Molybdenum Carbide Supported Platinum Catalysts for Water-Gas Shift: A Theoretical and Experimental Investigation

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Introduction

Early transition metals carbides are catalytically active in a variety of reactions, such as isomerization reactions, hydrogenation reactions, water-gas shift (WGS), hydrocarbon steam reforming, etc. [1]. Our group recently developed a method to load metal catalysts onto high surface area carbide and nitride supports, and demonstrated that Pt supported on Mo carbide (MoC) possessed extraordinary activities for WGS [2].

The objective of research described in this paper is to study the catalytic properties of Pt/MoC catalysts in order to offer insight into the function of carbide materials as catalyst supports. For this purpose, we tested the WGS activity of a series of supported Pt catalysts: Pt/MoC, Pt/TiO2, Pt/CeO2, and Pt/MoO3. The catalysts were characterized using H2 and CO temperature programmed reduction (TPR), scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), x-ray adsorption spectroscopy (XAS), and density functional theory (DFT) calculations.

Materials and Methods

High surface area MoC was synthesized from ammonia paramolybdate in 15% CH4/H2 gas stream using a temperature programmed reaction procedure. Platinum was deposited onto the carbides using a wet impregnation technique and a dihydrogen hexachloroplatinate (IV) salt solution. The catalysts were then reduced and passivated in a 1% O2/He stream, to prevent bulk oxidation of the support. The Pt/MoO3 was synthesized using a similar method. The other oxide supported catalysts were synthesized using a dry impregnation technique. Before measuring the WGS rates, the carbide catalysts were reactivated in a 15%CH4/H2 gas stream. The oxide supported catalysts were pretreated in a dilute H2 gas stream at 300°C. Reaction rates were measured using a reformate stream containing 11% CO, 21%H2O, 43% H2, 6% CO2 and 18% N2. The catalyst amounts and temperature ranges were adjusted to ensure rates were recorded in the differential reactor regime (conversion of less than 10%). A Cu/Zn/Al2O3 catalyst was also tested to benchmark the performance.

Results and Discussion

Rate measurements revealed that the Pt/MoC catalysts were the most active among the tested catalysts, including conventional Cu/ZnO/Al2O3 catalysts. These studies also revealed that if the support is only slightly changed from MoC to MoO2 the catalyst activity drops dramatically, see Figure 1. Characterization studies showed that the Pt particles on MoC were relatively small (<50nm) and uniformly dispersed, compared to particles on MoO2 which were much larger (~2µm). DFT calculations showed that Pt binds strongly to MoC, with energies that were comparable to the Pt cohesive energy and that these strong interactions lead to a high dispersion of Pt particles on the carbide support. On the other hand, the binding energy of Pt on MoO2 was much lower than the Pt cohesive energy resulting in large Pt particles and limited dispersion.

Furthermore, temperature programmed reaction measurements, the measurements of the electronic structure of Pt and the support, and DFT calculations showed that the carbide support has higher concentration of sites that can perform red-ox cycle at lower temperature that other tested oxide supports. This enhanced reducibility of the surface is a critical feature of the catalyst which contributes to the enhanced activity of the Pt/carbide systems.

We believe that both features of the Pt/MoC catalysts: (i) high dispersion of Pt and (ii) the enhanced reducibility are critical for the enhanced activity of Pt catalysts supported on carbide supports in WGS.

Significance

It is common practice in catalysis research to design catalysts by choosing different metals, choosing different supports, or forming alloys among other strategies. This project aims to offer a new variable into catalysts design, that of the changing the degree of oxidation, carburization, or nitridation of the support.

References

2. Dissertation of Timothy King, University of Michigan