

# Synthesis of High Surface Iron Decorated Molybdenum Carbide for Selective Hydrogenation of CO<sub>2</sub> to Light Olefins

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*Bipul Sarkar*  
[Dr. Bipul Sarkar] 09/10/2020  
Supervisor

*Sanat Kumar*  
[Dr. Sanat Kumar] 09/10/2020  
Head of Division

Submitted by  
**Himanshu Raghav**  
Catalytic Depolymerization Area (CDPA)  
Upstream and Wax Rheology Division (UWRD)  
CSIR- Indian Institute of Petroleum, Dehradun 248005

**Declaration:** I **Himanshu Raghav**, hereby certify that the work presented in this Report entitled “Synthesis of High Surface Iron Decorated Molybdenum Carbide for Selective Hydrogenation of CO<sub>2</sub> to Light Olefins” in partial fulfillment of the course requirement for award of the Degree of PhD, being submitted to CSIR-HARIT Unit, CSIR-Indian Institute of Petroleum, Dehradun, is an authentic record of Project Research work carried out by me at CSIR-IIP, Dehradun during the period January 2019 to August 2020 and under the supervision of Dr Bipul Sarkar.

Date 09/10/2020

*Himanshu Raghav*  
Signature of the Student

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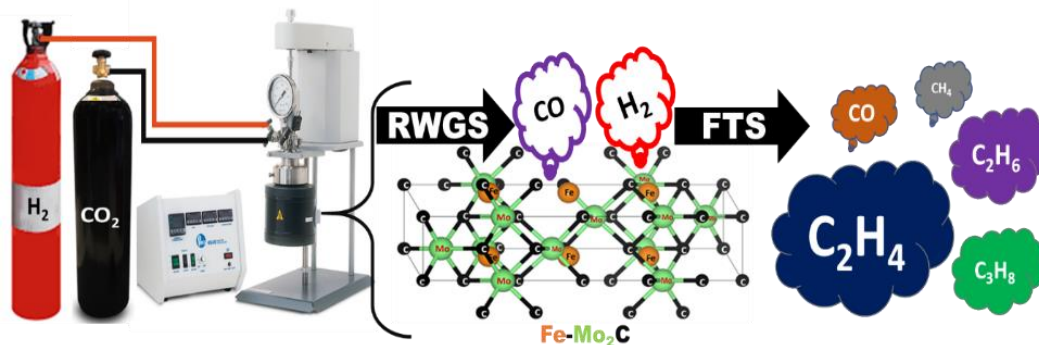
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## Abstract

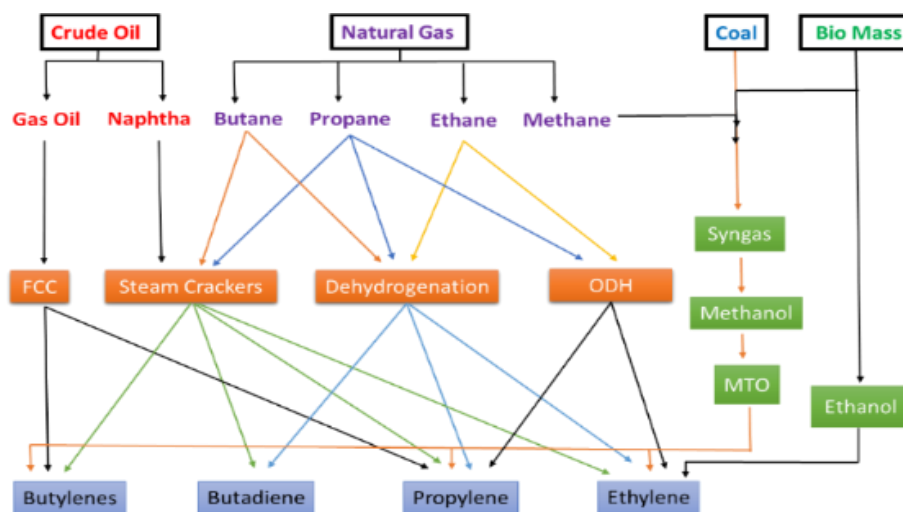
Production of olefins is a broad research field that is continuously expanding, as the demand is regularly increasing worldwide. Over the last few years, remarkable attention is paid to olefins production from various resources, particularly from rich sources, such as crude oil, natural gas, coal, and biomass. This work is related to light olefins



