Then TBHP (500 µL, 70 wt % in water) and water (6.5 mL) were added to the titration control system. The reaction mixture was stirred with TBHP titration feedstock at room temperature for 7 h. After the reaction, the solid catalyst was recovered by filtration, while the filtrate was extracted with 30 mL ethyl acetate (10 mL each time). The products were quantitatively analyzed by using an Agilent 7890A GC system equipped with a HP-5 capillary column and a FID detector. For the selective hydrogenation of nitroarenes, a mixture of nitroarenes (1 mmol), sodium hydroxide (0.2 mmol), tert-butanol (2 mL), dodecane (100 µL, the internal standard) and catalyst (0.7 mol%) was put into the autoclave, and the autoclave was flushed with hydrogen three times before the reaction. The mixture was vigorously stirred at 80 °C under a H_2 pressure of 3 MPa for a given reaction time. After the reaction, the mixture was analyzed with a gas chromatograph (Agilent 7890B) equipped with a 5% phenyl methyl siloxane capillary column (30 m × 320 μm × 0.25 µm).

3. Results and discussion

The metal dispersion in the M-N-C catalysts is strongly dependent on the pyrolysis temperature as well as the metal-support interaction. In our work, we employed nano-MgO as a sacrificial support, which interacts with the transition metal (Fe, Co, Ni) properly to prevent the metal aggregation during pyrolysis step and then can be removed by acid leaching, leaving the transition metal single atoms strongly bonded to the N-doped carbon support. Furthermore, it was found that the metal loading in the atomically dispersed M-N-C varied with the metal type, increasing in the order of Fe (1.6 wt%) < Co (3.6 wt%) < Ni (7.5 wt%). The single-atom dispersion was verified with both aberration-corrected HAADF-STEM and XAS. As shown in Figure 1, all the Co species are dispersed as single atoms in the Co-N-C catalyst, and the oxidation state of Co is in +2. By combined use of EXAFS, XANES, and DFT calculations, the exact structure of the Co-N-C is identified to be CoN4C8-1-2O2, 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-N4 plane (Figure 1). Such a unique structure gave rise to excellent activity, chemoselectivity and stability for the synthesis of aromatic azo compounds through hydrogenative coupling of nitroarenes (12 examples).

Different from the Co-N-C catalyst, the Fe center in the Fe-N-C catalyst has an oxidation state of +3. The high oxidation state of Fe species made it highly active and selective for the oxidation of C-H bonds of a broad scope of substrates at room temperature. Meanwhile, the structure of the Fe-N-C is quite complex. As shown in Figure 2, Mössbauer spectroscopy and KSCN titration experiments reveal that there are four different FeNx species (x = 4~6) in the atomically dispersed Fe-N-C catalysts, whose relative concentrations are critically dependent on the pyrolysis temperature. Among them, the most active Fe-N-C-700 catalyst is comprised of high-spin FeN6 (28.3%), low-spin FeN6 (53.8%) and medium-spin FeN5 (17.9%) species, where the FeN5 is at least one order of magnitude more active than the other two species although it accounts for only 28.3% of the total Fe species.

It is particular interesting that the atomically dispersed M-N-C catalyst is highly stable, even in harsh reaction conditions. To show the exceptional stability, the Ni-N-C catalyst was used for lignocellulose conversion to ethylene glycol at 245 °C, 6 MPa H_2 in hot water. It could be reused for more than 10 times without any loss in activity, while the Ni NPs supported on active carbon lost 50% activity in the second run.



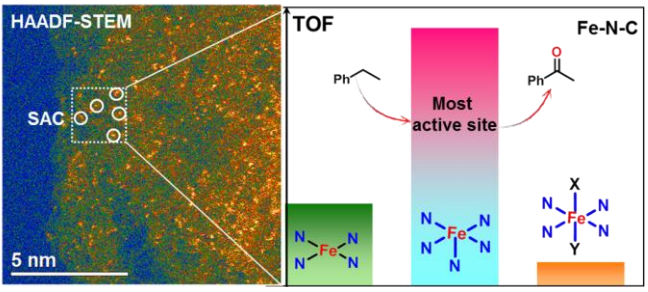


Figure 1. Atomically dispersed Co-N-C catalyst.

Figure 2. Atomically dispersed Fe-N-C catalyst

4. Conclusions

A new type of single-atom catalysts, atomically dispersed M-N-C catalysts were developed for a variety of selective organic transformations towards sustainable chemistry. The structures of M-N-C were identified and well correlated with the catalytic performances.

References

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