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# A highly active and synergistic Pt/Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalysts for Water-Gas Shift Reaction

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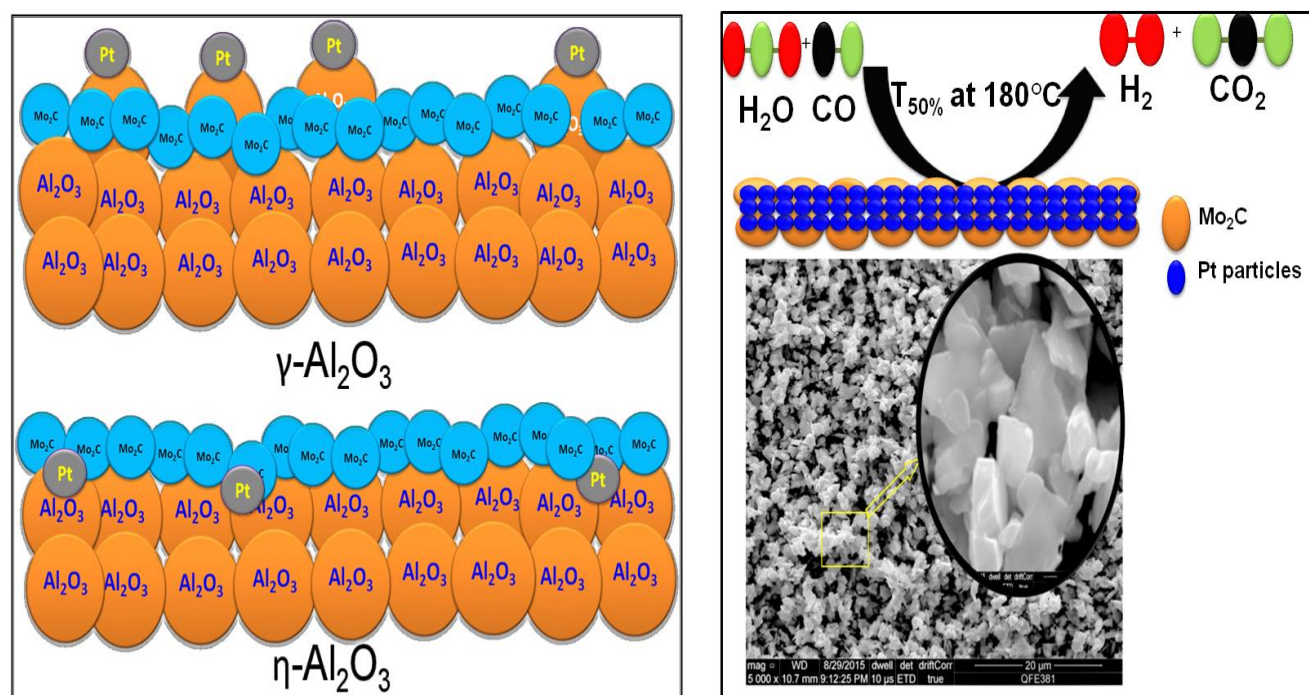
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## Abstract

Catalysts consisting of Pt and Cu supported on  $\text{Mo}_2\text{C}/\eta\text{-Al}_2\text{O}_3$ ,  $\text{Mo}_2\text{C}/\gamma\text{-Al}_2\text{O}_3$  or  $\text{Mo}_2\text{C}$  were prepared and used for the low-temperature water gas shift reaction. The catalysts were characterized by elemental analysis, X-ray diffraction (XRD), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The catalysts were studied in water gas shift reaction (WGSR) with a reaction mixture containing 11 % CO, 43 %  $\text{H}_2$ , 6%  $\text{CO}_2$ , 21 %  $\text{H}_2\text{O}$  (real feed composition mixture from the reformer) and balance He, with a reaction temperature range of 180-300 °C at a space velocity (SV) of 125,000  $\text{h}^{-1}$ . Catalyst supports ( $\eta\text{-Al}_2\text{O}_3$  and  $\gamma\text{-Al}_2\text{O}_3$ ), led to different synergetic effect between the two most active phases of Pt metal and  $\text{Mo}_2\text{C}$ . Pt/  $\text{Mo}_2\text{C}/\eta\text{-Al}_2\text{O}_3$  is a promising catalyst (44% conversion at 180°C) due to the close interaction between Pt and  $\text{Mo}_2\text{C}$  phases on the surface of the catalyst. The 4 Pt- $\text{Mo}_2\text{C}$  showed the highest activity where the temperature at which 50% conversion observed was at only 180 °C with SV of 125,000  $\text{h}^{-1}$  and constant stability over 85 hours.

**Keywords:** Water Gas Shift Reaction; Molybdenum carbide, Platinum, alumina, syngas.

## Graphical Abstract



Catalyst composition of Pt/ $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$  WGSR over Pt/ $\text{Mo}_2\text{C}$  catalyst

### Research highlights

- Molybdenum carbide is the active phase in water gas shift reaction
- The dispersion of  $\text{Mo}_2\text{C}$  during the carburization was enhanced with Pt
- Pt/ $\text{Mo}_2\text{C}$  catalysts are better than Cu/ $\text{Mo}_2\text{C}$  modified catalysts in WGSR.
- Using different acidic supports affect the synergetic effect between Pt and  $\text{Mo}_2\text{C}$ .
- Pt/ $\text{Mo}_2\text{C}$  showed higher catalytic activity than that of the commercial CuZnAl catalyst

## 1. Introduction

Nowadays, great attention is paid toward the water gas shift reaction (WGSR) as it offers a way of producing additional H<sub>2</sub> as well as eliminating harmful CO emissions in a variety of industrial applications to meet the safety and environmental requirements. The rise of bio-oil pyrolysis and subsequent methanol production makes a significant use of research into novel water-gas shift catalysts [1, 2]. The reaction feed for WGSR usually comes from of syngas (a mixture of CO and H<sub>2</sub>), generated by various processes such as biomass or coal gasification, methane steam or dry reforming, and methane partial oxidation.

At the industrial scale, the WGSR is carried out in two separate steps, high and low-temperature WGSR, to shift the equilibrium of the exothermic reaction into the desired direction. WGSR is used in preparing gases for fuel cells. High-temperature proton exchange membrane (HT-PEM) fuel cells can tolerate CO concentrations up to 3 vol.% [3], however, for low temperature (LT) fuel cells it is necessary to reduce CO concentration to less than 50 ppm for Pt electrode [4]. The drive for the production of synthetic fuels requires novel compact catalysts with a fast start-up time [5].

Noble metals supported onto reducible oxides represent a large class of novel WGSR catalysts. Choung et al.[6] observed a higher WGSR rate over a bimetallic Pt-Re catalyst supported onto a CeO<sub>2</sub>-ZrO<sub>2</sub> mixed metal oxide than the rates calculated by addition of individual rates over monometallic Pt and Re catalysts. The simultaneous addition of both Mo and Pt to WGSR catalysts supported on alumina (or silica) increases CO reaction rate at a temperature around 300 °C [7] which is related to decreasing CO binding energy over PtMo alloys. However, the authors observed a lower TOF over the bimetallic PtMo supported catalysts compared to Pt/CeO<sub>2</sub> catalyst.

Transition metal carbides such as Mo<sub>2</sub>C and Co<sub>2</sub>C have been established as active and selective catalysts for the WGSR [4, 8, 9]. Gnanamani et al.[10] studied the WGS reaction over alkali-

promoted  $\text{Co}_2\text{C}$  catalysts. They found that a  $\text{Na}/\text{Co}_2\text{C}$  catalyst showed a CO conversion of 76.3% at 240 °C. The authors suggested that the activity of the cobalt-based catalysts is primarily due to the carbide phases and the alkali metals (Na and K) promote catalytic activity by keeping cobalt in the reduced state. An active site density in  $\text{Mo}_2\text{C}$  catalysts is 25% greater than that in a commercial  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst. Therefore, the  $\text{Mo}_2\text{C}$  catalysts have a potential to replace the latter in a number of small-scale reactors for WGS [11]. Thin layers of  $\text{Mo}_2\text{C}$  catalysts supported onto a Mo substrate demonstrate catalytic activity in the WGS by 1–2 orders of magnitude higher than that of the commercial  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst [12, 13]. The catalytic activity of a bulk  $\text{Mo}_2\text{C}$  catalyst can further be improved by 4-5 times after the addition of small amounts of Pt [8]. The reaction rate over a  $\text{Pt}/\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$  catalyst of  $69.2 \mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$  was higher as compared to that of  $61.8 \mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$  over a  $\text{Cu}/\text{Zn}/\text{Al}_2\text{O}_3$  catalyst, while the turnover frequency (TOF) over the  $\text{Pt}/\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$  catalyst of was reported to be  $0.81 \text{s}^{-1}$  [9].

The highest WGS rate of  $284.6 \mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$  was observed at 240 °C over a non-supported  $\text{Pt}/\text{Mo}_2\text{C}$  catalyst [9]. The exceptionally high activity of the  $\text{Pt}/\text{Mo}_2\text{C}$  catalyst prepared by an aqueous wet impregnation method was due to the high density of active sites and the strong interaction between highly dispersed Pt nanoparticles and the  $\text{Mo}_2\text{C}$  support [4]. A high stability of the  $\text{Pt}/\text{Mo}_2\text{C}$  catalyst was also reported in the methanol electro-oxidation which has a similar reaction mechanism [14]. It was observed that Pt (i) increased the stability of  $\text{Mo}_2\text{C}$  support due to a strong chemical interaction and (ii) created a synergetic effect between the Pt nanoparticles and the  $\text{Mo}_2\text{C}$  phase.