production from CO<sub>2</sub> through the combined approach of reverse water-gas shift (RWGS) and CO hydrogenation *via* the Fischer–Tropsch (FT) process. Molybdenum carbide ( $\beta$ -Mo<sub>2</sub>C) that has a high surface area is attractive for use as support and plays an important role in this type of reaction. Catalysts based on Fe-  $\beta$ -Mo<sub>2</sub>C were formed by the wetness impregnation method and applied to the CO<sub>2</sub> hydrogenation reaction for selective light olefin production. The conversion of CO<sub>2</sub> and product selectivity was studied by changing operating conditions.

# Introduction

One of the main initiatives for fighting climate change is using CO<sub>2</sub> as a resource instead of waste. In recent times, carbon dioxide is considered a promising alternative feedstock of carbon to manufacture a lot of precious chemicals and fuels (alkanes, olefins, alcohols, and aromatics). Light olefins (C<sub>2</sub>–C<sub>4</sub>) are the basics building blocks for the chemical industry, linked with the increasing needs of the expanding global population. As olefins are predominately dependent on fossil resources and carbon-rich sources such as crude oil, natural gas, coal, biomass, their production is limited by the finite reserves and the associated economic and environmental concerns. The different routes for olefins production<sup>1</sup> are summarized in Figure 1.

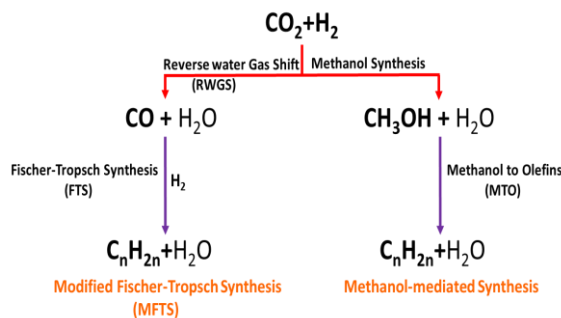


**Figure 1- Different routes for Olefins production from the carbon-rich source. [FCC (Fluid catalytic cracking), ODH (Oxidative dehydrogenation), MTO (Methanol to Olefins)]**

Currently, production of light olefins mainly involves steam cracking of either light hydrocarbon liquids or natural gas. The choice between gas or liquid feedstock depends on feedstock availability, cost, and by-product utilization. Although there is an expansion of production from alternative raw materials and processes, steam cracking and refinery (FCC) production will remain the dominant

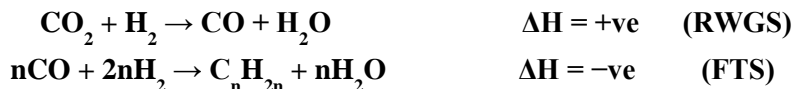
**Figure 2- CO<sub>2</sub> to Olefins through two competing pathways: MFTS and methanol mediated process**

process. So, we need an alternative route and feedstock for light olefins production. CO<sub>2</sub> is concerned as a C<sub>1</sub> source for an alternate



petrochemical building block, and having light olefins from carbon dioxide would be a commendable task. In this work, an attempt

has been made to hydrogenate CO<sub>2</sub> directly to light olefins *via* two competing pathways<sup>2</sup>: the modified Fischer-Tropsch synthesis and the methanol-mediated synthesis<sup>3</sup> (Figure 2). These pathways are distinguished by their intermediates: in the first route, CO<sub>2</sub> is reduced to CO via Reverse Water Gas Shift (RWGS), followed by a chain propagation via Fischer-Tropsch Synthesis. Modified Fischer Tropsch synthesis consists of two process reverse water-gas shift (RWGS) and Fischer-Tropsch (FT) synthesis<sup>4</sup>.



