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## **Partial Oxidation of Surrogate Jet-A Fuel over SiO<sub>2</sub> Supported MoO<sub>2</sub>**

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## Abstract

SiO<sub>2</sub> supported MoO<sub>2</sub> nanoparticle catalysts were synthesized by a sol-gel method for partial oxidation of *n*-dodecane. The MoO<sub>2</sub> nanoparticles are < 10 nm in size and show a resistance to sintering at 850°C (the typical reforming temperature of *n*-dodecane). The formation of Mo-O-Si bonds at the interface between the nanoparticle catalyst and its support can be used to explain the enhanced stability of the particles. As a result of maintaining the smaller particle size, the SiO<sub>2</sub> supported MoO<sub>2</sub> nanoparticles show improved reforming activity in terms of syngas generation compared to commercial MoO<sub>2</sub>, which has an average particle size in the order of micrometers. Commercial MoO<sub>2</sub> exhibits good initial activity up to a WHSV of 15 h<sup>-1</sup> and at space velocities beyond 20 h<sup>-1</sup> it behaves like a blank control. On the other hand, MoO<sub>2</sub> nanoparticles supported on SiO<sub>2</sub> show high initial reforming activity (e.g., 69% H<sub>2</sub> yield, 82% CO yield and 100% carbon conversion) at WHSV up to 30 h<sup>-1</sup>. Supported MoO<sub>2</sub> nanoparticle catalysts also show high reforming activity for the partial oxidation of *n*-dodecane at 850°C without deactivation for 24 h time-on-stream.

## Introduction

Comparison of U.S. energy consumption and production at the end of 2013, showed an energy deficit of around 15 quadrillion Btu [1]. This energy deficit can be partially addressed in the future by development of more efficient approaches to energy conversion, e.g., improving on conventional gas turbine and internal combustion engines [2]. These types of engines generate electricity via fuel combustion reactions, followed by converting the generated heat into mechanical energy and finally to electricity. Besides the Carnot efficiency limit, the transformation of chemical energy into electrical energy in turbine engines lead to large energy losses due to the involvement of multiple conversion steps [3].

Fuel cells can allow us to efficiently convert the chemical energy of logistic fuels into electrical energy [3]. A recent study conducted by Pacific Northwest National Laboratory (PNNL) has demonstrated that a fuel cell system can achieve an overall system efficiency > 60% when directly operated with liquid logistic fuels [4].

Amongst the different types of fuel cells, solid oxide fuel cells (SOFC) have garnered considerable interest, mainly due to their high operating temperature that allows the required redox reactions to be catalyzed by inexpensive non-noble metals such as nickel. Furthermore, SOFC can use either H<sub>2</sub> or a mixture of H<sub>2</sub> and CO (syngas) as the energy carrier. At anode the fuel reacts with oxygen ions transported from the cathode to generate electricity as

the main product and water, or a mixture of water and carbon dioxide, as by-products. Pure hydrogen can be obtained from syngas by treating it via water-gas shift reaction, followed by preferential CO oxidation and then separating H<sub>2</sub> and CO<sub>2</sub> [5]. The pure hydrogen stream can be fed to polymer electrolyte membrane (PEM) fuel cells. Therefore, syngas is the main intermediate energy carrier and it has the potential to power multiple types of fuel cell.

Syngas can be produced by reforming various types of carbon sources, including conventional logistic fuels such as gasoline, diesel and jet fuels [6-10]. In future, reforming of biofuels such as biodiesel can be a source of syngas [11]. The advantage of using biofuels is that it can offer a net zero carbon emission for the entire energy cycle by capturing the emitted CO<sub>2</sub> from the fuel cell system via photosynthesis [12]. The utilization of these sustainable liquid fuels for fuel cells in automobile applications is particularly important because the current storage and distribution infrastructure of fossil-based transportation fuels is compatible with liquid biofuels [13]. Thus, for automobile applications of fuel cells, we need on-board reformers that are compact and have the ability to efficiently convert liquid transportation fuels into syngas.

Three different reforming technologies can be considered for the production of syngas from liquid transportation fuels: steam reforming, partial oxidation, and autothermal reforming. Even though steam reforming is the most conventional approach to syngas generation, it is an endothermic process and, thus, requires external energy input. In addition, due to the requirement for additional space to store and distribute external water, steam reforming requires

a larger overall system size with added complexity. Autothermal reforming combines both steam reforming and partial oxidation, and therefore it faces the same challenges as the steam reformers. On the other hand, reformers for catalytic partial oxidation (CPO) are compact, have faster start-up and quick response times, making them an ideal candidate for on-board syngas generation [14]. However, in order to directly process liquid transportation fuels, CPO reformers require a catalyst, which has the ability to reform long chain hydrocarbons, is coke resistant, sulfur tolerant, and is stable at high reforming temperatures.

