

Advanced Catalysts for Fuel-Flexible Fuel Cells

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ABSTRACT

A far-reaching and long-term vision for next generation commercial air travel is the More Electric Airplane (MEA) concept, which allows greater fuel efficiency and lower greenhouse gas (GHG) emissions by substituting hydraulically and pneumatically driven systems with electrical ones. The increased electrical power demand in a MEA can be met by decentralizing the power-producing units using small individual devices such as fuel cells. Calculations show a 40% in-flight and a 75% on the ground saving in fuel by replacing the conventional gas turbine auxiliary power unit (APU) with a solid oxide fuel cell (SOFC). Molybdenum dioxide (MoO₂)-based catalysts represent a transformative approach to fuel-flexible fuel cell technology because of their ability to reform and electrochemically oxidize logistics fuels such as Jet-A, JP-5, and new bio-based aviation fuels.

Keywords: fuel cells, aviation fuels, catalyst, nanomaterials, oxides

1 INTRODUCTION

Fuel cells offer a number of advantages as an alternative energy production technology for both stationary and mobile applications. In commercial aviation, a concept called the more electric airplane (MEA) will allow greater fuel efficiency by substituting hydraulically and pneumatically driven systems by those based on electrical

energy. The increased electrical power demand in a MEA can be met by decentralizing the power-producing units using small individual devices such as fuel cells. Furthermore, existing commercial aircraft use a low efficiency gas turbine auxiliary power unit (APU) to provide electrical power for operating navigation systems and various other electronic devices. By replacing the conventional APU with a solid oxide fuel cell (SOFC) APU, improvements can be made in providing a means to obtain auxiliary power without consuming excessive amounts of fuel when the airplane is on the ground or when the load is increased on the main engines during flight. Thus, fuel cells may become the primary electrical power source with engine-driven generators serving a backup role on future airplanes.

An important practical requirement for the use of fuel cells on commercial and military airplanes is that they must operate using kerosene-based aviation fuels (such as Jet-A and JP-5), which are already on board. The existing approach for fuel cell systems operating on Jet-A fuel (the standard kerosene-based commercial aviation fuel) requires a fuel reformation process in which the Jet-A is mostly converted to hydrogen and carbon monoxide. This syngas mixture is fed into SOFCs where it is electrochemically converted to H₂O and CO₂, and produces electrical power. To develop a high performance fuel reforming system that can operate with Jet-A fuel, a catalyst with the following attributes is required:

- (1) High oxidation activity toward Jet-A fuel
- (2) High resistance to coking
- (3) Stability at high operating temperatures (i.e., higher than 700°C)
- (4) High sulfur tolerance (e.g., aviation fuels typically contain 500 ppm of sulfur)

Conventional nickel-based catalysts quickly deactivate under reforming environments due to coke formation and sulfur poisoning. However, we have developed a fuel-flexible molybdenum dioxide (MoO_2) based catalyst that has shown high catalytic activity for various processes involving long-chain hydrocarbons [e.g., 1,2] and bio-based aviation fuels.

Molybdenum is a transition metal oxide that has oxidation states ranging from +2 to +6, but the oxides exist mainly in one of two forms: molybdenum (IV) and molybdenum (VI) oxide. Molybdenum dioxide is unusual in that it possesses a significant metallic component to its interatomic bonding and, as shown in Figure 1, has an electronic conductivity comparable to that of many metals and highly conductive oxides such as ReO_3 [3]. Because of its high electronic conductivity, MoO_2 has been considered as an anode material in lithium ion batteries [e.g.,4].

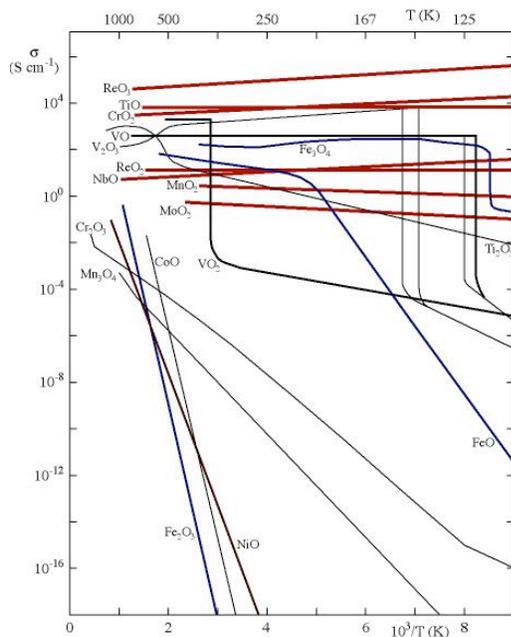


Figure 1: Temperature dependence of the electrical conductivity of several electronically conducting oxides.

MoO_2 crystallizes in a monoclinic structure, which deviates slightly from the rutile structure shown in Figure 2. The lattice parameters are $a = 0.56109\text{nm}$, $b = 0.48562\text{ nm}$, $c = 0.56285\text{ nm}$, $\beta = 120.95^\circ$ [3]. The upper (ball-and-stick) model shows the atom arrangement in rutile. The lower model illustrates how corner-sharing oxygen octahedra are linked.