Controlling the selectivity of olefins from CO<sub>2</sub> hydrogenation requires a basic understanding of the thermodynamics and kinetics of the reaction pathways mentioned above. RWGS has a positive ΔH value, so it is an endothermic reaction; thus, it requires higher temperatures, while Fischer–Tropsch synthesis has a negative ΔH value, it is an exothermic reaction, so favored lower temperatures. The thermodynamics of the reaction demonstrates that catalyst synthesis for the selective production of light olefins is a challenging task. In the second route, CO<sub>2</sub> is hydrogenated first to methanol and then converted to hydrocarbons. Both routes are compared in terms of catalyst development and reaction performance. To achieve the target optimizing catalyst design, integrating multifunctionalities for both CO<sub>2</sub> activation and C-C coupling. catalysts used for CO<sub>2</sub> hydrogenation available in the literature<sup>2</sup> (Figure-3).

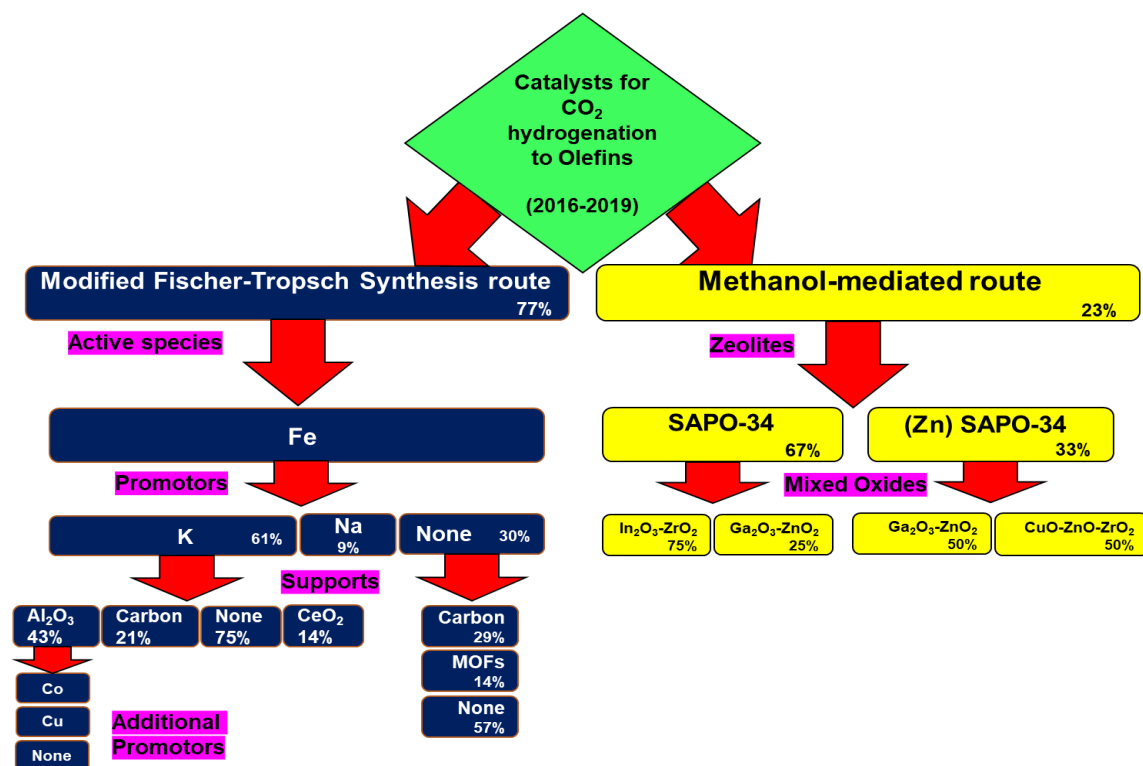


Figure-3. The percentages are calculated based on 26 papers published during 2016 - 2019

Iron-based catalysts are especially used in MFTS route. Whereas production of olefins through methanol-mediated route catalyst uses based on Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>.<sup>2</sup> In the performance of heterogeneous catalysts, supports play an important role. The support is used for the dispersion of the active phase and also participates in the reaction. In such a category, metal carbide a choice if doped with active functionality with nanoscale. Transition-metal carbides offering unique properties as supports for chemical catalysts and also have high surface areas. Carbide and nitride supported metal catalysts are reported to move for chemical reactions as well as, however, not restricted to water-gas shift, Fischer-Tropsch Synthesis, methanol steam reforming, and

hydrogen oxidation reactions. Molybdenum carbides are a perfect catalyst or support for the hydrogenation of CO<sub>2</sub>. It is especially appropriate as a heterogeneous catalyst as well as electrocatalyst in reduction processes. Based on all the assumptions, an iron decorated molybdenum carbide using SBA-15 template for better textural properties have been synthesised. The resulting catalyst was active for the above process due to their adsorption capacity, stability, and ability to support the active species of both reactions. Importantly, these materials are active for CO<sub>2</sub> hydrogenation.