MoO<sub>2</sub>-based catalysts have shown reforming activity for complex and heavy liquid hydrocarbons such as iso-octane, *n*-dodecane, gasoline and Jet-A fuel with both high coke resistance and sulfur tolerance [15-18]. Marin-Flores et. al. discussed the activity of unsupported nanoparticle MoO<sub>2</sub> for the partial oxidation of *n*-dodecane [16]. The catalyst showed excellent coking resistance and reforming activity with 80% conversion and 85% H<sub>2</sub> yield at 850°C, 1 atm, O<sub>2</sub>/C = 0.5 and weight hourly space velocity (WHSV) = 1.1 h<sup>-1</sup>. However, at the high reforming temperature of 850°C, MoO<sub>2</sub> is prone to sintering. In the literature two mechanisms are recognized for sintering [19]. In Oswald ripening atoms detach from smaller crystallites, migrate and attach to larger crystallites, resulting in crystal growth. The other mechanism involves migration of the entire crystallite followed by attachment and coalescence. Crystal growth can occur via either of these two mechanisms or as a culmination of both processes together. Although the sintering mechanism for MoO<sub>2</sub> nanoparticles is not exactly known, both

mechanisms are temperature dependent. The Tamman temperature,  $T_{\text{Tamman}}$ , represents the minimum onset temperature for sintering [19]:

$$T_{\text{Tamman}} \text{ (K)} = 0.5T_{\text{Melting point}} \text{ (K)} \quad \text{(Equation 1)}$$

Since the melting temperature of  $\text{MoO}_2$  is 1,370 K, according to Eqn. 1,  $\text{MoO}_2$  nanoparticles begin sintering above 685 K (i.e.,  $> 410^\circ\text{C}$ ). Since the typical reforming temperatures of logistic fuels are  $> 700^\circ\text{C}$ ,  $\text{MoO}_2$  nanoparticles would lose their active surface area quickly once the reaction starts. With the low active surface areas,  $\text{MoO}_2$ -based reforming systems can only operate at low WHSVs, which lead to low  $\text{H}_2$  production rate.

Sintering can be prevented either by supporting the nanoparticles on a high surface area support or alloying the nanoparticles with additional elements [19]. For this study, we chose to support  $\text{MoO}_2$  nanoparticles on  $\text{SiO}_2$  supports. Silica was chosen as the support because it offers a high surface area and it does not possess activity for fuel reforming [19-24]. Thus, it would not significantly alter the catalytic properties of the  $\text{MoO}_2$  nanoparticles. The support can prevent sintering by either entrapping the nanoparticles within the silica network or by forming chemical bonds across the hetero-phase interface. Jung et. al. synthesized silica-supported  $\text{TiO}_2$  nanoparticles via the sol-gel method and investigated the effect of the support on particle sintering. According to their study, the formation Ti-O-Si bonds improve the sintering resistance of  $\text{TiO}_2$  nanoparticles at high temperatures [25]. In this present study, we synthesized

SiO<sub>2</sub> supported MoO<sub>2</sub> nanoparticles utilizing a similar sol-gel method and investigated the effect of the silica support on the sintering of MoO<sub>2</sub> nanoparticles at high reforming temperatures. Finally we tested the activity of the supported catalyst for the partial oxidation of surrogate Jet-A fuel (i.e., *n*-dodecane) at various WHSVs. **The main objective of this study is to operate a MoO<sub>2</sub>-based reforming unit at the highest possible WHSV and achieve a high H<sub>2</sub> production rate.**

## **2. Experimental**

### **2.1 Catalyst Synthesis**

The supported catalysts used in this study were synthesized using the sol-gel approach. All the chemicals and reagents were obtained from Alfa Aesar. Ammonium heptamolybdate tetrahydrate (AHM) is the molybdenum precursor and tetraethyl orthosilicate (TEOS) is used as a silicon precursor. Samples with a composition of 10 mol% MoO<sub>3</sub>-SiO<sub>2</sub> were synthesized following the procedure described by Umbarkar et al. [26]. The resulting catalysts were reduced inside a quartz tube reactor using 10% H<sub>2</sub> in Ar at 450°C for 3 h. Pure SiO<sub>2</sub> was synthesized by the sol-gel method described above, except the molybdenum precursor was replaced by 20% (by volume) ammonium hydroxide solution. Unsupported nanoparticle MoO<sub>2</sub> was synthesized by the autoclave method described in Marin-Flores et. al [16] and it was used for our temperature programmed reduction (TPR) experiments.