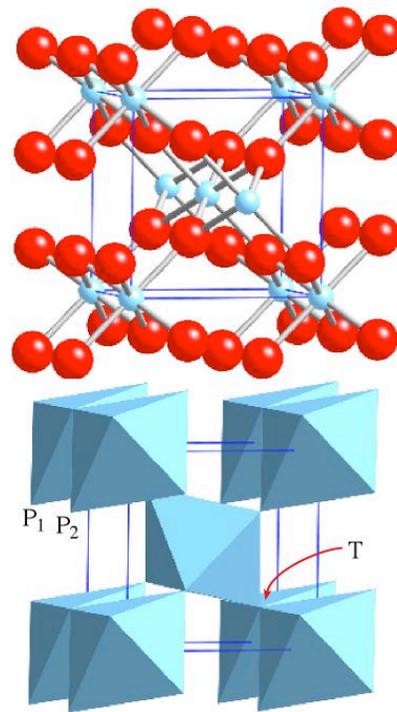


Figure 2: Rutile crystal structure viewed nearly parallel to the z-axis. Each of the pairs of overlapping octahedral (e.g., P_1/P_2) shares an edge. The two octahedral in the lower right thus have point T in common. The central octahedron touches each of the eight at the corners.

Although on-board applications for fuel cells may be some way off, there are near term applications for this technology including alternative-fuel fuel cells as range extenders or battery powered airport ground support equipment (GSE). The airport GSE market includes various types of specialty vehicles used to service aircraft during ground operations and fuel cells have the potential to provide significant lifecycle cost savings over lead acid battery and combustion engine systems.

2 RESULTS AND DISCUSSION

2.1 Synthesis and Characterization of MoO₂ Nanoparticles

The approach used in our group follows that of Chen et al. [5] who charged a MoO₃, ethylene glycol, water suspension in a Teflon[®]-lined stainless steel autoclave for 12 h at 180 °C. Ethylene glycol is the reducing agent in this method, however it is unclear whether the reaction takes place at the solid-liquid interface or fully in solution. A 3:1 volume mixture of deionized water and glycol was found to produce the most pure monoclinic MoO₂ phase. This product is nanocrystalline as shown in Figure 3.

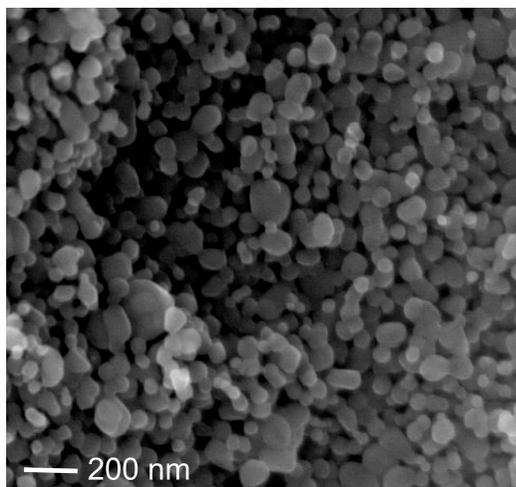


Figure 3: Scanning electron microscope image of nanoparticle MoO₂ synthesized by hydrothermal method.

2.2 Fuel Reforming

The catalytic performance of nanoparticle MoO₂ was compared to that of Ni metal and a commercial rhodium-based catalyst (1% Rh in Al₂O₃). The data was obtained at 850°C, 1 atm, and an O₂/C ratio of 0.6, using Jet-A fuel purchased from the regional airport and fed into the reactor at a weight hour space velocity (WHSV)=2.2 h⁻¹. The data obtained are shown in Figures 4. As seen, under these operating conditions, unsupported nickel displays a poor performance due to rapid coke formation, which eventually plugged the reactor after only 2 h of

operation. Nanoparticle MoO₂ and the rhodium-based catalyst exhibited more stable performances although with some differences in terms of selectivity. After 5 hours-on-stream, the rhodium catalyst produced higher yields of hydrogen (84.0%) and CO (80.5%), no methane and no C₂ compounds. Instead, MoO₂ yielded lower amounts of hydrogen (50.0%), CO (63.3%), and small concentrations of methane (2.6%) and ethylene (<0.5%) in the gas product. However, Figure 4 (c) also indicates that, in terms of conversion, both catalysts displayed similar performance with values of about 95%.

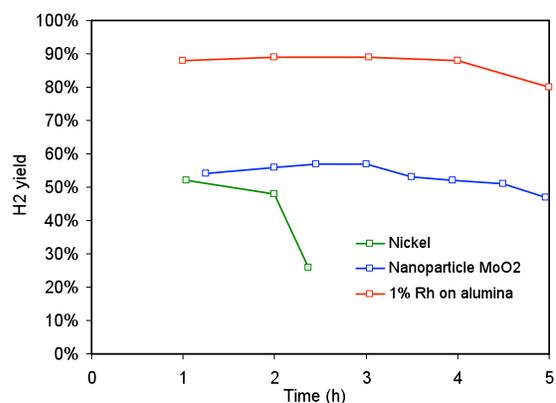


Figure 4(a). Comparison of H₂ yields for the partial oxidation of Jet-A fuel: nanoparticle MoO₂ versus unsupported nickel and 1% Rh on alumina (850°C, 1 atm, O₂/C=0.6, WHSV=2.2h⁻¹).