## Experimental Procedure

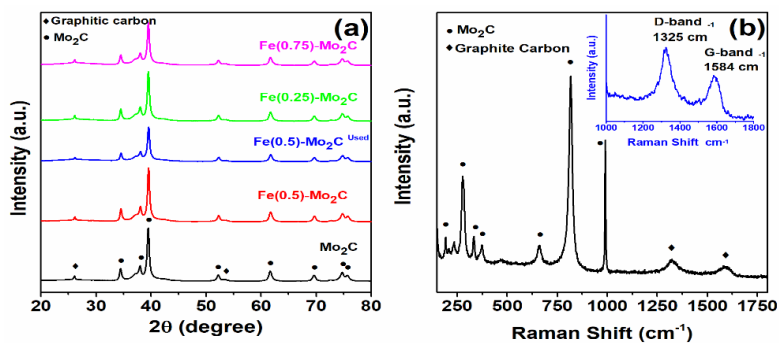
**Materials** - Pluronic P-123 (Sigma Aldrich), 2M HCl Solution, TEOS (Tetraethylorthosilicate AR grade), 98% (Sigma-Aldrich), Ammonium heptamolybdate tetrahydrate (Merck), Hydrofluoric acid 40%(Merck), Ferric nitrate Nonahydrate (PubChem). Mesoporous SBA-15 was synthesized according to a reported procedure<sup>5</sup>.

**Catalyst Preparation**- Fe-promoted catalysts were prepared by incipient wetness impregnation method using  $\beta$ -Mo<sub>2</sub>C as support. Support  $\beta$ -Mo<sub>2</sub>C was synthesized by taking an appropriate amount of ammonium heptamolybdate tetrahydrate dissolved in the desired amount of deionized water. SBA-15 was dissolved in deionized water separately. Both the resulting solutions were added into one beaker containing 200 ml deionized water under continuous stirring for 2h, and then the rotary evaporator was used for catalyst formation. The resulting material dry at 80°C for 12h. The obtained dried material was then loaded in a tubular furnace at 800°C for carbon deposition (40.10% hydrogen balance methane injected in the tubular furnace while the temperature was increased to 800°C in 4h and maintained at 800°C for 5h). After carbonization resulting material was leached by 10% hydrofluoric acid solution, then filtered and washed with distilled water several times until the pH of the filtrate solution was maintained at 7. The resulting sample was dried at 110°C for 24h. Finally, Mo<sub>2</sub>C was formed. Silicon was removed completely from the above sample. Then iron was uploaded in the different amounts on  $\beta$ -Mo<sub>2</sub>C by incipient wetness impregnation method and synthesized samples were calcined at 400°C. Thus Fe-Mo<sub>2</sub>C catalyst was formed.

## Results and Discussion

### Catalyst Characterization

The powder X-ray diffraction (PXRD) pattern of hexagonal-close-packed Mo<sub>2</sub>C or  $\beta$ -Mo<sub>2</sub>C and different wt.% iron-loaded  $\beta$ -Mo<sub>2</sub>C. The peaks located at 34.46°, 38.03°, 39.49°, 52.23°, 61.69°, 69.67°, 74.79°, 75.74° can be indexed to the planes (100), (002), (101), (102), (110), (103), (112) and (201) respectively facets of Mo<sub>2</sub>C (space group: P63/mmc) **Figure 4- (a) Powder XRD pattern of fresh Mo<sub>2</sub>C, Fe(0.5)- Mo<sub>2</sub>C, Fe(0.25)- Mo<sub>2</sub>C, Fe(0.75)- Mo<sub>2</sub>C and used Fe(0.5)- Mo<sub>2</sub>C. (b) Raman spectra of Mo<sub>2</sub>C**