## 2.2 Characterization

The catalysts were characterized using various techniques. Siemens D-500 X-Ray powder diffractometer with a Cu K $\alpha$  radiation was used for crystal structure analysis. The morphology of the powder samples was examined using both scanning electron microscopy (SEM; FEI Quanta 200F) and high-resolution transmission electron microscopy (TEM; JEOL JEM 2100 HR operated at 200kV). The samples for SEM were mounted on carbon tape and the SEM was operated at 30kV and a spot size of 3. TEM samples were prepared by dispersing the powders in acetone and drop casting them on 3 mm carbon coated grids. A Chemisorb 2720 equipped with a thermal conductivity detector (TCD) was used for temperature programmed reduction (TPR). A quantity, 30 mg, of sample was taken in a U-shaped quartz tube and degassed under He at a flow rate of 20 ml/min and at a temperature of 400°C for 30 min. Then the samples were cooled to 50°C in He under the same flow rate. For TPR, the sample was heated in flowing 5% H<sub>2</sub>/He from 50°C to 1000°C. BET surface area was measured by N<sub>2</sub> sorption experiments using a Micromeritics TriStar 3020 physisorption analyzer. Prior to measurements, the samples were degassed at 300°C, under vacuum ( $\leq$  100 Torr), for 1 hr. Diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) measurements were performed using a Nicolet iS50 FTIR. The catalyst samples were mixed with KBr and the measurements were conducted by obtaining 128 scans at 4 cm<sup>-1</sup> resolution.

## 2.3 Catalytic Activity

The reforming activity of the catalysts was measured in a quartz tube reactor set-up as described previously by Marin-Flores et al. [16]. The flow rates of reactants were adjusted to obtain the desired O<sub>2</sub>/C ratio. The gaseous products were analyzed using a gas chromatography (Molecular Sieve 5A Packed Column and HayeSep T Packed Column) with a TCD detector and the catalyst performance was evaluated in terms of H<sub>2</sub> yield, CO yield and carbon conversion, which are defined as shown below:

$$\text{H}_2 \text{ yield} = \frac{2 \times \text{moles of H}_2 \text{ produced}}{26 \times \text{moles of } n\text{-dodecane fed}} \times 100\%$$

$$\text{CO yield} = \frac{\text{moles of CO produced}}{12 \times \text{moles of } n\text{-dodecane fed}} \times 100\%$$

$$\text{Carbon Conversion} = \frac{\text{moles of (CO + CO}_2\text{ + CH}_4\text{ + 2} \times \text{C}_2\text{H}_4\text{) produced}}{12 \times \text{moles of } n\text{-dodecane fed}} \times 100\%$$

The WHSV was calculated by dividing the weight of the feed stream (i.e., a mixture of *n*-dodecane and air) per unit time by the weight of MoO<sub>2</sub>.

## 3. Results and Discussion

### 3.1 Catalyst Synthesis

Figure 1 shows the X-ray diffraction pattern for a sample obtained after calcination at 500°C. The diffractogram of the sample can be entirely indexed to orthorhombic MoO<sub>3</sub>, which is believed to form as a result of the complete conversion of the isopolymolybdate species to a pure Mo (VI) oxide. Based on the Scherrer equation, the average crystallite size is estimated to be 24 nm with

a standard deviation of 7 nm. The broad peak at  $2\theta$  below  $35^\circ$  represents the amorphous  $\text{SiO}_2$  support.