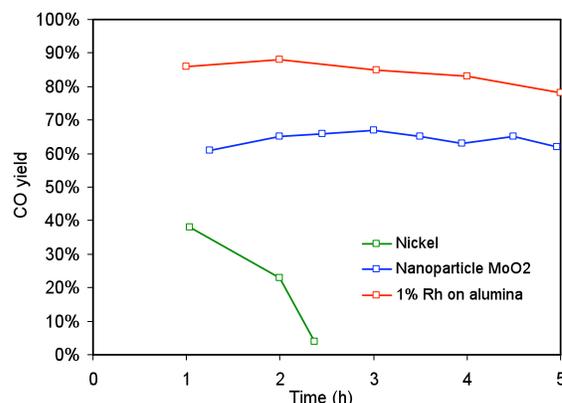


Figure 4(b). Comparison of CO yields for the partial oxidation of Jet-A fuel: nanoparticle MoO₂ versus unsupported nickel and 1% Rh on alumina (850°C, 1 atm, O₂/C=0.6, WHSV=2.2h⁻¹).

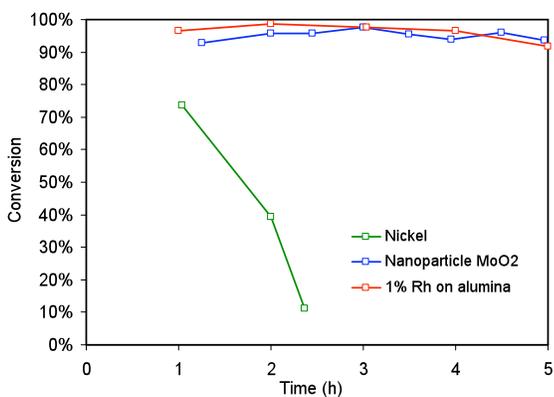


Figure 4(c). Comparison of total conversion for the partial oxidation of Jet-A fuel: nanoparticle MoO₂ versus unsupported nickel and 1% Rh on alumina (850°C, 1 atm, O₂/C=0.6, WHSV=2.2h⁻¹).

X-ray diffraction (XRD) analysis of a spent sample of nanoparticle MoO₂ indicates a barely detectable amount of Mo dioxide and, instead, a significant amount of Mo carbide (Mo₂C). On the other hand, X-ray photoelectron spectroscopy (XPS) analysis of the same sample reveals the presence of different oxidation states on the surface. In agreement with previous work [6], the presence of Mo²⁺ (carbide Mo) was not detected; however, approximately 20% of the Mo atoms are in the oxidation state Mo⁴⁺ (Mo dioxide), and 50% as Mo^{2.6+}. As concluded in the reference cited above and, in accordance with the Mars-van Krevelen mechanism of reaction, these two oxidation states are required to sustain the redox cycles taking place on the catalyst surface. These findings thus suggest a core-shell structure in the catalyst particles with the bulk formed by Mo₂C and the surface with the active sites (Mo⁴⁺ and Mo^{2.6+}) responsible for the catalytic activity.

An additional test was performed to measure the long-term activity of nanoparticle MoO₂ for the partial oxidation of Jet-A fuel. The operating conditions for this test were 850°C, 1 atm, O₂/C=0.7, and WHSV=0.8 h⁻¹ and the results are shown in Figure 5. As observed, after 24 h of operation, the catalyst exhibited stable performance with H₂ and CO yields of 43.3% and 58%, respectively, and a conversion of 99.9%. The concentrations of CH₄ and CO₂ were small

with values of 1.9% and 8.0%, and no C₂ compounds were detected during the test.

On the basis of these results, nanoparticle MoO₂ appears to very well cope with the issues related to the use of aviation fuels, such as coking deactivation and sulfur poisoning.

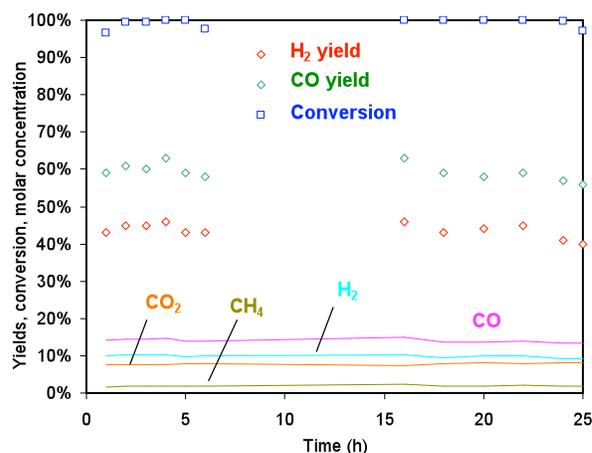


Figure 5. Long-term performance of nanoparticle MoO₂ for the partial oxidation of Jet-A fuel (850°C, 1 atm, O₂/C=0.7, WHSV=0.8h⁻¹).

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