We have studied precious metal catalysts [15] and molybdenum carbides [12, 16-19] in the medium temperature range. Among the precious metals, a  $\text{Pt}/\text{Mo}_2\text{C}$  catalyst has demonstrated the most promising results [5], with the temperature of 50% conversion ( $T_{50\%}$ ) of 180 °C at a space velocity (SV) of  $125,000 \text{h}^{-1}$ . Sabnis et al.[8, 20] studied WGS reaction over a  $\text{Pt}/\text{Mo}_2\text{C}$  catalyst and proposed a dual-site reaction mechanism. According to this mechanism, the

catalytic sites are located at the interface between the Mo<sub>2</sub>C and the Pt nanoparticles. The Mo<sub>2</sub>C phase adsorbs and activates water, while the Pt nanoparticle chemisorbs CO [8].

The present work aims at the development of novel Mo<sub>2</sub>C-containing catalysts with higher activity and stability in the WGS, by the addition of the Pt and Cu nanoparticles. Previously we obtained  $\eta$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with different surface and bulk characteristics from Al(NO<sub>3</sub>)<sub>3</sub> and AlCl<sub>3</sub> precursors, respectively [21, 22]. Herein, the structure-activity relationship over  $\eta$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported catalysts with different Mo<sub>2</sub>C loadings (33, 50 and 66 wt %) has been studied. While the alumina support allows fast scale-up via screen printing [23], the effect of the catalyst precursor is crucial in heterogeneous catalysis due to its effect on metal dispersion and close interaction between the active sites. Sabnis et al.[8], Wang et al.[9] and Schweitzer et al.[4], used an H<sub>2</sub>PtCl<sub>6</sub> precursor to prepare their Pt/Mo<sub>2</sub>C catalysts. However, it is well known that the catalysts derived from chlorine-containing precursors could be poisoned by chloride ions adsorbed on the metal surface. For example, the methane total oxidation conversion at 300°C over catalysts prepared from a Cl-containing precursor was much lower as compared to the catalysts prepared from chlorine-free precursors [24, 25].

Herein, we prepared a different range of catalysts using noble (Pt) or transition (Cu) metals loaded on Mo<sub>2</sub>C/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, Mo<sub>2</sub>C/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Mo<sub>2</sub>C for the low-temperature WGS. Using different acidic supports ( $\eta$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) in the catalyst composition, led to different synergetic effect between Pt and Mo<sub>2</sub>C. The prepared catalysts were used in WGS and compared with the commercial catalyst using a real feed composition mixture from the reformer (11 % CO, 43 % H<sub>2</sub>, 6% CO<sub>2</sub>, 21 % H<sub>2</sub>O).

## 2. Experimental

### 2.1 Catalyst preparation

The alumina supports ( $\eta$ -alumina and  $\gamma$ -alumina) were prepared as described in our previous work [21, 26-29] using aluminium nitrate or chloride precursor, after the precipitation by ammonia solution and calcination of the precipitate at 550 °C.

The supported Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> catalysts containing 33, 50 and 66 wt. % Mo<sub>2</sub>C were prepared by a wet impregnation of the respective alumina supports with a solution containing ammonium molybdate tetrahydrate precursor ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O; 81-83% as MoO<sub>3</sub>, Alfa Aesar). The mixture was sonicated at 80 °C (200 HT Crest ultrasonic bath), at a 45 kHz frequency for 3 h and resulted in a homogeneous paste. Then the mixture was dried at 120 °C overnight and calcined at 500 °C for 4 h under air with a heating rate of 2 °C min<sup>-1</sup>. After calcination, the sample was crushed, pelletized and sieved to obtain a 225-450  $\mu$ m fraction. Finally, the pellets were carburized in a flow of 15 vol.%, CH<sub>4</sub>/H<sub>2</sub> (50 ml.min<sup>-1</sup>) as the temperature was increased from the room temperature to 200 °C at a heating rate of 10 °C.min<sup>-1</sup>, and then from 200 to 590 °C at a rate of 1 °C.min<sup>-1</sup>. The temperature was kept at 590 °C for 2 hrs.

The second wet impregnation was used to introduce promoters. In this step, a solution containing Pt(NH<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub> or copper (II) acetate monohydrate precursors were used following the procedure described above. The Pt and Cu metal loading in the obtained catalysts were 4 and 20 wt%, respectively. The samples were designated as X Pt-Y Mo<sub>2</sub>C-Z where index X designates the Pt loading in wt%, index Y designates the Mo<sub>2</sub>C loading in wt% and index Z designates the type of alumina support E- ( $\eta$ -Al<sub>2</sub>O<sub>3</sub>) and G- ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>).

### 2.3 Catalyst characterization

The characterisation techniques are described in the supplementary information.

## 2.4 Catalyst activity measurements

Prior to the catalytic tests, the catalysts were pre-treated in a flow of 15% CH<sub>4</sub>/H<sub>2</sub> at a flow rate of 100 mL min<sup>-1</sup> at 590 °C for 2 h with a heating rate 10 °C min<sup>-1</sup>. In these experiments, 100 mg of catalyst (fraction size: 250-425 μm) was loaded in a fixed-bed reactor made of stainless steel (6 mm OD). The catalyst was placed between two plugs of quartz wool. A mixture of CO, CO<sub>2</sub>, H<sub>2</sub>, and helium was mixed with the corresponding water amount in order to achieve the desired feed gas composition of 11 vol.% CO, 43 vol.% H<sub>2</sub> and 6 vol.% CO<sub>2</sub>, 21 vol.% H<sub>2</sub>O, balance - He with a SV of 125,000 h<sup>-1</sup>. The liquid flow was controlled with a high-performance liquid pump. The products were analyzed by an in-line Perkin Elmer 500 GC equipped with a Hayesep column, thermal conductivity Detector (TCD) and a flame ionization detector (FID).

## 3. Results

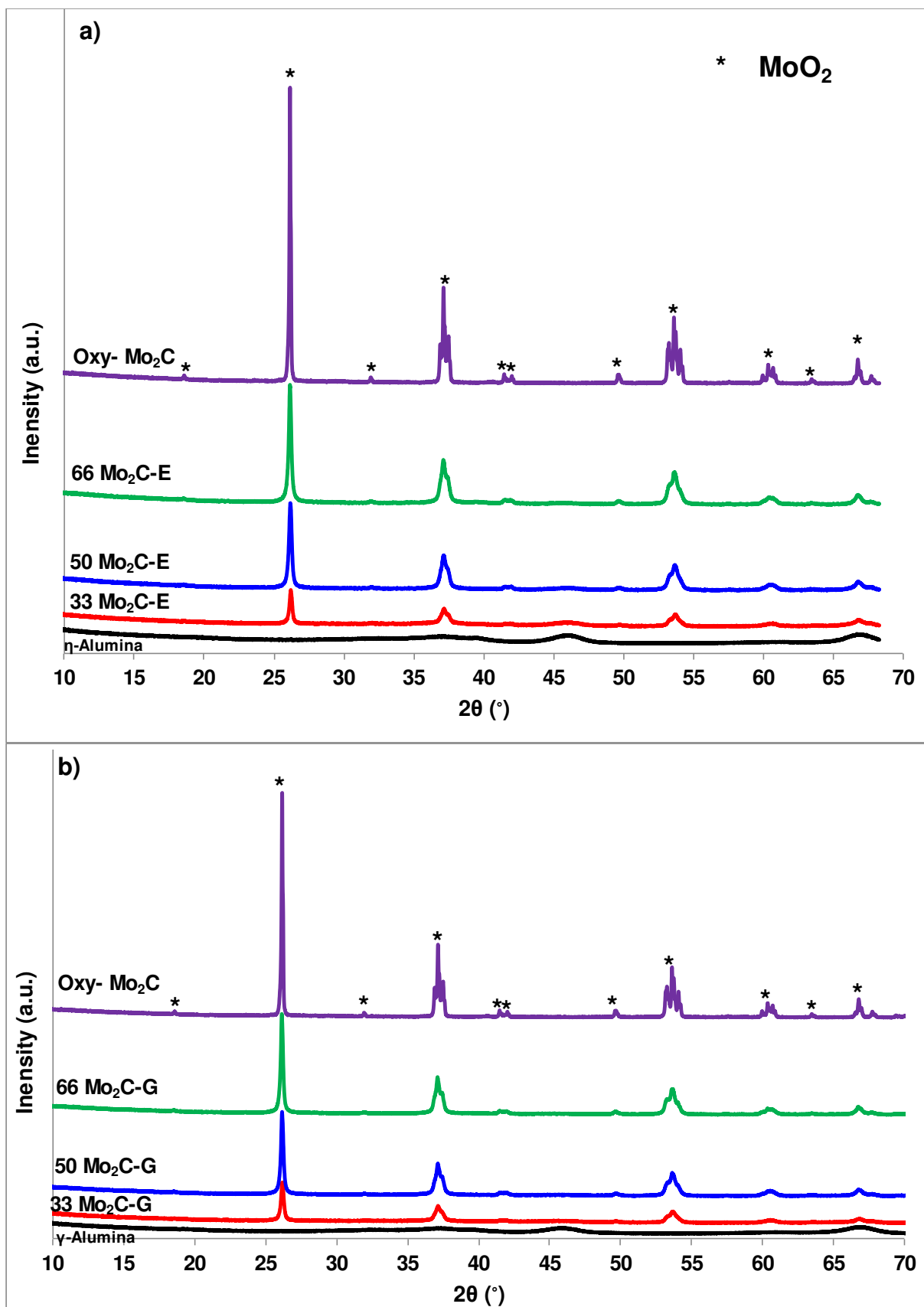
### 3.1. Catalyst characterization

#### 3.1.1. XRD analysis

Figure 1a, shows the XRD patterns of the η-Al<sub>2</sub>O<sub>3</sub>, Mo<sub>2</sub>C, 33 Mo<sub>2</sub>C-E, 50 Mo<sub>2</sub>C-E and 66 Mo<sub>2</sub>C-E catalysts. The XRD patterns of the η-alumina support and a bulk molybdenum carbide catalyst are shown for comparison. The alumina support shows the diffraction peaks corresponding to η-Al<sub>2</sub>O<sub>3</sub> (JCDD 04-0875). After exposure to air, the Mo<sub>2</sub>C phase was oxidized to monoclinic MoO<sub>2</sub> (JCPDS:32-0671) [30]. The appearance of the monoclinic MoO<sub>2</sub> phase can be explained as follows. After carburization process in the CH<sub>4</sub>/H<sub>2</sub> mixture, the molybdenum oxide species were fully converted into β-Mo<sub>2</sub>C [9]. Afterwards, β-Mo<sub>2</sub>C was converted into MoO<sub>2</sub> by a spontaneous oxidation reaction in the air as seen in Equation 1 and 2 with the final phase composition confirmed by the XRD results [4].