In order to obtain 10 mol%  $\text{MoO}_2\text{-SiO}_2$ , the calcined material needs to be reduced. In the literature, bulk  $\text{MoO}_3$  has been reduced between  $400\text{-}600^\circ\text{C}$  to obtain the  $\text{MoO}_2$  phase [27-29]. However, due to the presence of many suboxides (e.g.,  $\text{Mo}_{18}\text{O}_{58}$ ,  $\text{Mo}_8\text{O}_{23}$ ,  $\text{MoO}$ ) and the tendency of nanoparticles to have lower reduction temperatures than their parent bulk materials, temperature programmed reduction (TPR) experiments were performed to determine the suitable temperature for the reduction of  $\text{MoO}_3$  to  $\text{MoO}_2$  for our calcined samples [30]. The profile obtained in Figure 2a exhibits two major peaks: one at  $450^\circ\text{C}$  and another one centered around  $620^\circ\text{C}$ . Based on previous reports [27], the low temperature peak in the TPR profile can be attributed to the reduction of  $\text{MoO}_3$  to  $\text{MoO}_2$ , while the higher temperature peak is assigned to the reduction of  $\text{MoO}_2$  to Mo metal. The peak at  $450^\circ\text{C}$  has a noticeable shoulder at  $420^\circ\text{C}$ . Generally, the reduction  $\text{MoO}_3$  to  $\text{MoO}_2$  is considered a two-step reduction via an intermediate [27]. The shoulder at  $420^\circ\text{C}$  can be attributed to the reduction of  $\text{MoO}_3$  to the intermediate and then to  $\text{MoO}_2$  at  $450^\circ\text{C}$ . To prevent excessive reduction with the subsequent formation of metallic Mo, the temperature in the reduction step to produce silica-supported  $\text{MoO}_2$  was set to  $450^\circ\text{C}$ . Figure 2b shows the diffraction pattern of the sample obtained from the calcination step after the reduction under pure  $\text{H}_2$  at  $450^\circ\text{C}$  for 3 h. The diffractogram shows peaks that can be indexed exclusively to the monoclinic  $\text{MoO}_2$  phase along with the characteristic broad peak for silica at  $2\theta < 35^\circ$ . The average crystallite size of  $\text{MoO}_2$  calculated using

the Scherrer equation is 15 nm with a standard deviation of 7 nm.

### 3.2 Resistance to Sintering at 850°C

The effectiveness of silica as a support is determined by its ability to prevent sintering. For the sintering test, the synthesized catalysts were annealed under N<sub>2</sub> for 0.5 h at 850°C. XRD, TEM and BET surface area measurements were performed for the annealed catalysts and compared with as-synthesized catalysts (Table 1). Compared to a pure SiO<sub>2</sub> support, the surface area increases after the addition of MoO<sub>2</sub> over the SiO<sub>2</sub> support from 241 m<sup>2</sup>/g to 301 m<sup>2</sup>/g. However, the pore volume shows a decrease from 1.33 cm<sup>3</sup>/g to 1.08 cm<sup>3</sup>/g. The increase in the surface area can be attributed to the addition of MoO<sub>2</sub> nanoparticles, while the decrease in the pore volume can be due to the presence of MoO<sub>2</sub> crystallites occupying the **intra-particle** pores. The surface area decreases drastically from 301 m<sup>2</sup>/g for as-synthesized catalysts to 18 m<sup>2</sup>/g after annealing. The pore volume shows a similar trend and decreases to 0.04 cm<sup>3</sup>/g. The decrease in the surface area and pore volume can be explained due to the densification of the SiO<sub>2</sub> support (as seen later in the TEM images). Even though the silica support shows densification at high temperatures resulting in a low surface area, the nanoparticle MoO<sub>2</sub> does not show sintering and maintains its nanoparticle size at 850°C (as evident from both TEM and XRD crystallite size measurements).

Figure 3 shows representative TEM images of the samples used in this work. As shown in Figure 3a, as synthesized SiO<sub>2</sub> particles have an equiaxed

morphology with a size around 20 nm. In Figure 3b the initial MoO<sub>2</sub> nanoparticles dispersed on the silica before the annealing are clearly visible and are  $\leq 10$  nm, which is in good agreement with the estimates from the XRD data. Comparison of Figures 3a and 3b shows that the SiO<sub>2</sub> particles have sintered during the reduction process. The post-annealing sample at 850°C shown in Fig. 3c suggests that the annealing process was not able to produce significant changes in the morphology of the MoO<sub>2</sub> nanoparticles: the size after annealing is  $\leq 10$  nm.

