Molybdenum Dioxide: A Reforming Catalyst 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 (MoO_2)-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 and JP-5.

Keywords: molybdenum dioxide, fuel cells, catalyst, nanoparticles

1   INTRODUCTION

Because of growing concerns over global climate change and national energy security, a reduction in the use of fossil fuels is imperative. These concerns are greatly impacting future aircraft design and commercial manufacturers such as Boeing are working on cleaner, quieter and more fuel-efficient airplanes. A concept called the More Electric Aircraft (MEA) can allow greater fuel efficiency by substituting hydraulically and pneumatically driven systems with electrical ones. The increased electrical power demand in MEA can be met by decentralizing the power-producing units using small individual devices such as fuel cells. Such distributed electrical power systems can reduce the amount of electrical wiring needed by shortening the distance between the power generator and the power consumer. With the reduction in electrical wiring there is a concomitant reduction in weight, which further increases fuel efficiency. Furthermore, existing 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 fuel cell APU, a significant improvement can be made in providing auxiliary power without consuming as much fuel when the airplane is on the ground and reducing the load on the main engines during flight. Thus, fuel cells may become the primary power source for on-board electrical power and engine-driven generators become backup sources on all future aircraft.

Of the many available fuel cell systems, there is a significant advantage in using solid oxide fuel cells (SOFCs) that can directly work with aviation fuels such as Jet-A and JP-5. To develop such SOFCs, an anode catalyst is needed that possesses the attributes listed in Table I [1]:

Table I: Anode Catalyst Requirements for Direct Jet-A SOFCs

High oxidation activity toward Jet-A fuel	Resistance to coking
High oxygen ion and electronic conductivities	Tolerance to high sulfur concentrations

Conventional Ni-based catalysts quickly deactivate under the Jet-A fuel oxidation environment due to coke formation and sulfur poisoning. The use of molybdenum dioxide (MoO_2)-based catalysts represents a transformative approach to fuel-flexible fuel cell technology. Unlike previously studied transition metal oxides (e.g., CeO_2) in SOFC applications, MoO_2 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 [2].

Due to its unique combination of properties, MoO_2 has been found to display a 40% improvement in reforming conversion of premium gasoline compared to that of Ni metal [3]. Additionally, the capability of MoO_2 to selectively transfer lattice oxygen to the hydrocarbons reduces the amount of carbon accumulated on the catalyst surface and minimizes coke formation during the reformation of logistics fuels.

Molybdenum dioxide crystallizes in a monoclinic structure, which deviates slightly from the rutile structure shown in Figure 2. The lattice parameters are $a = 0.56109$nm, $b = 0.48562$ nm, $c = 0.56285$ nm, $\beta = 120.95°$ [4]. The upper (ball-and-stick) model shows the atom arrangement in rutile. The lower model illustrates how corner-sharing oxygen octahedra are linked.
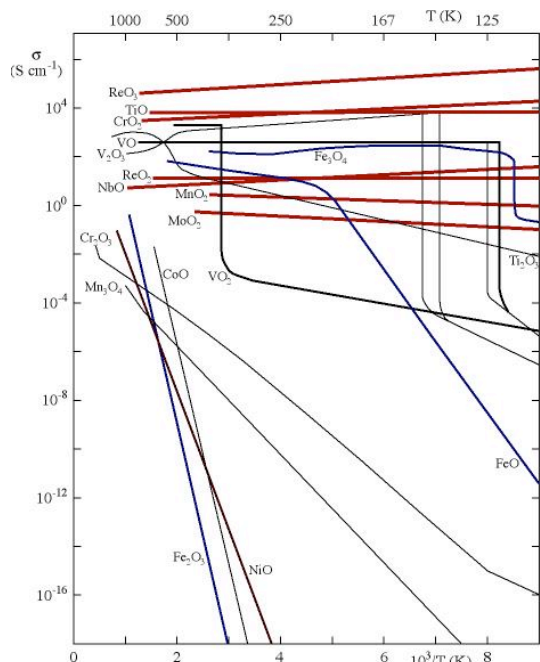
Figure 1: Temperature dependence of the electrical conductivity of several electronically conducting oxides.
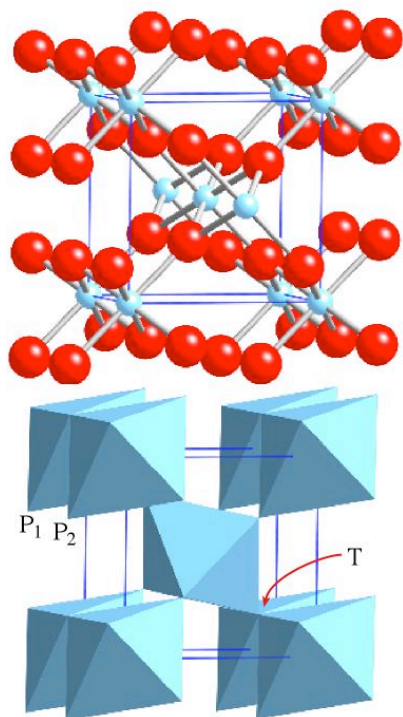