The corresponding diffraction lines of MoO<sub>2</sub>, especially those at 2θ= 26.12, 37.11 and 53.58° appeared in both of the studied molybdenum catalysts. The intensity of these lines increased as the molybdenum loading increased from 33 to 66% on η-Al<sub>2</sub>O<sub>3</sub> support.



**Figure 1:** XRD patterns of a)  $\eta$ - $\text{Al}_2\text{O}_3$ , Oxy- $\text{Mo}_2\text{C}$  (passivated  $\text{Mo}_2\text{C}$ ), 33  $\text{Mo}_2\text{C}$ -E, 50  $\text{Mo}_2\text{C}$ -E and 66  $\text{Mo}_2\text{C}$ -E; b)  $\gamma$ - $\text{Al}_2\text{O}_3$ ,  $\text{Mo}_2\text{C}$ , 33  $\text{Mo}_2\text{C}$ -G, 50  $\text{Mo}_2\text{C}$ -G and 66  $\text{Mo}_2\text{C}$ -G.

Figure 1b shows the XRD patterns of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Mo<sub>2</sub>C, 33 Mo<sub>2</sub>C-G, 50 Mo<sub>2</sub>C-G and 66 Mo<sub>2</sub>C-G catalysts. The XRD patterns of the  $\gamma$ -alumina support and a bulk molybdenum carbide catalyst are shown for comparison. The pure alumina support showed the diffraction peaks corresponding to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase (JCDD 10-0425). Once again the bulk Mo-containing catalyst showed monoclinic MoO<sub>2</sub> phase (JCPDS:32-0671) [30]. It is obvious that three of these diffraction lines ( $2\theta = 26.12, 37.11$  and  $53.58^\circ$ ) appeared in the alumina supported Mo<sub>2</sub>C catalysts and these diffraction lines increased in intensity as the molybdenum loading increased from 33 to 66 wt.%. From a previous work [21], the pore volume of  $\eta$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were 0.5 and 0.35 cm<sup>3</sup>.g<sup>-1</sup>, respectively, which suggest a higher Mo<sub>2</sub>C dispersion on  $\eta$ -Al<sub>2</sub>O<sub>3</sub> than that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

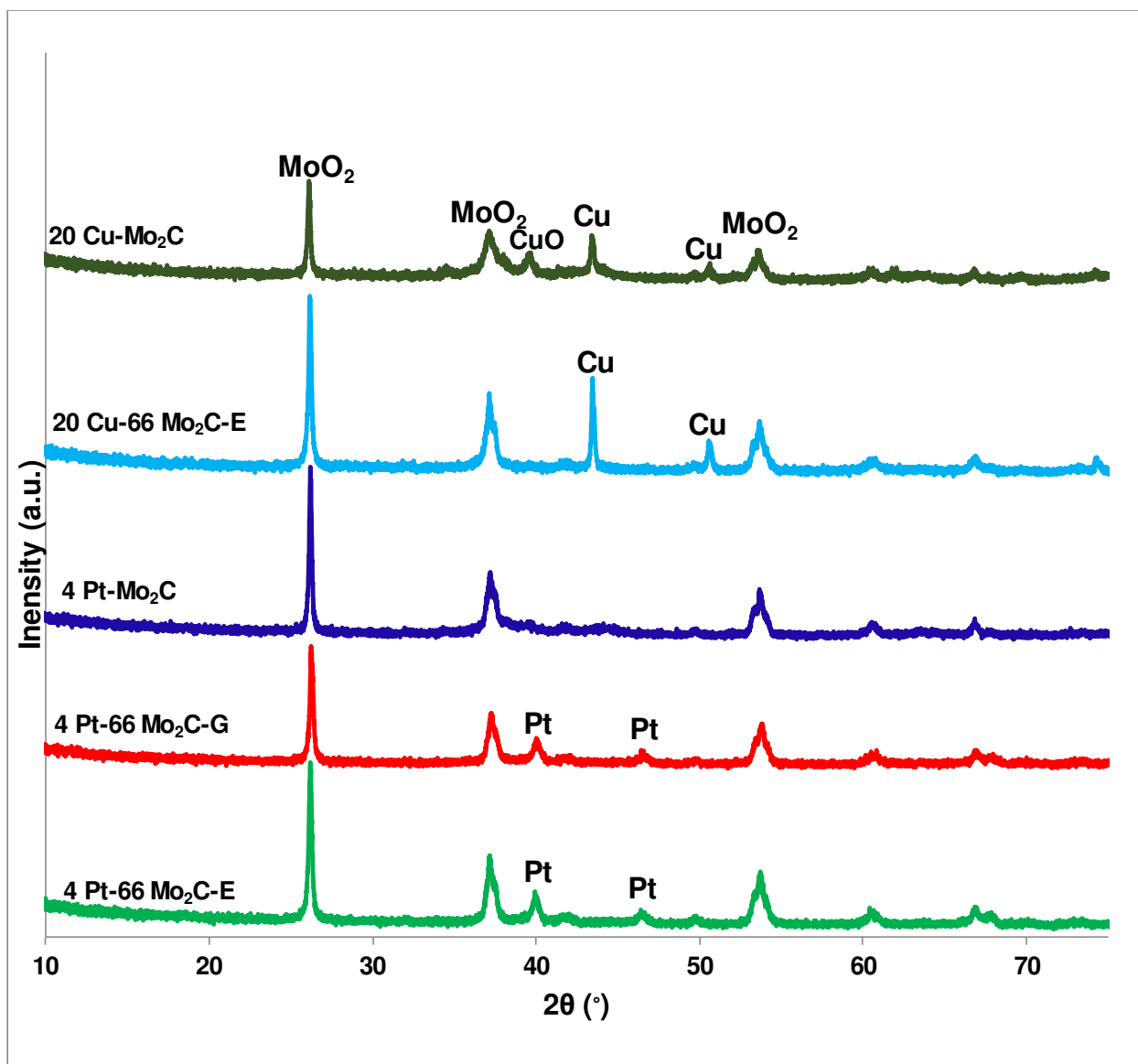
Table 1 shows the surface area of the pure supports along with the Mo<sub>2</sub>C loaded on  $\eta$ -Al<sub>2</sub>O<sub>3</sub> or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. The BET surface areas of the highest loading Mo<sub>2</sub>C on  $\eta$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports are 100 and 79 m<sup>2</sup>.g<sup>-1</sup>, respectively. The higher surface area in case of  $\eta$ -Al<sub>2</sub>O<sub>3</sub> is due to its higher pore volume than that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> resulting from a higher Mo<sub>2</sub>C dispersion. It is obvious that the surface area decreased with increasing the Mo<sub>2</sub>C loading in both  $\eta$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports by 58 and 95 m<sup>2</sup>.g<sup>-1</sup>, respectively, while the pore volume decreased by approximately 0.05 cm<sup>3</sup>.g<sup>-1</sup>. This decrease in the surface area and pore volume suggested that Mo<sub>2</sub>C are filling the pores or deposits on alumina supports.

**Table 1:** Surface area of the supports along with the metals loaded on Mo<sub>2</sub>C/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, Mo<sub>2</sub>C/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Mo<sub>2</sub>C catalysts.

Catalyst Abbreviation	S <sub>BET</sub> (m <sup>2</sup> .g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> .g <sup>-1</sup> )
33 Mo <sub>2</sub> C-E	159	0.27
50 Mo <sub>2</sub> C-E	130	0.24
66 Mo <sub>2</sub> C-E	101	0.21
33 Mo <sub>2</sub> C-G	175	0.18
50 Mo <sub>2</sub> C-G	131	0.16
66 Mo <sub>2</sub> C-G	79	0.13
4 Pt-66 Mo <sub>2</sub> C-E	63	0.10
4 Pt-66 Mo <sub>2</sub> C-G	37	0.06
20 Cu-66 Mo <sub>2</sub> C-E	51	0.11
20 Cu-66 Mo <sub>2</sub> C-G	52	0.07
20 Cu -Mo <sub>2</sub> C	21	0.03
4 Pt-Mo <sub>2</sub> C	61	0.10
Mo <sub>2</sub> C	70	0.11

Figure 2 shows the XRD patterns of Pt or Cu modified Mo<sub>2</sub>C or Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> supports. Again, the main three diffraction lines appeared in all of the prepared catalysts. 4 Pt-66 Mo<sub>2</sub>C-E and 4 Pt-66 Mo<sub>2</sub>C-G catalysts showed two extra diffraction peaks at  $2\theta = 39.61$  and  $46.42^\circ$  which corresponding to the reflections (111),(200), respectively, of face-centred cubic (fcc) structure of platinum metal [31, 32] (JCPDS PDF 04-0802). The appearance of platinum diffraction peaks on those two previous supports confirmed a Pt deposition with relatively large particle size over the alumina surface compared with 4 Pt-Mo<sub>2</sub>C catalyst which showed no appearance of Pt diffraction peaks; this is may be due to the synergetic effect between Pt and Mo<sub>2</sub>C [14, 33]. In copper modified catalysts, Cu metal diffraction lines (JCPDS 04-0836) appeared at  $2\theta = 43.60$  and  $50.81^\circ$  corresponding to (111) and (200), respectively. The 20 Cu-Mo<sub>2</sub>C catalyst showed an extra diffraction line at  $2\theta = 39.51^\circ$  corresponding to copper oxide phase [34].