In order to understand the role of the silica support in preventing sintering of nanoparticle MoO<sub>2</sub> at high temperatures, DRIFTS and activation energy measurements (via TPR) were performed. Figure 4 shows the transmittance spectra for SiO<sub>2</sub> and as-synthesized 10 mol% MoO<sub>2</sub>-SiO<sub>2</sub>. The SiO<sub>2</sub> spectrum (Figure 4a) shows three characteristic peaks at 802 cm<sup>-1</sup>, 956 cm<sup>-1</sup> and 1095 cm<sup>-1</sup> corresponding to symmetric  $\nu(\text{Si-O-Si})$ ,  $\nu(\text{Si-O-H})$  and asymmetric  $\nu(\text{Si-O-Si})$ , respectively [31]. For 10 mol% MoO<sub>2</sub>-SiO<sub>2</sub> samples, the high intensity peaks of SiO<sub>2</sub> suppress peaks that are characteristic for MoO<sub>2</sub> nanoparticles (e.g., 739 cm<sup>-1</sup> (Mo-O), 696 cm<sup>-1</sup> (O-Mo-O), 960 cm<sup>-1</sup> (Mo=O) and 860 cm<sup>-1</sup> (Mo-O-Mo)). Nevertheless, the as-synthesized 10 mol% MoO<sub>2</sub>-SiO<sub>2</sub> sample shows peaks for SiO<sub>2</sub> (802 cm<sup>-1</sup> for symmetric  $\nu(\text{Si-O-Si})$  and 1095 for asymmetric  $\nu(\text{Si-O-Si})$ ) and a peak shift for  $\nu(\text{Si-O-H})$  towards higher wavenumber to 965 cm<sup>-1</sup>. This shift can be explained by replacement of H with Mo to form Si-O-Mo [32]. A similar shift has been reported in the literature for silica supported TiO<sub>2</sub>, where the formation Ti-O-Si bonds improves the sintering resistance [25]. Based on our DRIFTS data,

we can speculate that the formation of Si-O-Mo bonds at the MoO<sub>2</sub>-SiO<sub>2</sub> interface could anchor the MoO<sub>2</sub> nanoparticles and prevent sintering.

The energy of activation, E<sub>a</sub>, for the reduction process was measured for supported and unsupported nanoparticle MoO<sub>2</sub> using the Kissinger equation [33], in order to further investigate the effect of the MoO<sub>2</sub>-SiO<sub>2</sub> interaction observed in DRIFTS:

$$\text{Ln} \left[ \frac{\psi}{T_{\text{max}}^2} \right] = \frac{-E_a}{RT_{\text{max}}} + \text{Ln} \left[ \frac{AR}{E_a} \right] \quad (\text{Equation 2})$$

In the Kissinger equation (Eqn. 2)  $\psi$  is the heating rate,  $T_{\text{max}}$  is the peak temperature, A is a pre-exponential factor, and R is the gas constant. Samples of both catalysts were reduced at different  $\psi$  and E<sub>a</sub> was calculated using the slope of the straight line resulting from the plot of  $\text{Ln} [\psi/T_{\text{max}}^2]$  versus  $1/T_{\text{max}}$ . The TPR profiles of unsupported and silica-supported MoO<sub>2</sub> are shown in Figure 5a and 5b, respectively. Figure 5c displays the data appropriately arranged to determine E<sub>a</sub> for the reduction of both samples with H<sub>2</sub>. As seen, for the unsupported MoO<sub>2</sub> sample, the value of E<sub>a</sub> was found to be  $99 \pm 3$  kJ/mol whereas for the silica supported MoO<sub>2</sub> sample the value obtained was  $104 \pm 6$  kJ/mol. Thus, the reducibility of MoO<sub>2</sub> with and without the support appears to be very similar, which suggests that the interaction is present only at the interface and it does not affect the bulk property of the catalysts.

To further investigate the effect of the interfacial interaction, the dispersion of MoO<sub>2</sub> over SiO<sub>2</sub> was calculated for the annealed sample using Eqn. 3. The

assumptions are that the crystallites have a circular cross section and the surface density is 14.69 Mo atoms/nm<sup>2</sup> for MoO<sub>2</sub>:

$$\% \text{ Dispersion} = \frac{\text{Mo atoms on crystallite surface}}{\text{Total Mo atoms in crystallite}} \quad (\text{Equation 3})$$

Based on this calculation, the dispersion of MoO<sub>2</sub> over SiO<sub>2</sub> for as-synthesized 10 mol% MoO<sub>2</sub>-SiO<sub>2</sub> sample was 21%. This low dispersion value can further explain why the interaction at the interface does not affect the bulk catalytic properties. Thus, we propose that the prevention of sintering of the nanoparticles is mainly caused by the interfacial interaction between MoO<sub>2</sub> and SiO<sub>2</sub>. The interaction is strong enough to prevent sintering and grain growth of the MoO<sub>2</sub> nanoparticles, but it does not affect the bulk properties due to the low dispersion.

