Partial Oxidation of Jet Fuel Over Molybdenum Dioxide

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Introduction

The production of hydrogen for fuel cell applications using hydrocarbon sources has become a challenging task due to a number of issues that need to be addressed. The search for a highly active catalytic material with high coking resistance, sulfur tolerance and thermal stability is still an ongoing quest. Marin-Flores and Ha have recently reported molybdenum dioxide (MoO_2) to exhibit high activity for the partial oxidation of isooctane [1], proceeding to full conversion at 700°C and 1 atm. The high activity shown by MoO_2 can be explained in terms of a Mars-van-Krevelen-type mechanism [2], which involves redox cycles taking place on the catalyst surface. The unusual metallic character displayed by this oxide is thought to be responsible for its high catalytic activity as it enhances the formation of hydrogen atoms, which in turn accelerates the hydrocarbon decomposition. Based on the information mentioned above, we decided to investigate the catalytic behavior of MoO_2 for the partial oxidation of jet fuel, which is a process of higher complexity.

Materials and Methods

Activity tests were performed in a 12 mm fixed-bed tubular (quartz) reactor. The liquid fuel was vaporized at 350°C and fed into the vaporizer using a syringe pump. A mass flow rate controller was employed to control the amount of air. The off-gas was cooled down to separate condensable compounds and the dry gas product was analyzed using an SRI chromatograph to monitor H_2, CO, CO_2, and CH_4 concentrations.

The MoO_2 catalyst was purchased from Alfa Aesar. The catalyst samples were subjected to a 30-min pretreatment with pure hydrogen at 450°C prior to usage in activity tests. XRD measurements were performed on a Philips diffractometer. XPS spectra were obtained with an AXIS-165 manufactured by Kratos Analytical Inc. BET surface area measurements were made using a Coulter SA-3100 characterization machine.

Results and Discussion

BET surface area after H_2-pretreatment was found to be 2.7 m^2/g. XPS surface analysis results are summarized in Table 1. With this information the surface concentration of active sites (Mo^{4+}) on the catalyst sample turned out to be 7.89×10^{18} sites/g.

Table 1. XPS surface analysis of pretreated catalyst sample

	Surface Composition			Mo3d spectrum		
Species	**Mo**	**C**	**O**	**Mo^{4+}**	**Mo^{5+}**	**Mo^{6+}**
At%	28	22	50	29	41	29

Previous work using MoO_2 as catalyst and isooctane [1] as fuel indicated that the dioxide phase can be deactivated by loss of active sites due to phase transitions. Thus, under certain operating conditions the dioxide can become either molybdenum carbide (Mo_2C) or molybdenum trioxide (MoO_3). To optimize the catalyst performance the dioxide phase needed to be stabilized. To achieve this, a thermodynamic analysis was carried using the criterion of minimization of Gibbs free energy and considering n-dodecane as jet fuel surrogate. This led us to determine an operating window within which the dioxide phase was stable as well as the conditions required to maximize the hydrogen production. Thermodynamic predictions were validated with in-situ XRD measurements and activity tests. The dioxide phase appears to be stable at 700°C and at oxygen to carbon ratios (O/C) ranging from 0.5 to 1. Plus, higher hydrogen concentrations should be obtained as the O/C ratio becomes smaller.

To corroborate these results, jet fuel partial oxidation was performed using n–dodecane at 700°C and at an O/C ratio of 0.54. The results are shown in Figure 1. The turnover frequency (TOF) obtained for MoO_2 in this test was 0.91 s^{-1} (molecules of H_2 per active site per second).

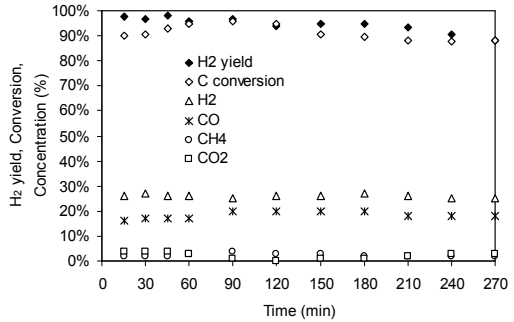

Figure 1. MoO_2 catalytic performance for the partial oxidation of jet fuel surrogate (n-dodecane) at 700°C, 1 atm and O/C=0.54.

The complexity of the jet fuel surrogate was also increased by adding tetralin (benzocyclohexane) as aromatic compound. For a mixture 50% dodecane-50% tetralin the hydrogen yield and conversion obtained were above 90%. Activity tests with actual jet fuel were also carried out in this work, producing a TOF of 0.51 s^{-1} at 800°C and 1 atm. However, given the complexity of this mixture, there are still some stability issues to be overcome.

Significance

In light of these results, MoO_2 emerges as a promising catalyst for the partial oxidation of jet fuel, which is a process intended to optimize the fossil fuel consumption. This is of particular interest for both aircraft industry and army.

References

1. Marin-Flores, O.G., Ha, S., accepted in *Appl. Catal. A: General*, 2008
2. Vannice M., *Catal. Today* 123 18 (2007)