Table 1 shows the surface area of the Cu or Pt-modified Mo<sub>2</sub>C or Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> supports. Interestingly, the surface area of the pure Mo<sub>2</sub>C decreased on loading previously, it was 4 wt% from 70 to 61 m<sup>2</sup>.g<sup>-1</sup>, and the pore volume remained relatively constant, confirming the synergetic effect between Pt and Mo<sub>2</sub>C [14, 33]. The same effect occurred with 20 Cu-Mo<sub>2</sub>C as the surface area decreased to 21 m<sup>2</sup>.g<sup>-1</sup>. Conversely, the surface area of all other catalysts dramatically decreased with loading 4 wt% Pt. For instance, the surface area of 66 Mo<sub>2</sub>C-E and 66 Mo<sub>2</sub>C-G catalysts were 101 and 79 m<sup>2</sup>.g<sup>-1</sup>, respectively and decreased by loading Pt to 63 and 37 m<sup>2</sup>.g<sup>-1</sup>, respectively. The same effect occurred upon loading 20 wt% Cu over these two catalysts as the surface area decreased to 51 and 52 m<sup>2</sup>.g<sup>-1</sup>, respectively.

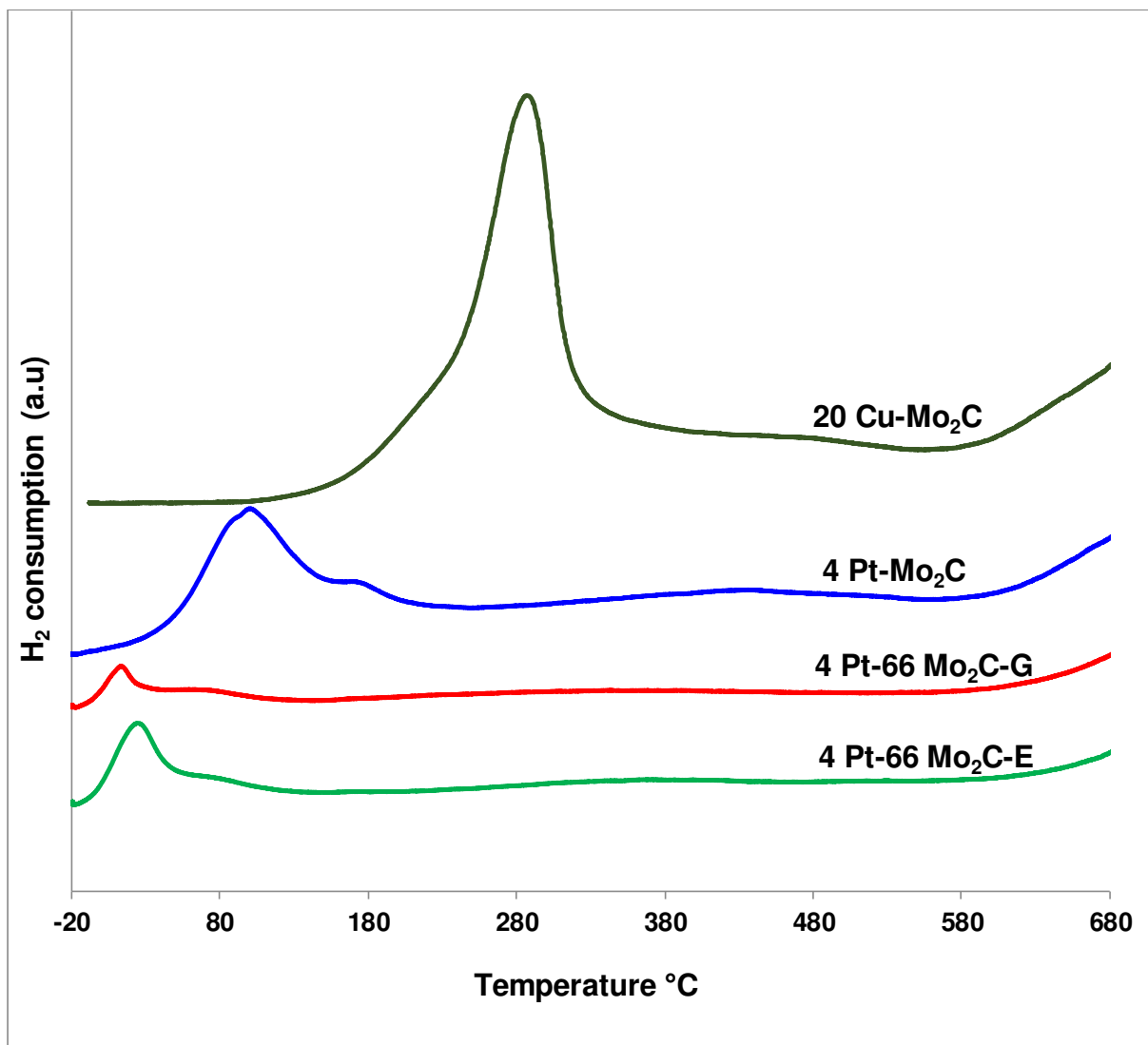


**Figure 2:** XRD patterns of 4 Pt-66 Mo<sub>2</sub>C-G, 4 Pt-66 Mo<sub>2</sub>C-E, 4 Pt-Mo<sub>2</sub>C, 20 Cu-66 Mo<sub>2</sub>C-E and 20 Cu -Mo<sub>2</sub>C.

### 3.1.2. H<sub>2</sub>-TPR analysis

Figure 3 shows the H<sub>2</sub>-TPR profiles of 4 Pt-66 Mo<sub>2</sub>C-G, 4 Pt-66 Mo<sub>2</sub>C-E, 4 Pt-Mo<sub>2</sub>C and 20 Cu-Mo<sub>2</sub>C catalysts as each catalyst showed one reduction peak at 20, 9, 88 and 280 °C, respectively. It is well known that using the reducible supports is more active than that of irreducible supports in WGS [4]. It is apparent that all the Pt-containing catalysts reduced much easier than that of Cu containing catalyst. Among the Pt-containing catalysts, 4 Pt-Mo<sub>2</sub>C

catalyst showed the largest reduction peak which should facilitate the oxidation-reduction cycle and consequently improve the catalytic activity of the catalyst followed by the reduction peak of 4 Pt-66 Mo<sub>2</sub>C-E catalyst. Using the same molybdenum precursor and carburization procedures, pure Mo<sub>2</sub>C was prepared by Wang et al.[9] and Schweitzer et al.[4] and H<sub>2</sub>-TPR characterization showed a single reduction peak at 250 °C. In our work, loading 4% Pt enhanced the reduction process where the reduction peak shifted to a lower temperature at 88 °C compared to the literature.



**Figure 3:** H<sub>2</sub>-TPR profiles of 4 Pt-66 Mo<sub>2</sub>C-G, 4 Pt-66 Mo<sub>2</sub>C-E, 4 Pt-Mo<sub>2</sub>C and 20 Cu -Mo<sub>2</sub>C.