### 3.3 Catalyst Activity for Partial Oxidation of *n*-dodecane

Activity tests for the partial oxidation of *n*-dodecane were conducted for both unsupported MoO<sub>2</sub> (commercial MoO<sub>2</sub>) and supported nanoparticle MoO<sub>2</sub> on SiO<sub>2</sub>. The reaction conditions were chosen based on the thermodynamic and experimental analysis performed by Marin-Flores et al. for the partial oxidation of *n*-dodecane over unsupported MoO<sub>2</sub> nanoparticles [18]. According to their experimental results and thermodynamic calculations, the highest stability for the MoO<sub>2</sub> phase can be achieved at 850°C and 1 atm using O<sub>2</sub>/C ratios between 0.5 and 1.0. However, if the O<sub>2</sub>/C ratio is too high and closer to 1.0, the production rate of syngas is low due to the formation of large concentrations of H<sub>2</sub>O and CO<sub>2</sub>. On the other hand, if the O<sub>2</sub>/C ratio is too low and closer to 0.5, the tendency for the coke formation significantly increases. Therefore, an O<sub>2</sub>/C ratio

of 0.7 was used for the present study in order to stabilize the MoO<sub>2</sub> phase without becoming detrimental for the syngas production.

Figure 6a shows % H<sub>2</sub> yield, % CO yield and % carbon conversion for the partial oxidation of *n*-dodecane over commercial MoO<sub>2</sub> at different WHSVs after operating the catalyst for 4.5 h. Figure 6a also includes the blank run for comparison purposes. In the absence of the catalyst (blank run), 21% H<sub>2</sub> yield, 75% CO yield and 95% carbon conversion were measured. According to the thermodynamic calculations performed by Marin-Flores et al., the equilibrium H<sub>2</sub> and CO yields are between 80-85% under the given reforming conditions [18]. Thus, the H<sub>2</sub> yield for the blank run is much lower compared to the equilibrium H<sub>2</sub> yield, while the CO yield is just slightly lower than the equilibrium CO yield. In addition to H<sub>2</sub> and CO, the blank run also produced 3% CH<sub>4</sub> yield, 15% C<sub>2</sub>H<sub>4</sub> yield and 19% CO<sub>2</sub> (not shown in Figure 6a). The main reaction taking place in the reformer at 850°C for the blank run is thermal cracking, which leads to the formation of C<sub>1</sub> and C<sub>2</sub> products. Even though the carbon conversion is high at 95%, its selectivity towards H<sub>2</sub> gas generation is too low for fuel cell applications as seen by the low hydrogen yield of 21%.

According to Figure 6a, commercial MoO<sub>2</sub> provides 100% carbon conversion for WHSVs ranging between 6 and 20 h<sup>-1</sup>. Conversion increases by 5% compared to that of the blank run irrespective of the WHSV. When compared to the blank run, the H<sub>2</sub> yield for commercial MoO<sub>2</sub> at WHSV of 15 h<sup>-1</sup> significantly increases from 21% to 55%. However, there is almost no change in CO yield (75% to 76%), while CO<sub>2</sub> yield only increases by 6%. This increase in H<sub>2</sub> yield for



commercial MoO<sub>2</sub> can be partially explained by the enhanced reforming activities toward CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> compounds over the MoO<sub>2</sub> surface as no CH<sub>4</sub> yield is observed and C<sub>2</sub>H<sub>4</sub> yield drops from 15% to 12% in the product stream when the commercial MoO<sub>2</sub> catalyst was used at WHSV of 15 h<sup>-1</sup>. Moreover, the fuel mixture, in the absence of the catalyst, would continuously decompose in the gas phase as it flows through the reactor. The blank test suggests that most of the fuel is fully decomposed in the gas phase to either CO or CO<sub>2</sub> with low H<sub>2</sub> selectivity at the outlet of the reactor. However, in the presence of the catalyst the partially decomposed fuel molecules or carbon fragments react over the catalyst bed before they have a chance to fully decompose to either CO or CO<sub>2</sub> in the gas phase. Compared to the blank test, our activity test results indicate that this catalytic partial oxidation reaction favors the production of H<sub>2</sub> (probably by decreasing H<sub>2</sub>O selectivity) that leads to a higher H<sub>2</sub> yield. As the WHSV increases from 15 to 20 h<sup>-1</sup>, the H<sub>2</sub> yield decreases and eventually becomes comparable to the blank run as shown in Figure 6a. The loss of selectivity towards H<sub>2</sub> at high WHSV of 20 h<sup>-1</sup> for the commercial MoO<sub>2</sub> can be attributed to its larger particle size (50-200nm) and low surface area (4 m<sup>2</sup>/g) [16]. With an increase in WHSV, the amount of fuel that flows over the catalyst bed per unit time increases. Due to the low surface area of the commercial MoO<sub>2</sub>, it does not offer enough active sites to catalytically reform all the fuel molecules at high WHSV values. Therefore, a large portion of the fuel molecules undergo gas phase decomposition, rather than catalytic partial oxidation and thus produce a lower % H<sub>2</sub> yield. The diffractograms from the spent samples shown in Figure 6b

indicate that the MoO<sub>2</sub> phase is the predominant crystalline phase with a small amount of Mo<sub>2</sub>C present in all cases.

