Defective ZnO-Supported Gold Catalysts: Facilitating CO Oxidation via Vacancy Defects Implantation

Ming-Han Liu[1, 2], Chung-Yuan Mou[2, *] and Chia-Min Yang[1]
[1] Department of Chemistry, National Tsing Hua University, No. 101, Sec. 2, Kuang-Fu Rd., Hsinchu 30013, Taiwan
[2] Department of Chemistry, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd., Taipei, 10617, Taiwan
*e-mail: cymou@ntu.edu.tw

We prepare defects-tunable twin-brush-like ZnO supported gold catalysts (denoted as Au/TB-ZnO) for elucidating the pivotal role of vacancy defects in catalysts. The metal size and oxidation state of gold were modulated by adjusting vacancy ratio of support, i.e., $[V_o\bullet]/[V_{Zn}\bullet]$, therefore, giving an enhanced catalytic activity in CO oxidation with two orders of magnitude higher than the activity of conventional ZnO supported gold catalyst. It was found that the higher vacancy ratio endows defective ZnO with much more doping of gold on ZnO (sub)surface, forming numbers of "Au-O-Au_{Zn}" linkages and further speeding up the reaction of CO oxidation via Mars–van Krevelen (MvK) mechanism. It is believed that the manipulation of support defects density may provide a new strategy for improving catalytic properties of conventional catalysts.

Introduction

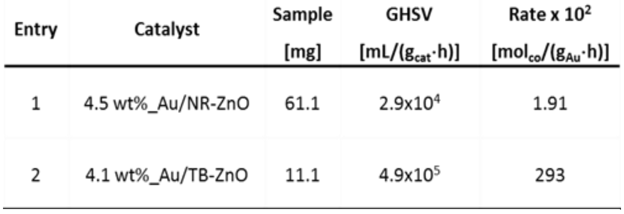
Supported gold catalysts owe their excellent activity to the small size and specific metal-support interaction. Understanding the interaction of gold and support therefore is a key topic in the development of highly active supported gold catalysts. Previously, we have demonstrated a strong-metal-support -interaction (SMSI) on ZnO nanorod supported gold catalyst, namely Au/NR-ZnO for giving insights to the tuning of CO catalytic activity under different atmosphere pretreatments.[1] The activity of Au/NR-ZnO thus increased when the electrons transferred from cluster gold to the oxygen vacancies (V_o) of NR-ZnO upon oxygen pretreatment. Accordingly, it is envisaged that the activity of gold catalyst might be affected by tuning the amount of support defects. Herein, we choose twin-brush-like ZnO (TB-ZnO) as a defects-tunable support for preparing gold catalysts. TB-ZnO (~1.2 μm in size) shows assembled bundles of small nanorods at both halves of the twin-brush form of particles. The vacancy ratio, i.e., $[V_o\bullet]/[V_{Zn}\bullet]$ of TB-ZnO was systematically manipulated by adjusting calcination conditions. Moreover, catalytic performance of defective ZnO supported gold catalysts was evaluated in catalysis of CO oxidation.

Experimental

Rod-like [2] and twin-brush-like [3] ZnO were synthesized according to previous literatures. Gold clusters were deposited on the calcined ZnO supports by deposition-precipitation (DP) method. Briefly, for 5 wt% loading, 10 mL of 0.5 wt% $HAuCl_4$ solution was firstly neutralized to pH value of 7. Afterwards, it was dropped slowly into a solution containing 1 g of ZnO, followed by adjusting pH value to 9~10. The solution was kept stirring for 2 days at room temperature. The samples were washed and collected by centrifugation with deionized water.

Results and Discussion

Zinc-vacancy-free rod-like ZnO was chosen as a comparable support for preparing gold catalyst. Regardless of incommensurate vacancy defect concentrations, both materials (i.e., NR-ZnO and TB-ZnO) display rod-like morphology with (10-10) nonpolar surfaces of ZnO being the main exposed facets. By controlling deposition of gold clusters, two comparable ZnO-supported gold



Entry	Catalyst	Sample [mg]	GHSV [mL/(g_{cat}·h)]	Rate x 10^2 [mol_{co}/(g_{Au}·h)]
1	4.5 wt%_Au/NR-ZnO	61.1	$2.9x10^4$	1.91
2	4.1 wt%_Au/TB-ZnO	11.1	$4.9x10^5$	293