space group number-194 and JCPDS 00-035-0787)<sup>6</sup>. In the XRD pattern, no peaks are observed related to molybdenum oxides or metallic molybdenum, demonstrating the high purity of the  $\beta$ -Mo<sub>2</sub>C sample. Meanwhile, the

additional peak observed at 26.10° and 53.8°, can be attributed to the (002) and (004) plane demonstrating the formation of graphitic carbon. Besides, the degree of graphitization in Mo<sub>2</sub>C was confirmed by the Raman spectroscopy (Fig. b). The peak at 1325 cm<sup>-1</sup> corresponds to the D-band, and G-bands at about 1584 cm<sup>-1</sup> is associated with amorphous carbon materials (sp<sup>2</sup> vibrations of perfect graphite carbon). The intensity ratio between the G-band and D-band peaks (I<sub>G</sub>/I<sub>D</sub>) is proportional to the degree of graphitization. The value of I<sub>D</sub>/I<sub>G</sub> is 1.28 for β-Mo<sub>2</sub>C samples meaning a high degree of graphitization in the composite.

## Catalyst Screening

The study of the effect of working conditions (temperature, pressure, and reaction time) on the CO<sub>2</sub> conversion and product selectivity over the synthesized catalysts. All reactions were performed in a Parr reactor. 1gm catalyst was used in each reaction, and reactions were performed at 40 bar and 300-400 °C and the reactant gas mixture H<sub>2</sub>/CO<sub>2</sub> in 3/1 ratio and reaction time 2-3 h. The reaction products were observed in the gas phase and analyzed by gas chromatography (GC) with a thermal conductivity detector (TCD) for inorganic gases and for hydrocarbons GC with flame ionization detector (FID).

**Table 1. Summary of performance of different wt% Fe promoted Mo<sub>2</sub>C catalysts (Fe-Mo<sub>2</sub>C) for CO<sub>2</sub> hydrogenation to olefins.**

Sl. No	Catalyst	Conv. (mol %)	Selectivity (mol%)					X <sub>CO</sub> (x10 <sup>-7</sup> )	X <sub>CH<sub>4</sub></sub> (x10 <sup>-7</sup> )
			CO	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>		
1	Fe(0.25)-Mo <sub>2</sub> C	5.6	4.7	1.7	18.7	64.3	10.3	3.20	1.16
2	Fe(0.5)-Mo <sub>2</sub> C	4.2	8.2	5.0	16.8	65.9	3.2	4.19	2.56
3	<b>Fe(0.5)-Mo<sub>2</sub>C<sup>a</sup></b>	<b>7.3</b>	<b>1.7</b>	<b>0.9</b>	<b>14.6</b>	<b>79.4</b>	<b>4.1</b>	<b>1.51</b>	<b>0.80</b>
4	Fe(0.5)-Mo <sub>2</sub> C <sup>b</sup>	9.8	0.5	2.1	4.6	92.0	0.8	0.59	2.51
5	Fe(0.75)-Mo <sub>2</sub> C	7.1	3.3	1.8	19.7	64.1	11.1	2.85	1.56

Condition: catalyst wt.-1 g (powder); reaction temp.-300°C; pressure-4 MPa H<sub>2</sub>:CO<sub>2</sub>- 3:1; time-2 hours. <sup>a</sup> after 3h of reaction time; <sup>b</sup> at 400°C. X<sub>CO</sub> and X<sub>CH<sub>4</sub></sub> is the rate of formation of CO and CH<sub>4</sub>, respectively. The relative standard deviation (RSD) is ±3%.

**Conclusion**- The (β-Mo<sub>2</sub>C) phase has the strongest metallic nature and is highly Stable with more ionic character. It behaves both as support and a co-catalyst for CO<sub>2</sub> hydrogenation. Iron-loaded β-Mo<sub>2</sub>C catalysts show good performances in CO<sub>2</sub> conversion into olefins. The 0.5 wt. % Fe supported on Mo<sub>2</sub>C shows a CO<sub>2</sub> conversion of 7.3% at 300°C after 3h, while the same catalyst Fe (0.5)-Mo<sub>2</sub>C at 400°C after 2h CO<sub>2</sub> conversion reaches 9.8%.

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