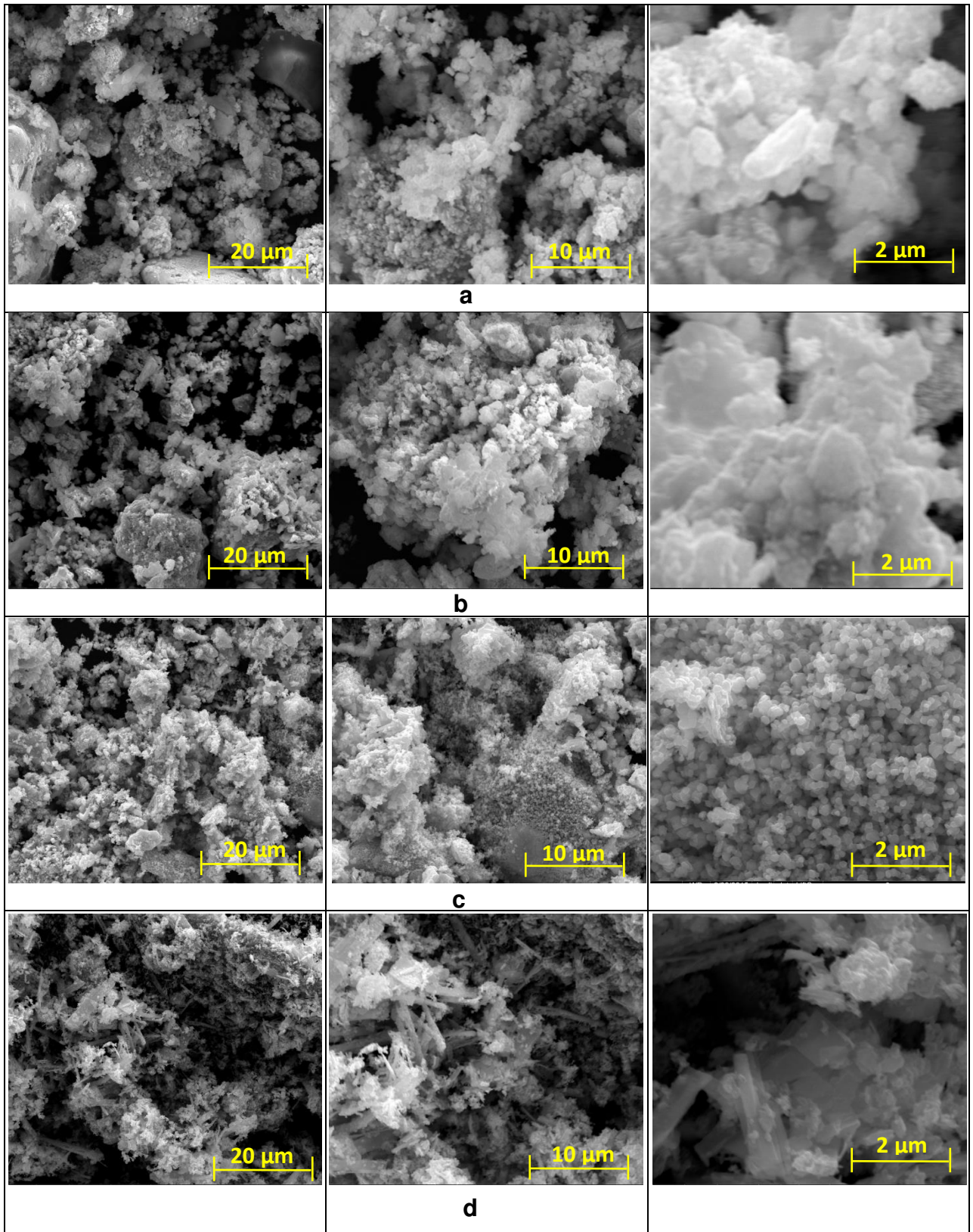
### 3.1.3. SEM-EDX analysis

Figure 4 shows the SEM images of 4 Pt-66 Mo<sub>2</sub>C-E, 4 Pt-66 Mo<sub>2</sub>C-G, 4 Pt-Mo<sub>2</sub>C, and 20 Cu - Mo<sub>2</sub>C catalysts. The particles formed clusters in 4 Pt-66 Mo<sub>2</sub>C-E, 4 Pt-66 Mo<sub>2</sub>C-G, and 20 Cu - Mo<sub>2</sub>C catalysts. While the catalyst 4 Pt-Mo<sub>2</sub>C catalyst showed good particle size distribution. Moreover, the 4 Pt-Mo<sub>2</sub>C catalyst showed smaller particle size than that of the original Mo<sub>2</sub>C catalyst as seen in Figure 5.

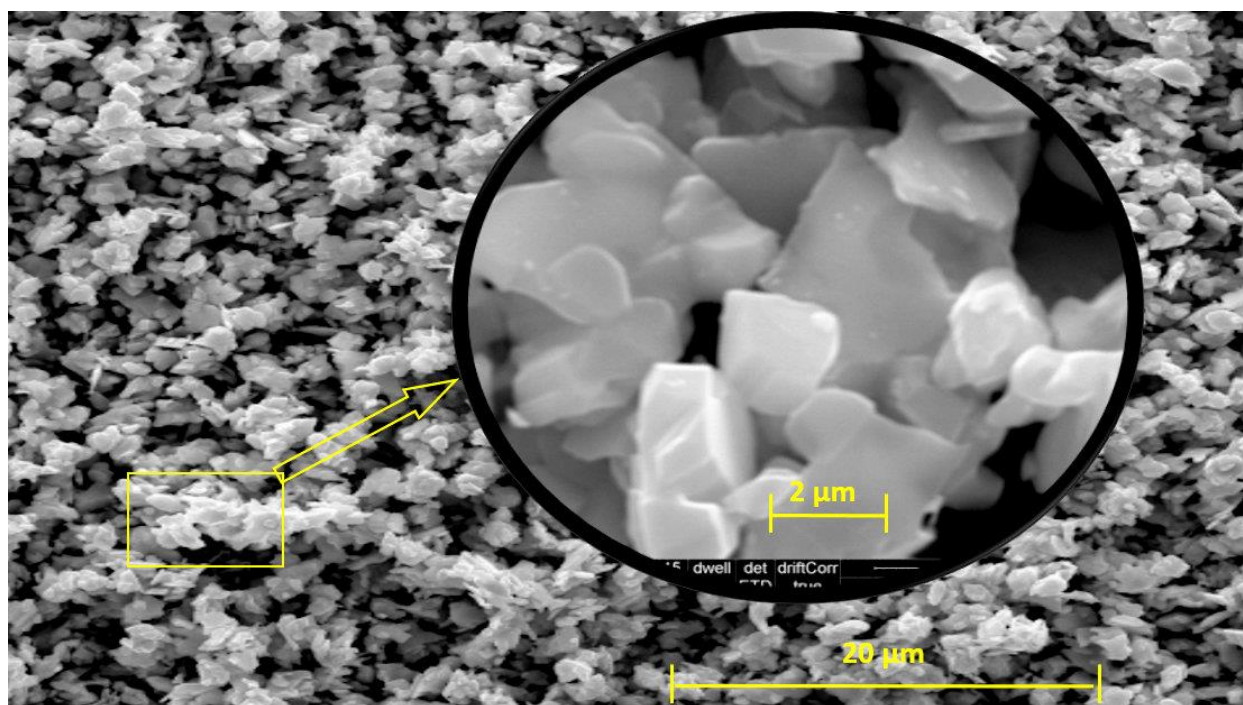
Table 2 shows the EDX data of Mo<sub>2</sub>C, 4 Pt-66 Mo<sub>2</sub>C-E, 4 Pt-66 Mo<sub>2</sub>C-G, 4 Pt-Mo<sub>2</sub>C and 20 Cu - Mo<sub>2</sub>C catalysts. EDX showed that 4 Pt-Mo<sub>2</sub>C offered the best Pt particle size distribution by showing 4.3 wt% of Pt. While 4 Pt-66 Mo<sub>2</sub>C-E and 4 Pt-66 Mo<sub>2</sub>C-G catalysts showed Pt content around 5.5 % and this agrees with the SEM images that showed a cluster formation on the surface of these two catalysts. The copper loading in 20 Cu - Mo<sub>2</sub>C was 20 wt%; EDX result showed 18.6% and this is may be due to the poor copper dispersion as shown by SEM images in Figure 4.

**Table 2:** EDX data of Pure Mo<sub>2</sub>C, 4 Pt-66 Mo<sub>2</sub>C-E, 4 Pt-66 Mo<sub>2</sub>C-G, 4 Pt-Mo<sub>2</sub>C and 20 Cu - Mo<sub>2</sub>C.

	Pt (wt. %)	Mo (wt. %)	O (wt. %)	Al (wt. %)	Cu (wt. %)
Mo <sub>2</sub> C	--	69.5	30.5	--	--
4 Pt-66 Mo <sub>2</sub> C-E	5.1	52.0	35.3	7.5	--
4 Pt-66 Mo <sub>2</sub> C-G	5.5	48.3	35.9	10.3	--
4 Pt-Mo <sub>2</sub> C	4.3	64.6	31.1	--	--
20 Cu - Mo <sub>2</sub> C	--	54.4	27.0	--	18.6



**Figure 4:** SEM images for a) 4 Pt-66 Mo<sub>2</sub>C-E, b) 4 Pt-66 Mo<sub>2</sub>C-G, c) 4 Pt-Mo<sub>2</sub>C, and d) 20 Cu-Mo<sub>2</sub>C at a different level of magnifications using ETD detector.



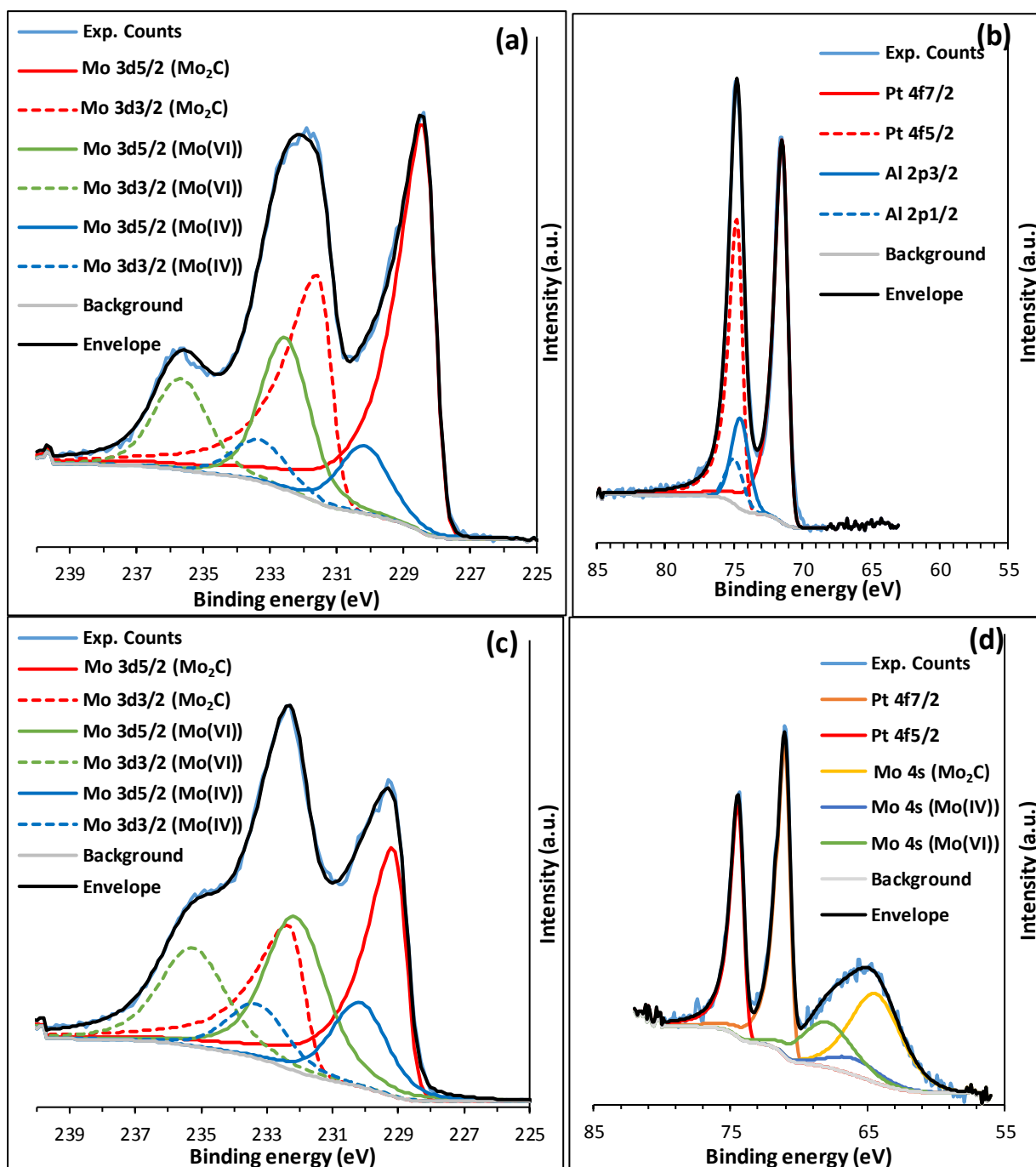
**Figure 5:** SEM image of the pure Mo<sub>2</sub>C catalyst.