For supported MoO<sub>2</sub>, the activity tests were performed for the partial oxidation of *n*-dodecane at the same reaction conditions used for the unsupported MoO<sub>2</sub>. The results as a function of WHSV are shown in Figure 7a. At a WHSV of 20 h<sup>-1</sup>, the supported MoO<sub>2</sub> shows average values of ~100% for H<sub>2</sub> yield, CO yield and carbon conversion. Using MoO<sub>2</sub> nanoparticles supported on SiO<sub>2</sub> not only produces complete carbon conversion it also shows an improvement in the selectivity towards syngas production (i.e., an increase in H<sub>2</sub> and CO yields). The H<sub>2</sub> yield and CO yield are higher than their respective equilibrium values by 15 to 20%. This discrepancy indicates that there are many reactions (both gas phase and heterogeneous catalytic reactions) occurring over the catalyst bed of the reactor in a very complex way, which were not all accounted for by the previous thermodynamic studies [18].

Furthermore, no CO<sub>2</sub> yield was observed over the supported nanoparticle MoO<sub>2</sub> at a WHSV of 20 h<sup>-1</sup> (data not shown), whereas commercial MoO<sub>2</sub> shows a performance similar to the blank run with 20% CO<sub>2</sub> yield. As explained earlier, in the case of commercial MoO<sub>2</sub>, the performance is similar to the blank run at high space velocities, due to the lower surface area that enhances the undesired gas phase reaction. In the case of the supported MoO<sub>2</sub>, the high surface area allows a large volume of fuel molecules to be processed per a unit time via surface partial oxidation and the undesired gas phase reaction is reduced. Additionally, the nanoparticle size effect can also contribute to the enhanced catalytic

reforming activity of the supported MoO<sub>2</sub>. This particle size effect is a well-known phenomenon in the literature [37-39]: changing the particle size of the catalyst changes the selectivity towards desired products. Consequently, H<sub>2</sub> and CO yields of the supported MoO<sub>2</sub> are much higher than those of the commercial MoO<sub>2</sub> at the high WHSV of 20 h<sup>-1</sup>.

Marin-Flores et al. also showed similar results for unsupported MoO<sub>2</sub> nanoparticles for the partial oxidation of *n*-dodecane under reforming conditions similar to our present study except at WHSV < 10 h<sup>-1</sup> [16]. Because unsupported MoO<sub>2</sub> nanoparticles can easily sinter at the reforming temperature, the active surface area would significantly decrease at the beginning of the reaction and the reforming activity would be similar to that of the blank run if a high WHSV is used. However, the supported MoO<sub>2</sub> nanoparticles synthesized in our study maintain their nanoparticle size and high surface area due to the interaction between the nanoparticles and the silica support, thus providing much improved reforming activity at the high WHSV of 20 h<sup>-1</sup>.

As the WHSV is increased to 30 h<sup>-1</sup>, the average conversion remains at 100% while the average yields of H<sub>2</sub> and CO drop to 82% and 69%, respectively. A further increase in the WHSV to 51 h<sup>-1</sup> leads to an increase in average yields of both H<sub>2</sub> and CO, which reached values of 96% and 97%, respectively. This increase in syngas generation can be attributed to the phase change of MoO<sub>2</sub> into Mo<sub>2</sub>C, as seen in the diffractograms in Figure 7b. The MoO<sub>2</sub> is the stable phase up to WHSV of 30 h<sup>-1</sup> and it transforms to Mo<sub>2</sub>C at WHSV of 51 h<sup>-1</sup>. The phase change at the high WHSV of 51 h<sup>-1</sup> is consistent with the thermodynamic

study done by Marin-Flores et al. [18]. For the initial reforming performance, it seems that the supported Mo<sub>2</sub>C nanoparticles are more active than that of supported MoO<sub>2</sub> nanoparticles toward the partial oxidation of *n*-dodecane. However, the phase change at the high WHSV is detrimental to the long-term performance of the catalyst as MoO<sub>2</sub> is the more stable catalyst at high WHSVs than Mo<sub>2</sub>C. This is due to the high oxygen mobility of MoO<sub>2</sub>, where lattice oxygen is more active than gas phase oxygen for reacting with the carbon molecules. Therefore, in the case of MoO<sub>2</sub>, the lattice oxygen is readily available for scavenging any deposited carbon on the catalyst surface, whereas in the case of Mo<sub>2</sub>C, the carbon deposits slowly build on the surface and eventually deactivates the catalyst.