Figure 2: Rutile crystal structure viewed nearly parallel to the z-axis. Each of the pairs of overlapping octahedral (e.g., P_1/P_2) shares an edge. The two octahedral in the lower right thus have point T in common. The central octahedron touches each of the eight at the corners.

2 RESULTS AND DISCUSSION

Figure 3(a) shows a scanning electron microscope (SEM; FEI Sirion operated at 15 kV) image of the MoO_2 nanoparticles used in this study. Figure 3(b) is a transmission electron microscope (TEM; Phillips CM200 operated at 200 kV) image of the as-prepared nanoparticles. The material is synthesized by combining MoO_3 with an aqueous solution of ethylene glycol in an autoclave at 180°C for 12h [5]. Pure nanoparticle MoO_2 is produced directly without the need for any post-synthesis reduction. The nanoparticles are equiaxed with an average particle size of 20nm. X-ray diffraction and electron diffraction in the transmission electron microscope were used to confirm the formation of MoO_2 as the only reaction product.
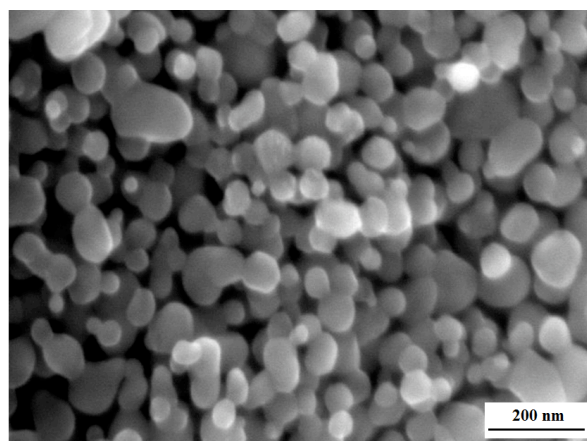

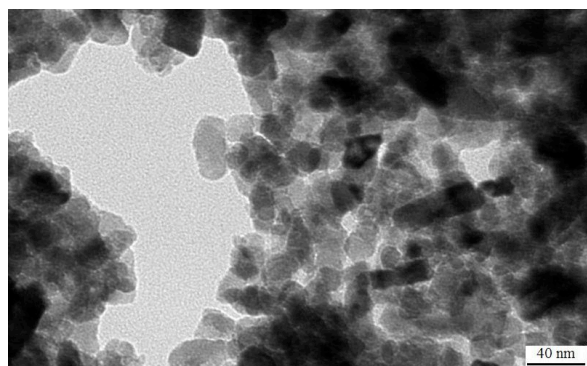Figure 3(a): SEM image of nanoparticle MoO_2.

Figure 3(b): TEM image of nanoparticle MoO_2.