#### *3.1.4. Understanding the catalyst structure using XPS analysis*

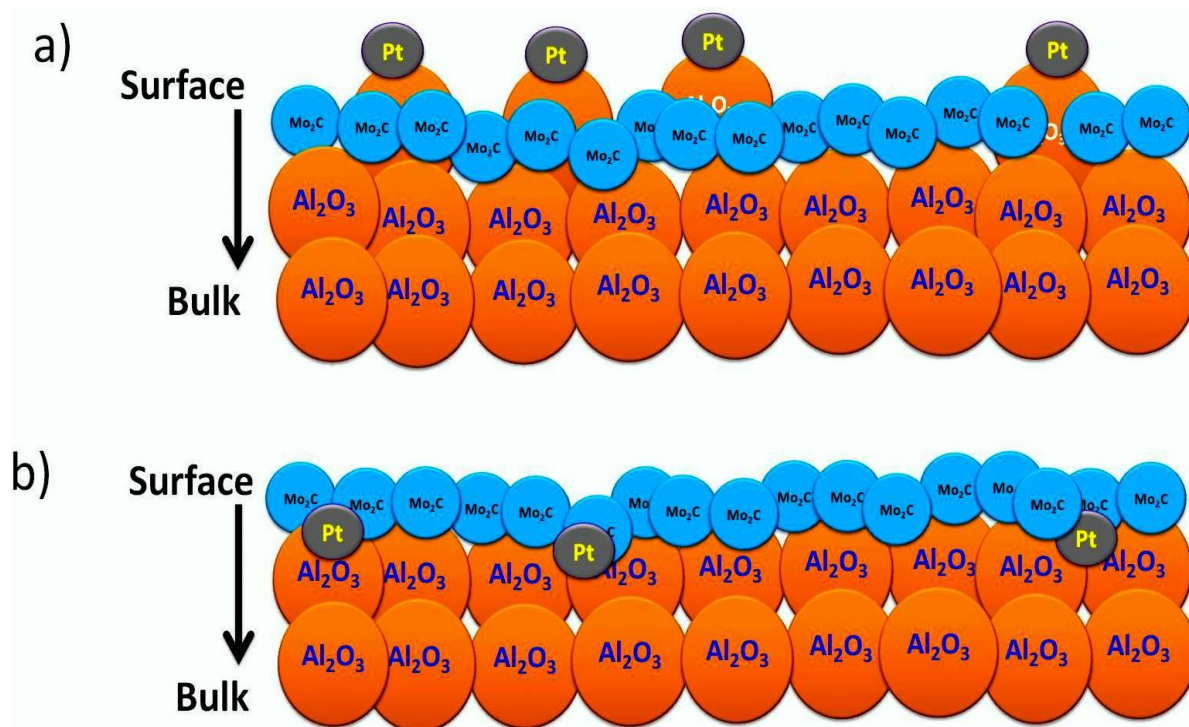
To understand the catalyst structure and molybdenum carbide behaviour of 4 Pt-66 Mo<sub>2</sub>C-G, 4 Pt-66 Mo<sub>2</sub>C-E, XPS and XRD analyses were utilised. X-ray photoelectron spectra of the partially oxidised samples (left in air for short time) are presented in Figure 6. The Mo peak for the 4 Pt-66 Mo<sub>2</sub>C-G sample shows the presence of Mo in three oxidation states; as Mo<sub>2</sub>C, MoO<sub>2</sub> and MoO<sub>3</sub> in the molar ratio of 64:11:25, respectively. Figure 6b shows that Pt was present in the metallic form on the catalyst surface. Moreover, there is a small peak of Al which was also observed at the binding energy of around 120 eV and corresponded to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support material. Interestingly, the survey spectrum showed Mo to Al mass ratio of 5.8, while the nominal sample composition provided the value of 2.2. A significantly higher relative amount of Mo observed on the surface-specific photoelectron spectroscopy indicates that the Mo compounds efficiently covered the surface of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support. The Pt to Mo mass ratio was about 0.057 which agrees with the nominal ratio of 0.060.

Figure 6c shows the Mo 3d peak of the 4 Pt-66 Mo<sub>2</sub>C-E catalyst, where three oxidation states of Mo can be observed in the molar ratio of 46:17:37 for Mo<sub>2</sub>C, MoO<sub>2</sub> and MoO<sub>3</sub>, respectively. The 4 Pt-66 Mo<sub>2</sub>C-E sample compared to the 4 Pt-66 Mo<sub>2</sub>C-G one shows a lower amount of Mo<sub>2</sub>C and an increased MoO<sub>3</sub>. In contrast to the 4 Pt-66 Mo<sub>2</sub>C-G sample, the 4 Pt-66 Mo<sub>2</sub>C-E sample Figure 6d shows the presence of Mo peak close to that for Pt, but no Al. The latter is surprising considering the nominal Al content of 30 wt%. However, considering that XPS is a very surface-specific method, the absence of Al on the spectra can be explained by full coverage of the η-Al<sub>2</sub>O<sub>3</sub> support with Mo which is feasible considering high Mo content. The possibility of η-Al<sub>2</sub>O<sub>3</sub> coverage is also supported by the very low Pt to Mo mass ratio observed of 0.006 for the 4 Pt-66 Mo<sub>2</sub>C-E sample, while the nominal loading was 0.060. Thus, the possible interaction between Pt and Mo<sub>2</sub>C which are the two active sites in WGS in the case of 4 Pt-66 Mo<sub>2</sub>C-E is shown in Scheme 1. On the other hand, 4 Pt-66 Mo<sub>2</sub>C-G showed an interaction between Pt and γ-Al<sub>2</sub>O<sub>3</sub> on the surface of the catalyst as shown in Figure 6 b and Scheme 1. Therefore, XPS results revealed that by using different acidic supports (η-Al<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub>) in the catalyst composition, this led to different interaction because Pt in the catalyst was substantially below the Mo<sub>2</sub>C surface as confirmed by the survey spectra and showed in Scheme 1 along with and synergetic effect between the two most active phases of Pt metal and Mo<sub>2</sub>C which is greater in the case of 4 Pt-66 Mo<sub>2</sub>C-E (η-Al<sub>2</sub>O<sub>3</sub>) catalyst than that of 4 Pt-66 Mo<sub>2</sub>C-G (γ-Al<sub>2</sub>O<sub>3</sub>). We reported earlier that η-Al<sub>2</sub>O<sub>3</sub> and γ-Al<sub>2</sub>O<sub>3</sub> catalysts can be prepared from different precursors of aluminium nitrates and chloride, respectively [21]. The produced catalysts showed different surface morphology and acidity with η-Al<sub>2</sub>O<sub>3</sub> showed higher acidity and better morphology than that of the γ-Al<sub>2</sub>O<sub>3</sub> catalyst. η-Al<sub>2</sub>O<sub>3</sub> showed a total acidity and the acid site density of 8.56 x10<sup>20</sup> (sites.g<sup>-1</sup>) and 3.8 x10<sup>18</sup> (sites.m<sup>-2</sup>), while γ-Al<sub>2</sub>O<sub>3</sub> showed values of 6.91 x10<sup>20</sup> (sites.g<sup>-1</sup>) and 2.5 x10<sup>18</sup> (sites.m<sup>-2</sup>), respectively. Furthermore, η-Al<sub>2</sub>O<sub>3</sub> offered a larger pore volume of 0.5 cm<sup>3</sup>.g<sup>-1</sup>

compared with that of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> of 0.35 cm<sup>3</sup>.g<sup>-1</sup>. The superior morphology and acidity of  $\eta$ -Al<sub>2</sub>O<sub>3</sub> offered a better dispersion of Pt with a close interaction with Mo<sub>2</sub>C.



**Figure 6:** X-ray photoelectron spectra for the 4 Pt-66 Mo<sub>2</sub>C-G sample (a) Mo 3d, (b) Pt 4f peaks and for the 4 Pt-66 Mo<sub>2</sub>C-E sample, (c) Mo 3d and (d) Pt 4f peaks.

