Au@ZIF-8: CO Oxidation over Gold Nanoparticles Deposited to Metal−Organic Framework

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There has been a rapidly growing interest in Au catalysts since the extraordinary activity of Au supported on metal oxides was reported for CO oxidation.[1] Gold nanoparticles (NPs) supported on metal oxides, zeolites, mesoporous materials, and activated carbons (AC) have been widely studied as catalysts in the past two decades.[2−4] On the other hand, metal−organic frameworks (MOFs) are promising multifunctional materials, which are thermally robust and in many cases highly porous. The spatial organization of metal ions and organic ligands leads to rationally designed frameworks with nanosized channels and cavities, analogous to that found in zeolites. Moreover, proper selection of the structural subunits and their connected ways allows flexible and systematic modification of the pore structure of MOFs. Over the past decade, research efforts have been mostly aimed at preparing new MOF structures and studying their applications in gas storage and separation.[5,6] Taking into account the similarity to zeolites, a logical application of MOFs, especially by embedding noble metal (Pd, Pt, Au, etc.) NPs into the pores of MOFs, could be to solid catalysts. It is expected that the crystalline porous structures of MOFs limit the migration and aggregation of metal clusters/NPs. So far, there are a limited number of reports on MOFs as catalysts[7] and extremely rare works on embedding noble metal NPs within pores of MOFs as catalysts for liquid phase heterogeneous catalytic reactions.[8,9] Only two examples of Au-supported MOFs were reported, whereas neither of which was found to be active for gas phase catalytic reaction.[9]

Herein, we report Au NPs deposited to a zeolite-type MOF by a simple solid grinding method.[9b] This work represents the first example of an active catalyst in CO oxidation by using a microporous metal−organic framework (MMOF) as a support for noble metal NPs. The ZIF-8 framework (Zn(MeIM)$_2$, MeIM = 2-methylimidazole), one of representative MMOFs, was used as a support. We have chosen ZIF-8 because it holds an intersecting three-dimensional structural feature, high thermal stability (over 500 °C), large pore size (diameter of 11.6 Å), and large surface area (BET, 1413 m^2/g), which are desirable for depositing small Au NPs.[10,11]

The pretreated ZIF-8 and desired quantitative volatile organogold complex (to give 0.5, 1.0, 2.0, and 5.0 wt % Au loadings, respectively), (CH$_3$)$_2$Au(acac) (easily adsorbed/reacted on the surface of the support, acac = acetylacetonate),[12a,b] were ground uniformly in an agate mortar in air for ~35 min at room temperature. Then the as-prepared sample was treated in a stream of 10 vol% H$_2$ in He at 230 °C for 2.5 h to yield Au@ZIF-8.[11]

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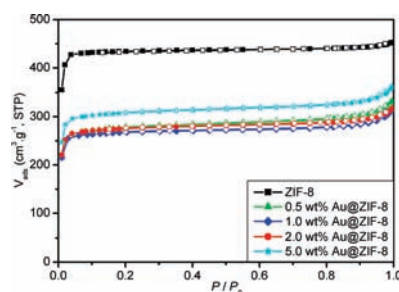[‖] Tokyo Metropolitan University.

Figure 1. Nitrogen adsorption isotherms of ZIF-8 and Au@ZIF-8 samples with different Au loadings measured at 77 K. Empty markers represent the desorption isotherms.

No diffractions were detected for Au NP species from powder XRD patterns after H$_2$ reduction in Au@ZIF-8 samples with different Au loadings,[11] which indicates Au loadings are too low or Au NPs are too small in all samples. The latter proved to be more probable by UV−vis spectrum examination of Au@ZIF-8 samples.[11] The intensity of the absorption peak at ~530 nm originated from surface plasmon slightly increases with an increase in the particle size, accompanied by a decrease in the peak width. Such features observed coincide with the prediction of the Mie thoery.[12c] Weak surface plasmon absorption by 5.0 wt % Au@ZIF-8 suggests the formation of small Au NPs, whereas the absence or weaker plasmon bands for other samples indicate smaller Au NPs together with lower Au loadings. These features were also consistent with the results of TEM observations mentioned below.

The specific surface areas of Au@ZIF-8 with different Au loadings were determined by the N$_2$ physisorption measurement (Figure 1), which shows a type I isotherm according to IUPAC classification for all samples. The appreciable decrease in surface area indicates that the cavities of the host framework possibly with the locally distorted environment are occupied by highly dispersed Au NPs or/and blocked by Au NPs which are located at the surface, as in the case of metal NPs loaded to MOF-5, SNU-3, and zeolitic materials.[13] A slight increase in surface area observed for 5.0 wt % and higher Au loading samples[11] may be attributed to the aggregation of Au NPs, which leads to a lower occupation of the cavities.