The catalytic activity of MoO_2 under partial oxidation conditions was performed as follows [6]. The catalyst samples, in powder form supported by a quartz wool plug, were placed inside a 12 mm fixed-bed tubular (quartz) reactor. No catalyst pretreatment was applied prior to the

activity tests. The liquid (fuel) feed was fed into the furnace at 500°C, where it was vaporized and mixed with air, employed as the oxygen source. A silicon carbide bed inside the furnace was used to enhance the mixing of the reactants. A calibrated syringe pump and a mass flow controller allowed the control of the flow rates of liquid fuel and air, respectively. The exit stream was cooled down to 5°C to separate water, non-reacted fuel, and other possible condensable products from the gas product. Figure 4 shows the catalytic activity of MoO_2 for the partial oxidation of n-dodecane (a model jet fuel compound). The catalyst shows very high fuel conversion and H_2 and CO yields (fuel conversion 80%; H_2 yield 85%; CO yield 85%) and is stable over an extended period of time.
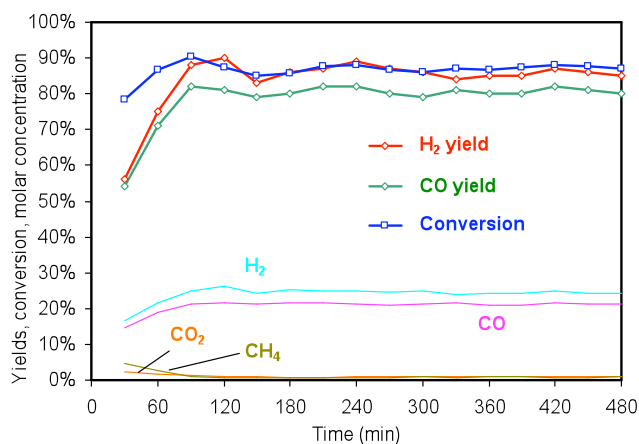

Figure 4: Catalytic activity of MoO_2 for partial oxidation of n-dodecane.

After the partial oxidation process the samples were examined using SEM to determine the presence, if any, of coke formation. The samples were compared to a commercial Ni-based catalyst that had been operated under the same conditions. The results are shown in Figure 5. As observed, the commercial Ni catalyst exhibits a significant carbon deposit in the structure, which indicates its poor resistance to coking deactivation and agrees with the continuous decay observed in the performance (not shown). Instead, MoO_2 shows no significant amount of coke formation, which explains the stable performance obtained during the reforming process [see also, Ref. 7]. Energy dispersive X-ray spectroscopy (EDS) data, also shown in Figure 5, support these observations as they indicate a much larger amount of carbon in the nickel catalyst as compared to that obtained in the MoO_2 catalyst.

The effect of the concentration of a model sulfur compound (benzothiophene, BT) on the catalytic performance of MoO_2 obtained during the partial oxidation of n-dodecane is reported in Figure 6.
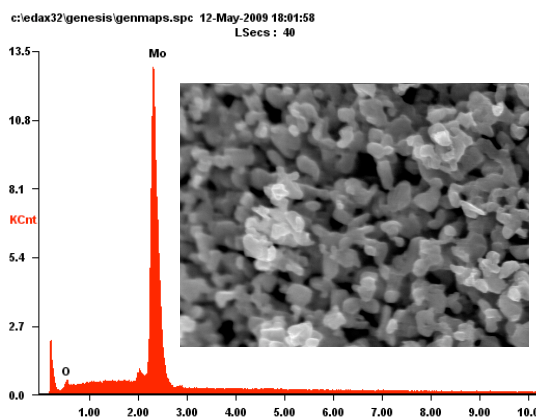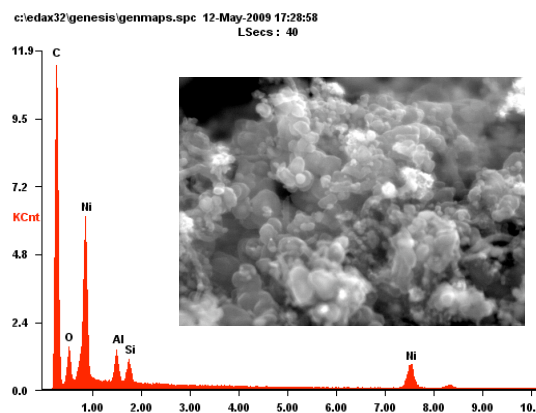