Table 1: Catalytic activities (20 °C) of ZnO-supported gold catalysts

catalysts, i.e., Au/NR-ZnO and Au/TB-ZnO were obtained with the same particle size of gold for further catalytic evaluation. Therefore, the active metal size and external facets of support for both two catalysts are regarded as identical factors in catalysis. In the catalytic evaluation of CO oxidation, Au/TB-ZnO showed an enhanced activity in CO oxidation of 153 times higher than the catalytic activity of Au/NR-ZnO (Table 1). According TPR analysis, it can be unraveled that there are two kinds of gold species on the Au/TB-ZnO surface included metallic gold nanoparticles and implanted ionic gold within ZnO structure. However, there is no detection of ionic gold on Au/NR-ZnO catalyst. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization straightforwardly indicated the appearance of MvK mechanism on the surface of Au/TB-ZnO. Furthermore, to control the catalytic activity of supported gold, the vacancy ratio of ZnO was modulated by varying calcination conditions, and further displaying an rising tendency in activity with increasing vacancy ratio. (Figure 1a) In addition, the gold catalysts with higher activities possess the higher percentage of trivalent gold species and much smaller gold clusters. (Figure 1b)

Conclusion

In conclusion, the activity improvement of Au/TB-ZnO in comparison with Au/NR-ZnO is mainly attributed to the occurrence of MvK mechanism at the perimeter of gold particles via breaking large amount of "Au-O-Au$_{Zn}$" linkage, which are formed by gold implanting in zinc vacancies of ZnO crystal lattice. Most importantly, these "Au-O-Au$_{Zn}$" linkages (occurring in Au/TB-ZnO) are rather fragile than the "Au-O-Zn" bonding (occurring in Au/NR-ZnO) at the perimeter of gold nanoparticles. The catalytic performance of gold catalyst in CO oxidation was systematically manipulated for the first time by tuning the vacancy ratio of [V$_o$•] to [V$_{Zn}$•]. The enhanced activity of gold catalyst in CO oxidation is associated with the decreasing of gold size and increasing of the content of active Au^{3+} species. Accordingly, the catalytic record and its catalytic behavior will stand a landmark not only for ZnO-supported gold catalysts but also for the conventional outstanding Au/TiO$_2$ catalysts. From now on, the strategy to manipulate catalyst vacancy density and/or ratio may pave a new way to effectively control active metal size and tune the content of surface active species among metal-oxide supported catalysts.

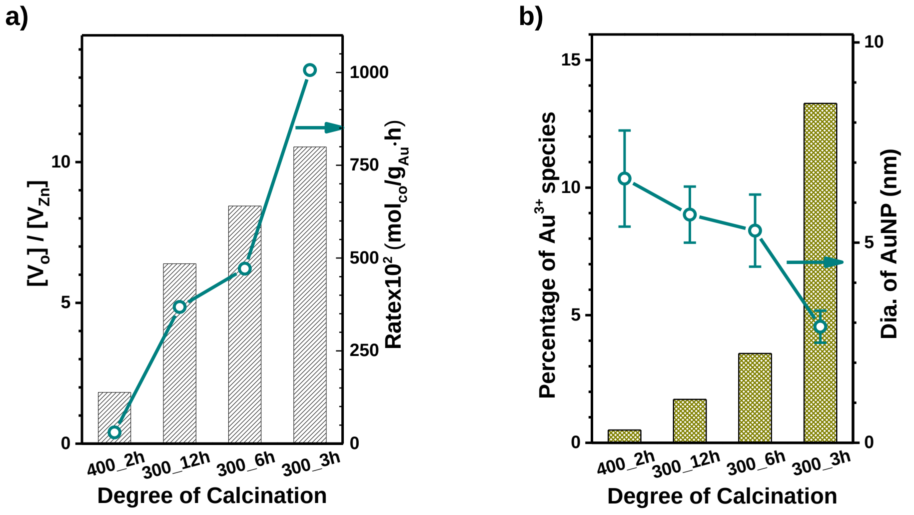


Figure 1: Specific rate of CO oxidation (a) and particle size of active gold (b) affected by defective ZnO supports with different vacancy ratios of [V$_o$•]/ [V$_{Zn}$•]

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