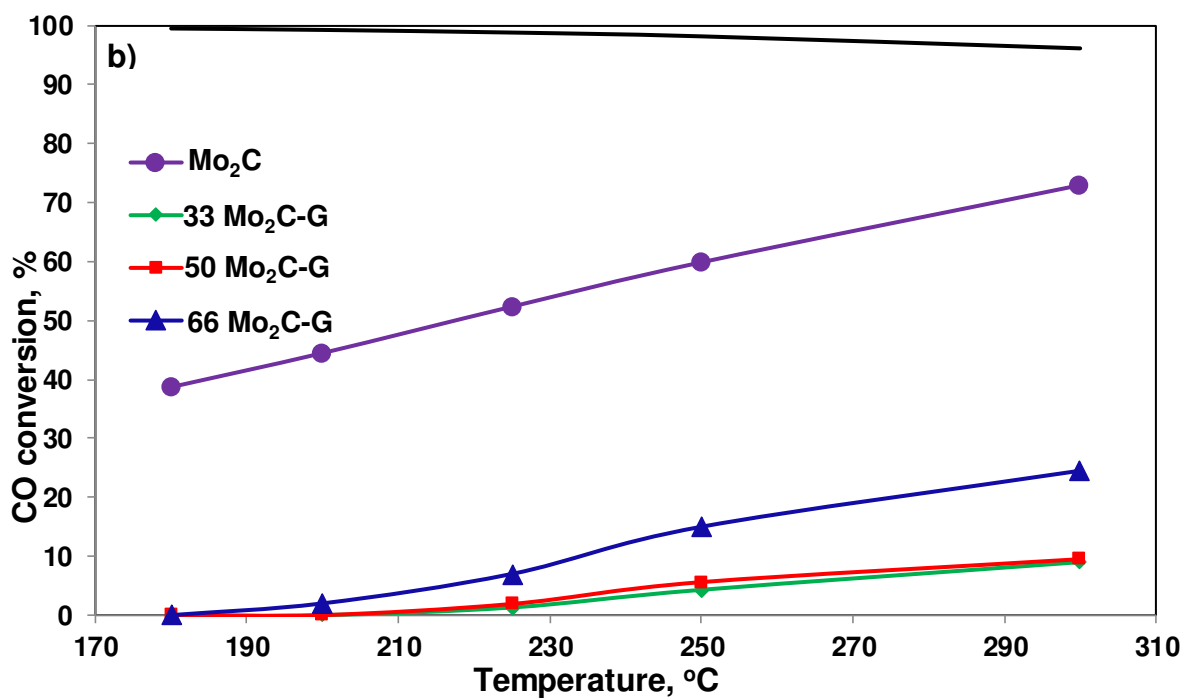
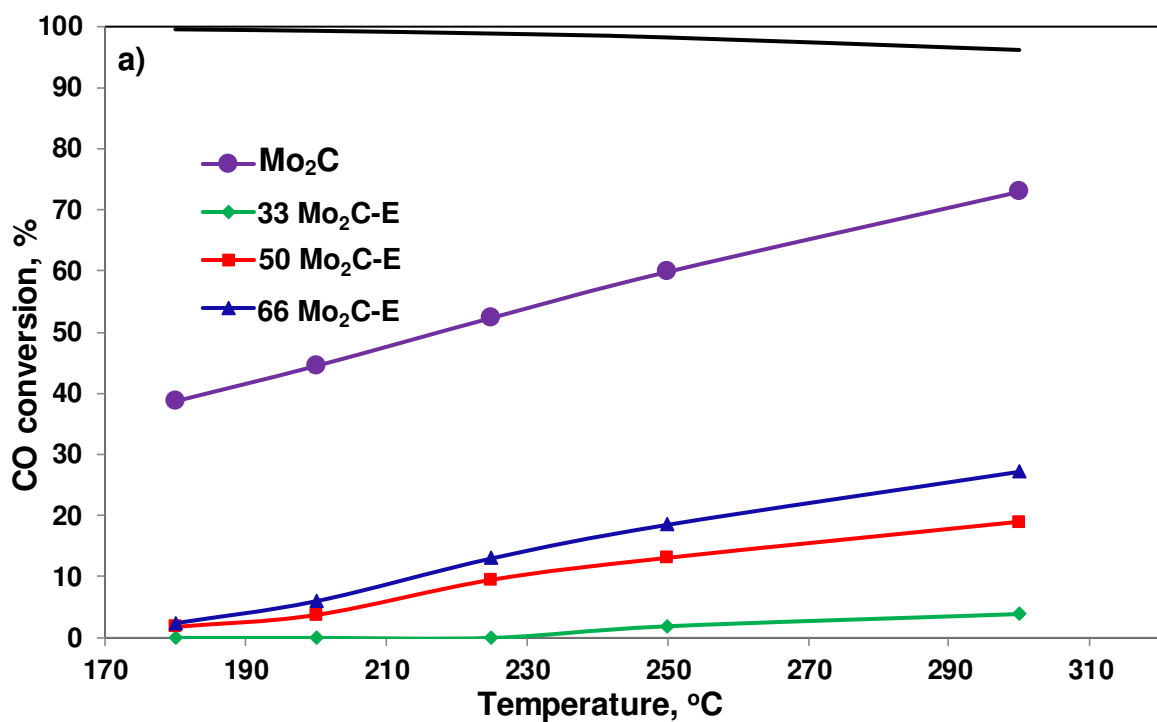


**Scheme 1:** Schematic representation of the structure of 4 Pt-66 Mo<sub>2</sub>C-G (a) and 4 Pt-66 Mo<sub>2</sub>C-E (b) catalysts derived from the XPS results.

Namiki et al.[35] used *in-situ* XPS and DRIFTS techniques to study the mechanism of WGS over Mo<sub>2</sub>C catalyst and found that the WGS on the carburised Mo<sub>2</sub>C/Al<sub>2</sub>O<sub>3</sub> preceded the redox route based on the dissociation of H<sub>2</sub>O and CO. Therefore, a good WGS catalyst indicates a facile reduction/oxidation cycle between the two phases of Mo<sub>2</sub>C and MoO<sub>x</sub> under reaction conditions, thus we investigated the nature of the re-oxidation of Mo<sub>2</sub>C phase. The *in-situ* XRD study shown in Figure S1 (supplementary) demonstrate that the carburized catalyst then left in air for a short time (4 Pt-66 Mo<sub>2</sub>C-E, reduced) has Pt, Mo<sub>2</sub>C and MoO<sub>3</sub> phases. Even gentle heating to 100 °C in the air (4 Pt-66 Mo<sub>2</sub>C-E, fresh) results in a significant decrease in the relative intensity of the Mo<sub>2</sub>C reflections and increase in MoO<sub>2</sub> indicating the quick oxidation of the carbide.

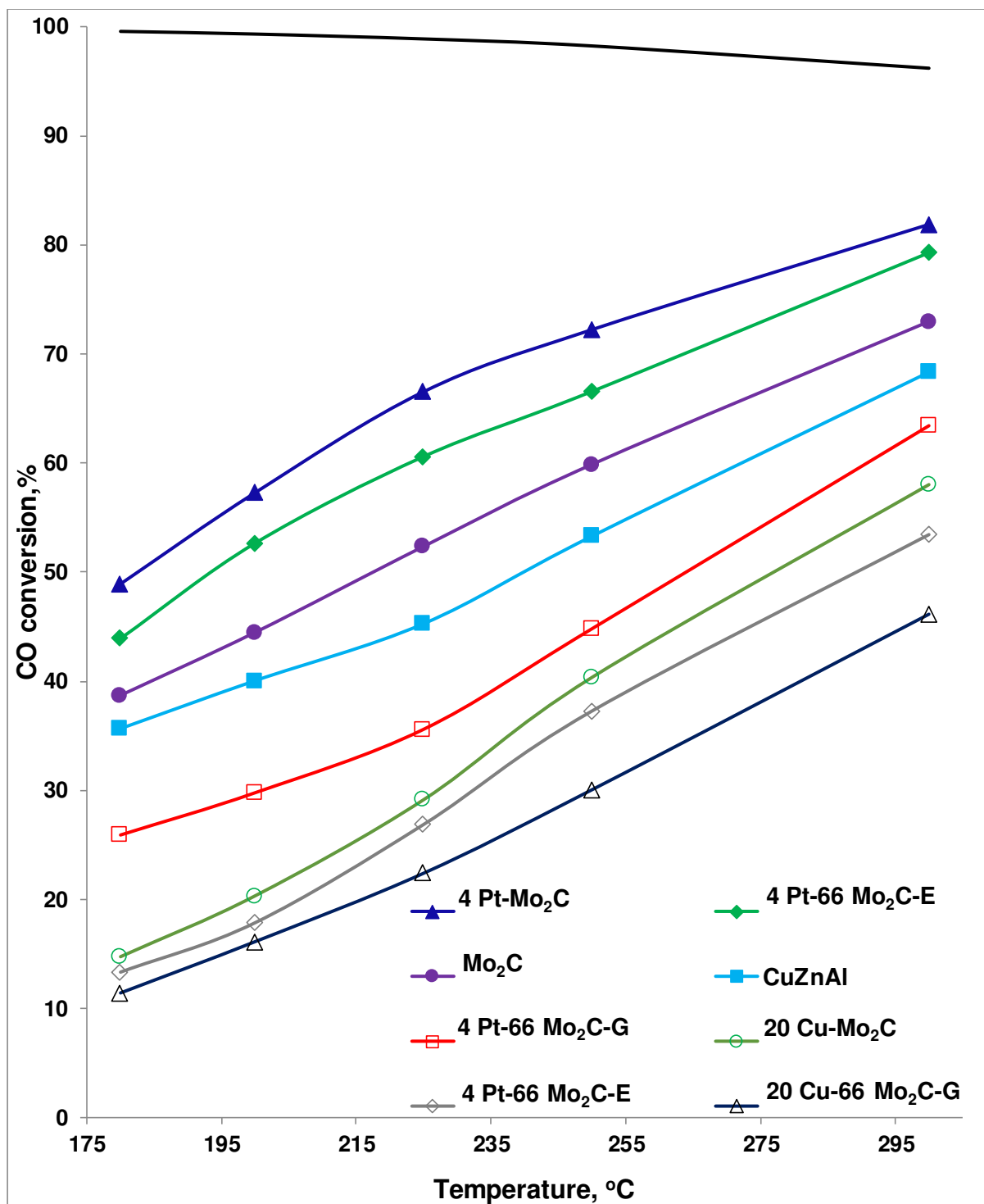
#### 4. Catalytic activity

It was reported that Mo<sub>2</sub>C showed higher catalytic activity than that of commercial catalyst for WGSR [4]. Herein, we used different supports with copper or platinum loadings as described in Table 1. Figure 7 a shows the catalytic activity profiles for WGSR over Mo<sub>2</sub>C, 33 Mo<sub>2</sub>C-E, 50 Mo<sub>2</sub>C-E and 66 Mo<sub>2</sub>C-E catalyst with different Mo<sub>2</sub>C loadings over the temperature range 180-300 °C. The conversion increases with increasing either the reaction temperature or the Mo<sub>2</sub>C loading, which can be explained as Mo<sub>2</sub>C is the only active site for the WGSR and is responsible for the dissociation of water to react with the CO species. The same trend is noticed in the 33 Mo<sub>2</sub>C-G, 50 Mo<sub>2</sub>C-G, 66 Mo<sub>2</sub>C-G and Mo<sub>2</sub>C catalysts as shown in Figure 7b but with less catalytic activity at the same Mo<sub>2</sub>C loading and different support. For instance, the conversion at 300 °C for 66 Mo<sub>2</sub>C-E and 66 Mo<sub>2</sub>C-G are 27.17 and 24.1, respectively. The higher activity in the presence of η-Al<sub>2</sub>O<sub>3</sub> support can be attributed to the synergetic effect between Pt and Mo<sub>2</sub>C as shown from the XPS results in Figure 6 and Scheme 1 along with the higher pore volume of 0.5 for η-Al<sub>2</sub>O<sub>3</sub> and 0.35 for γ-Al<sub>2</sub>O<sub>3</sub>. Although Mo<sub>2</sub>C, 66 Mo<sub>2</sub>C-E and 66 Mo<sub>2</sub>C-G showed the highest catalytic activity in the previous series of catalysts, those catalysts still require further promotion to achieve better catalytic activity and stability during the WGSR. Thus, 4 wt.% Pt and 20 wt.% Cu metals were added to that catalyst where the final prepared catalysts designated as 4 Pt-Mo<sub>2</sub>C, 4 Pt-66 Mo<sub>2</sub>C-E, 4 Pt-66 Mo<sub>2</sub>C-G, 20 Cu-Mo<sub>2</sub>C, 20 Cu-66 Mo<sub>2</sub>C-E and 20 Cu-66 Mo<sub>2</sub>C-G.