The Au@ZIF-8 samples obtained are catalytically active in CO oxidation. To the best of our knowledge, this is the first report of a porous MOF as an active support for noble metal NPs for gas phase catalysis.[8,9] In principle, the CO oxidation activity is improved with increasing Au loadings, as shown in Figure 2 (left); the temperatures for 50% conversion are approximately 225, 200, 185, and 170 °C, respectively for 0.5, 1.0, 2.0, and 5.0 wt %
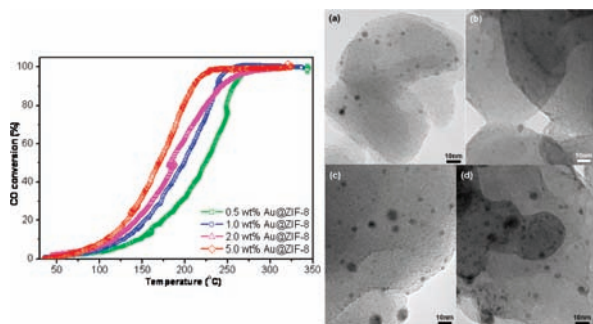
Figure 2. Conversion−temperature curves for CO oxidation over Au@ZIF-8 catalysts with different Au loadings (left) after repeated catalytic runs (see text). TEM images of 1.0 wt % (a and b) and 5.0 wt % (c and d) Au@ZIF-8 before (a and c) and after (b and d) catalytic reaction (right).
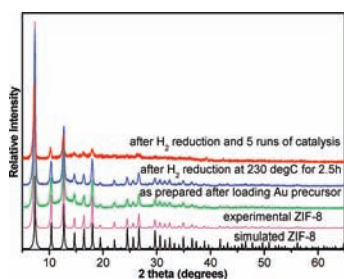

Figure 3. Powder XRD patterns of ZIF-8 and representative 1.0 wt % Au@ZIF-8 treated under different conditions.

Au@ZIF-8 samples. In these experiments, the CO oxidation activity was repeatedly examined from room temperature to 315−340 °C. The catalytic activity appeared from the second run and became reproducible after 3rd−4th runs (Figure 2, left). It is worth noting that thermal activation at a suitable temperature (>300 °C) seems necessary for stable activity in our experiments. Accordingly, we assume that the high thermal stability of ZIF-8 could be one of the important factors for the genesis of CO oxidation activity.[8,9]

Figure 2 (right) shows the typical TEM images for 1.0 and 5.0 wt % Au@ZIF-8 before and after reaction. Since the migration or/and aggregation of Au NPs stuck in crystalline porous structures in ZIF-8 is prevented, Au NPs are close to monodisperse and the mean diameter estimated by size distribution even decreases slightly after reaction,[11] indicating no sintering of Au NPs during the reaction, which can also be confirmed by the preserved catalytic activity in the following runs.[11] The mean diameters are 3.4 ± 1.4 and 3.1 ± 0.9 nm for 1.0 wt % Au@ZIF-8 before and after reaction, respectively. However, for a 5.0 wt % sample, even though most Au NPs are still very small, a few Au NPs aggregate in various degrees, resulting in a much wider standard deviation. The average diameters are 4.2 ± 2.6 and 3.5 ± 2.4 nm before and after catalysis, respectively.[11] It is worth noting the crystalline order of the ZIF-8 host matrix mostly remains unchanged after loading Au NPs and several runs of reaction, as shown by the comparison of the powder XRD patterns in Figure 3, and simultaneously, no obvious diffractions from Au NPs were observed from Au@ZIF-8 after catalysis, which agrees with TEM observation. Scanning electron microscopic (SEM) observation for 1.0 wt % Au@ZIF-8 indicates the size and morphology of the ZIF-8 support almost remained the same after reaction.[11]

In summary, a zeolite-type MOF was employed as a support for preparing nanoparticulate Au catalysts by a simple solid grinding method, for the first time, which was used as a catalyst in the gas phase CO oxidation and exhibited considerable activity. The present results might bring light to new opportunities in the development of high-performance gold catalysts by using rapidly growing MOFs as supports. Due to the large surface area, tunable size and shape of the pores as well as functional group-modified walls of the pores,[8b] incorporation of noble metal NPs in MOFs will provide great potential as candidates for novel heterogenerous catalysts. Work is underway to explore the catalytic mechanism in detail and expand ZIF-8 to other host MOFs for Au NPs and their catalysis.

Supporting Information Available: Details of experiments and catalytic activity measurements, UV−vis spectra, PXRD patterns, photographs, SEM and TEM images, reproducible acitvites of Au@ZIF-8 as well as stability of host ZIF-8. These materials are available free of charge via the Internet at http://pubs.acs.org.

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