

Removal of Organo-sulfur Impurities at Low-temperatures using Au-ZnO nanocomposites as Catalytic Adsorbent

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Introduction & Significance

Sulfur compounds occur as a natural contaminant in all the major fuel feedstock including crude oil, coal, natural gas and biomass-derived syngas. These impurities are often associated with problems like equipment corrosion, downstream catalyst poisoning, and environmental pollution. Accordingly, the sulfur content in the fuel is often strictly regulated by environment-protection agencies around the world. One way of removing sulfur is to use solid adsorbents to selectively separate sulfur-components from raw fuel. Metal oxides are typically used for reactive adsorption of such organo-sulfur compounds. Poor reaction kinetics, however, requires high operating temperatures (>400°C), which results in large energy costs accompanied with chemical reduction and physical degradation of the adsorbent, resulting in lower capacity and underutilization of the adsorbent¹⁻³. As a consequence, developing adsorbents that can have high-sulfur removal capacity at low-temperature is highly desirable.

Zinc oxide is known for its favorable thermodynamics for its reaction with sulfur containing compounds, which provides it with high sulfur-removal capacity. However, sluggish kinetics of this fluid-solid reaction ($\text{ZnO} + \text{C}_x\text{H}_z\text{S}_y \rightarrow \text{ZnS}$) does not favor low temperature application, which necessitates use of a catalyst for accelerating reaction. This study investigates the role of noble metals as catalysts that can synergistically enhance the reactivity of a host metal oxide towards organo-sulfur impurities.

Nanometer-sized gold has recently proven to be an efficient heterogeneous catalyst with high catalytic activity for selective reduction/oxidation reactions including CO oxidation, selective hydrocarbon oxidation, methanol synthesis, water-gas shift reaction and hydrogenation reactions. Gold is the only known metal to reversibly adsorb H_2S , a common sulfur impurity in the raw syngas or natural gas feedstock. Well-dispersed nano-sized gold is thought to have strong interaction with the supporting metal oxide. It has been proposed in theory, as early as 1988, that metal can change the defect equilibrium of metal oxides making them more reactive⁴. It should be noted here that in bulk of the literature, effect of this metal-metal oxide interaction has been studied only with respect to chemical reactions happening at the surface with bulk of the metal oxide remaining unreacted. In this study, the entire bulk of ZnO undergoes a solid-state transition to form ZnS. Moreover, the reaction of sulfur containing molecule with Au-ZnO has not been studied before. Thus this study not only shows how to make the nanocomposites more practical for applications involving reactive adsorption where bulk oxide undergo reactive transition (resulting in higher adsorption capacity), it also examine the underlying phenomenon of oxide-metal interaction in context to its effect on solid-state reactivity, an area entirely unexplored in previous literature. The model system of Au-ZnO nanocomposites investigated involves thioacetamide as a model-sulfur containing organic molecule. The reactive performance is examined by monitoring the rate of disappearance of ZnO and extent of ZnS formed in a given time.

Materials and Methods

Au-ZnO solid nanocomposites were prepared by incipient impregnation method. The nominal amount of gold loaded on the support was 2 wt%. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution (10mM) was added dropwise into a solution containing pre-synthesized ZnO nanoparticles dispersed in water (95% within 10-40nm., Alfa-Aesar Nanotek®) under vigorous stirring and room temperature. After 10-15 minutes of stirring, the solution flask is put into a sonicator bath and NaBH_4 is introduced into the solution via rapid injection. The color of the contents of the flask turned from white to pink. The solution was left in sonicator bath for around 5 minutes, after which, it is stirred again for 2 hours. After aging for 2 hours, the resultant suspension was centrifuged and the precipitant was washed with deionized water at least two times and finally, the washed precipitant is re-dispersed in water using sonication at room temperature. The pH value of all the samples, as measured, was found to range within 6.7 to 7.1. The mean size of gold nanoparticle, as measured using TEM imaging, is 3.76 nm

XRD, DRIFTS, XPS, TEM STEM-EDS and UV-VIS Absorption spectroscopy were used to characterize the fresh composites.

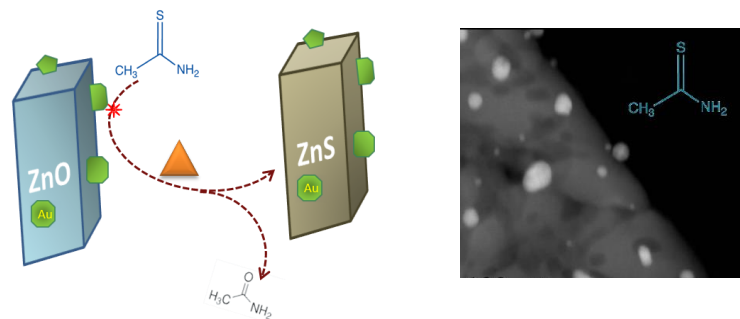


Figure 1: a) Schematic showing the observed overall conversion during the reaction between Au-ZnO and thioacetamide (TAA). (b) Representative STEM images of Au-ZnO nanocomposites (Average Au size is 3.76nm and ZnO is 40nm)

Results and Discussion

Figure 1 shows a schematic of the overall desulfurization reaction. Overall reaction involved is $\text{ZnO} + \text{C}_2\text{H}_5\text{NS}$ (TAA) = $\text{ZnS} + \text{C}_2\text{H}_5\text{NO}$. Conversion to ZnS was evaluated by comparing the progressively increasing area under the ZnS (111) during the XRD analysis. The extent of final conversion at a given temperature were measured by calculating the ratio of area-averaged intensity of ZnS (111) to ZnO (101), while the initial rates were measured by measuring the temporal decrease in the absorbance value of ZnO excitonic peak. **Figure 2** shows XRD of the Au-ZnO sample treated with TAA representative of the extent of conversion achieved at different temperatures.

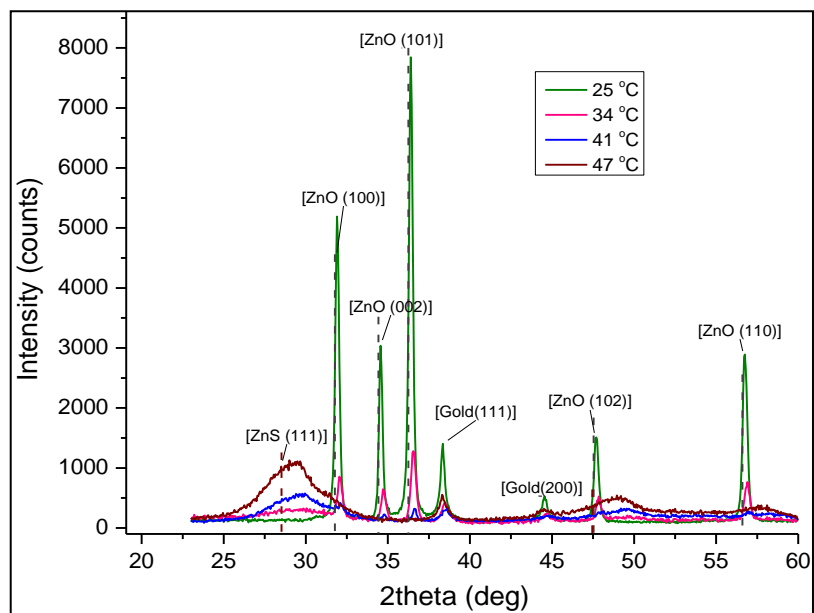


Figure 2: XRD of sulfided Au-ZnO composites at different temperatures

References

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