Properties of Molybdenum Supported on Low Acidity Zeolites for Catalytic Dehydrogenation

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Introduction
Dehydrogenation of ethane and propane from shale gas has the potential to meet the increasing global demand for light olefins. Dehydrogenation is performed industrially on platinum or chromia/alumina catalysts [1], but platinum is expensive and chromia is toxic [2], which creates a need for alternative catalysts that are both inexpensive and non-toxic.

It is well known that metal carbides can be used as catalysts for dehydrogenation of alkanes [3]. Specifically, molybdenum carbide supported on alumina and silica can react with numerous hydrocarbons, including propane, producing olefins [4]. Molybdenum carbide supported on H-[Al]ZSM-5 is also used to convert methane to benzene [5]. The primary product, ethylene, reacts rapidly on the zeolite acid sites to produce benzene and other aromatic species. Here we show that by using H-[B]ZSM-5, a material with very weak acidic properties [6], as a support for molybdenum carbide nanoparticles, a novel catalyst that retains high activity for C-H bond activation can be prepared.

Materials and Methods
Molybdenum was added on the support by the incipient wetness impregnation method using ammonium heptamolybdate as the source of Mo. The material was calcined in air at 823K for 5 hours and then carburized in methane (20%, H<sub>2</sub> balance) at 923K for 4 hours prior to catalytic testing. The resulting materials contain 5.8 wt% of molybdenum.

The catalysts were tested over a range of temperatures (673-802K), pressures (20-60 bar), and weight hourly space velocities (WHSV) (90-350 g<sub>C5</sub>/g<sub>cat</sub>-hr) using n-pentane as the reactant. A high-pressure liquid chromatography pump was used to feed n-pentane (Fisher, 99.7% purity) into a packed-bed microreactor (4.6 mm ID) and the reactor effluent was analyzed using an online gas chromatograph.

Results and Discussion
A number of pure and supported molybdenum carbides were investigated for the dehydrogenation of n-pentane. Figure 1 compares the reaction rates (left) and pentene carbon selectivity (right) of pentane conversion on several molybdenum carbide catalysts. The pentene carbon selectivity is defined as the percent of the total carbon in the products contained within pentenes. Two samples provided the highest reactivity and selectivity toward pentenes: Mo<sub>C</sub>/B-ZSM-5 (zeolite support) and Mo<sub>C</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. These two catalysts (Figure 1) also exhibited an induction period, with the highest reaction rates observed approximately at 1 h time on stream. This increase in reactivity indicates that the most active form of the catalyst is formed in the reactor by interaction with the reactant. For both the alumina and the B-ZSM zeolite supports, there was a slow deactivation rate occurring over the 5 hours on stream investigated, but unlike the other catalyst tested, the selectivity of the dehydrogenation product from the zeolite support did not change with time on stream.

Figure 1. Rates and pentene carbon selectivity of pentane conversion on various molybdenum carbide catalysts. Conditions: 40 bar, 0.5 mL/min of pentane, 723 K, m<sub>cat</sub> = 100 mg, WHSV = 188 g<sub>C5</sub>/g<sub>cat</sub>-hr, residence time ~0.6 s.

The Mo(B)/ZSM-5 catalyst showed the highest conversion of all the catalysts investigated, while maintaining the same high selectivity towards the dehydrogenation product as exhibited on Mo(γ-Al<sub>2</sub>O<sub>3</sub>). Furthermore, by using B-ZSM-5, the secondary bimolecular reactions observed in acidic [Al]ZSM-5, which include oligomerization and dehydrocyclization reactions, were suppressed, preserving the olefinic product. Further structural, spectroscopic and catalytic investigations are on-going.

Significance
The novel molybdenum-containing low acidity [B]ZSM-5 zeolites prepared here are capable of activating pentane and other hydrocarbons (not shown) with a high selectivity towards the dehydrogenation product. This new catalyst has the potential for applications in industrial dehydrogenation or hydrotreating, particularly in the presence of other species such as sulfur or nitrogen.

References