In order to elucidate the above phenomena, 24 h activity tests were performed at WHSV of 30 and 51 h<sup>-1</sup> for the supported MoO<sub>2</sub>. Fig. 8a shows the catalyst performance at WHSV of 30 h<sup>-1</sup> for the supported MoO<sub>2</sub> sample. As seen, the catalyst exhibits a stable performance without any signs of deactivation over a period of 24 h, with a conversion of 100% and average H<sub>2</sub> and CO yields of 63% and 75%, respectively. The diffractogram of the sample at the end of the test (data not shown) indicates the presence of only the MoO<sub>2</sub> phase.

However, in case of WHSV 51 h<sup>-1</sup> for the supported MoO<sub>2</sub>, the catalyst shows higher H<sub>2</sub> and CO yields with 100% carbon conversion for the first 5 h on-stream (like that shown in the initial performance data in Figure 7a) and then it slowly deactivates over the next 21 h time-on-stream. This decrease in the performance over 21 h is attributed to excessive coke formation, which became

evident as it was easily observed on the reactor walls. The XRD pattern of the spent sample (data not shown) indicated the presence of only Mo<sub>2</sub>C.

Therefore, according to our 24 h activity test data, the catalyst shows both good initial activity and good stability at WHSV of 30 h<sup>-1</sup>, where it maintains the MoO<sub>2</sub> phase. However, if the WHSV increases to 51 h<sup>-1</sup>, the supported MoO<sub>2</sub> nanoparticles are first transformed into Mo<sub>2</sub>C followed by the gradual decreases in the performance (e.g., decrease of H<sub>2</sub> yield, CO yield and carbon conversion).

DRIFTS were obtained for the spent catalysts at WHSV of 30 h<sup>-1</sup> in order to determine if the interaction between MoO<sub>2</sub> and SiO<sub>2</sub> was still present. As seen in Figure 9, the spent catalysts also show the peak that is characteristic of the Mo-O-Si bond at 965 cm<sup>-1</sup>. Thus, the catalysts maintain the interphase interaction between SiO<sub>2</sub> and MoO<sub>2</sub> during the reforming test, which is essential for maintaining nanoparticle MoO<sub>2</sub> and producing a high syngas generation rate over the 24 h period.

## **Conclusions**

High surface area silica supported MoO<sub>2</sub> catalysts were synthesized by the sol-gel method. The surface area eventually drops to 18 m<sup>2</sup>/g after annealing at 850°C. The reduction in surface area is solely due to the sintering of silica and not due to sintering of the MoO<sub>2</sub> nanoparticles. As observed in TEM images, the MoO<sub>2</sub> crystallite size ranges from 2-10 nm. DRIFTS for the synthesized catalysts shows the presence of Mo-O-Si bonds, which helps in anchoring the MoO<sub>2</sub> nanoparticles to the silica surface and thus preventing sintering at high

temperatures. The presence of an interaction between silica and MoO<sub>2</sub> at the interface does not affect the bulk property of the catalyst, as the activation energy for MoO<sub>2</sub> reduction is almost the same for both supported and unsupported catalysts. The low dispersion of the nanoparticles over the silica support might also play a contributing role to maintaining the bulk catalytic activity.

The supported MoO<sub>2</sub> nanoparticles show good catalytic activity and high selectivity towards syngas generation at high WHSVs with near 100% conversion, H<sub>2</sub> yield and CO yield at WHSV of 20 h<sup>-1</sup>. The increase in selectivity towards syngas generation for supported MoO<sub>2</sub> nanoparticle is due to the maintenance of a high surface area at the reforming temperature.

Silica supported MoO<sub>2</sub> nanoparticles show good initial catalytic activity up to WHSV of 30 h<sup>-1</sup>. At a WHSV of 51 h<sup>-1</sup>, the MoO<sub>2</sub> transforms to Mo<sub>2</sub>C. This phase change leads to an increase in syngas generation for the initial operation time, but deactivation due to severe coking occurs over a period of 24 h. The activity test for silica supported MoO<sub>2</sub> catalysts at WHSV of 30 h<sup>-1</sup> shows the good reforming performance over 24 h time-on-stream experiments with 100% conversion, 63% H<sub>2</sub> yield and 76% CO yield. The spent catalyst at WHSV of 30h<sup>-1</sup> shows solely the MoO<sub>2</sub> phase. Therefore, in order to maintain a good catalytic activity over a long-term operation, the catalyst needs to be operated in conditions such that it retains the MoO<sub>2</sub> phase.

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