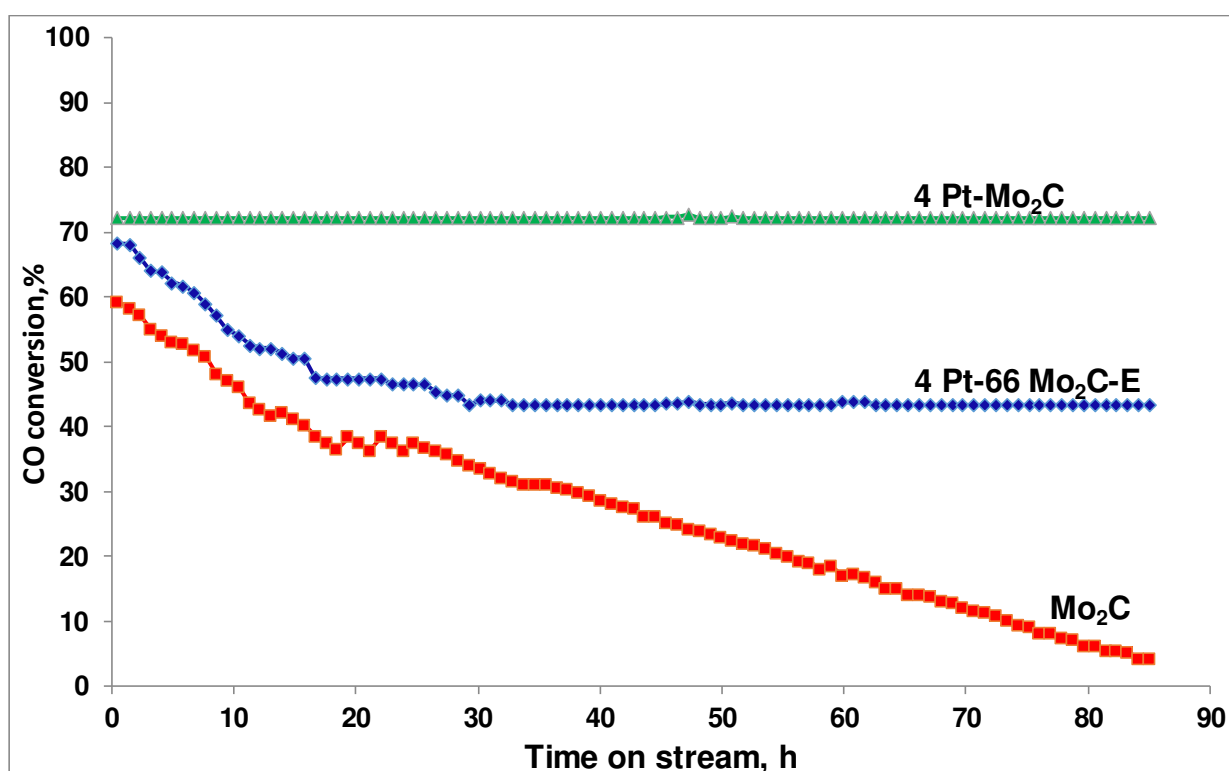
**Figure 7:** Catalytic activity profiles for WGS over a) Mo<sub>2</sub>C, 33 Mo<sub>2</sub>C-E, 50 Mo<sub>2</sub>C-E and 66 Mo<sub>2</sub>C-E; b) Mo<sub>2</sub>C, 33 Mo<sub>2</sub>C-G, 50 Mo<sub>2</sub>C-G and 66 Mo<sub>2</sub>C-G along with the equilibrium line in black colour. Reaction conditions: temperature, 180-300 °C; SV ~ 125,000 h<sup>-1</sup>. 11% CO, 43% H<sub>2</sub>, 6% CO<sub>2</sub>, 21% H<sub>2</sub>O, and balance He.

Figure 8 shows the catalytic activity for WGS over different catalysts of 4 Pt-Mo<sub>2</sub>C, 4 Pt-66 Mo<sub>2</sub>C-E, Mo<sub>2</sub>C, 4 Pt-66 Mo<sub>2</sub>C-G, 20 Cu -Mo<sub>2</sub>C, 20 Cu-66 Mo<sub>2</sub>C-E, 20 Cu-66 Mo<sub>2</sub>C-G along with the commercial CuZnAl catalysts. In all catalysts, the CO conversion increased with increasing the reaction temperature. All the copper catalysts loaded Mo<sub>2</sub>C or Mo<sub>2</sub>C-alumina support exhibit low activity at reaction temperatures below 250 °C and have lower conversion than the Pt-based catalysts. For instance, at a reaction temperature of 300 °C, 20 Cu -Mo<sub>2</sub>C and 4 Pt-Mo<sub>2</sub>C have catalytic conversions of 58 and 81.9 %, respectively. Such differences can be attributed to the active site in metal/Mo<sub>2</sub>C catalysts is bi-functional for WGS as proved by Sabnis et al.[20]. Moreover, the reducibility of the catalyst can play a big role in the catalytic activity, as confirmed by the TPR results, where the reduction temperature for 20 Cu -Mo<sub>2</sub>C was 280 °C whereas for 4 Pt-Mo<sub>2</sub>C is 88 °C.



**Figure 8:** Catalytic activity profiles for WGS over 4 Pt-Mo<sub>2</sub>C, 4 Pt-66 Mo<sub>2</sub>C-E, Mo<sub>2</sub>C, 4 Pt-66 Mo<sub>2</sub>C-G, 20 Cu-Mo<sub>2</sub>C, 20 Cu-66 Mo<sub>2</sub>C-E, 20 Cu-66 Mo<sub>2</sub>C-G and CuZnAl catalysts along with the equilibrium line in black colour. Reaction conditions: temperature, 180-300 °C; SV ~ 125,000 h<sup>-1</sup>. 11% CO, 43% H<sub>2</sub>, 6% CO<sub>2</sub>, 21% H<sub>2</sub>O, and balance He.

For the catalyst to meet the commercialization requirements, it should offer good stability behaviour during the operating conditions. Figure 9 shows a comparison of the stability of  $\text{Mo}_2\text{C}$ , 4 Pt-66  $\text{Mo}_2\text{C}$ -E and 4 Pt- $\text{Mo}_2\text{C}$  at a reaction temperature of  $250^\circ\text{C}$  for 85 h. The catalytic activity of 4 Pt-66  $\text{Mo}_2\text{C}$ -E and 4 Pt- $\text{Mo}_2\text{C}$  is similar at time zero on stream but with time on stream, the CO conversion over 4 Pt-66  $\text{Mo}_2\text{C}$ -E decreased from 68 to 43% after 30 h then stabilised for the next 55 h, while 4 Pt- $\text{Mo}_2\text{C}$  was stable over the reaction time which is in agreement with the results of Yan et al.[14].



**Figure 9:** Comparison of the stability of  $\text{Mo}_2\text{C}$ , 4 Pt-66  $\text{Mo}_2\text{C}$ -E and 4 Pt- $\text{Mo}_2\text{C}$ . Reaction conditions: temperature,  $250^\circ\text{C}$  for 85 hr; SV  $\sim 125,000 \text{ h}^{-1}$ . 11% CO, 43%  $\text{H}_2$ , 6%  $\text{CO}_2$ , 21%  $\text{H}_2\text{O}$ , and balance He.

Compared with the literature, our results show 4-5 times higher activity with the  $T_{50\%}$  for Pt-Mo<sub>2</sub>C was 180°C which is lower than in previous research work performed over the Pt/CeO<sub>2</sub> catalyst, which showed the  $T_{50\%}$  value of 400°C [36]. On the addition of Pt, the stability experiments showed no decrease in the catalyst activity over 85 hours at 250 °C.

## 5. Conclusion

Herein different Pt and Cu based catalysts at different supports (Mo<sub>2</sub>C, 4 Pt-66 Mo<sub>2</sub>C-E and 4 Pt-66 Mo<sub>2</sub>C-G) were studied for low-temperature water gas shift reaction. The prepared catalysts were used in WGSR and compared with the commercial catalyst using a real feed composition mixture from the reformer (11 % CO, 43 % H<sub>2</sub>, 6% CO<sub>2</sub>, 21 % H<sub>2</sub>O). It was found that the 4 Pt-Mo<sub>2</sub>C catalyst has the highest activity and the most stable catalyst over 85 hours at 250 °C. XPS results revealed that by using different acidic supports ( $\eta$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) led to different interaction and synergetic effect between the two most active phases of Pt metal and Mo<sub>2</sub>C.

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**Conflict of Interest Statement:** The authors declare no conflict of interest.

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