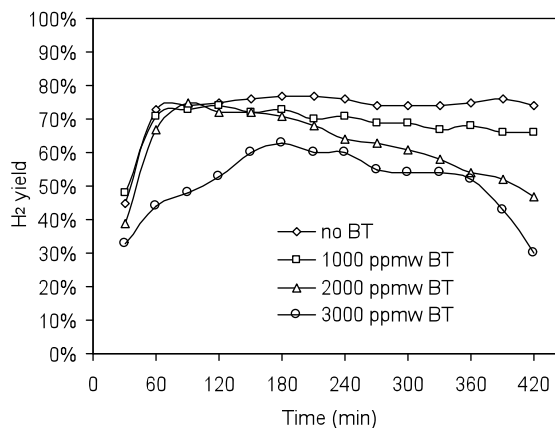Figure 5: SEM-EDX analysis of spent samples: (a) Ni catalyst, (b) MoO_2.

Figure 6: H_2 yield of MoO_2 for partial oxidation of n-dodecane with various concentration of benzothiophene (BT) as a model sulfur compound.

As seen, concentrations of up to 1000 ppmw of BT in the fuel appear to barely affect the catalytic activity of MoO_2 producing a drop of about 10% in the H_2 yield, with respect to that obtained without BT in the fuel after 7 hours of operation. The CO yield displays a similar behavior although the decline in this parameter was only

approximately 5%, after the same time on stream. However, the total fuel conversion exhibits a different trend, remaining unaffected after the same period of time. Higher concentrations of sulfur compound intensify these patterns. Thus, 3000 ppmw of BT provokes a drop in the hydrogen yield of approximately 40%, whereas CO yield and conversion reduce by 45% and 30%, respectively. The performances obtained at different BT concentrations are higher than that obtained in absence of catalyst (blank run), which only produced 5% hydrogen yield, 40.3% CO yield, and 56.4% total conversion.

The catalytic activity of MoO_2 is the result of a series of redox cycles taking place on the catalyst surface, as described by the Mars-van Krevelen mechanism [e.g., 8], which is illustrated in Figure 7.
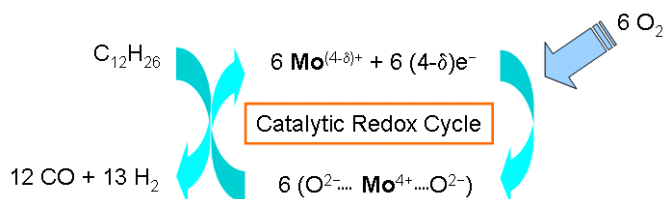

Figure 7: A proposed Mars-van Krevelen reaction mechanism for the partial oxidation of *n*-dodecane over MoO_2 nanoparticle.

The oxidation of the fuel is performed on the Mo^{4+} sites and embodies the insertion of nucleophilic oxygen ions O^{2-} from the lattice structure to the hydrocarbon molecules. Consequently, the Mo^{4+} site is reduced to $Mo^{(4-\delta)+}$ and oxygen vacancies are created on the catalyst structure. The reduced sites, $Mo^{(4-\delta)+}$, are then reoxidized by the gas oxygen fed into the system. In doing so, the oxygen ions produced are able to replenish the oxygen vacancies created in the previous step.

3   CONCLUSIONS

In summary, MoO_2 represents an exciting new catalyst for fuel flexible fuel cells. The material demonstrates enhanced coking and sulfur tolerance in the harsh environments that would be encountered in using logistics fuels such as Jet-A and JP-5. Catalytic behavior is believed to occur via a Mars-van Krevelen mechanism, which is facilitated through oxygen diffusion within the oxygen sub-lattice of MoO_2.

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