Graphical Abstract

**Probing the Active Sites for Water-Gas Shift over Pt/Molybdenum Carbide using
Multi-Walled Carbon Nanotubes**

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Abstract

Pt/Mo₂C is known to have water-gas shift (WGS) rate per total mole of Pt that is higher than on any oxide-supported Pt catalyst. The difficulties for the characterization of Pt/Mo₂C were overcome by preparing the carbide using Multi-Walled Carbon Nanotubes (MWCNT), which showed the expected kinetics. X-ray absorption spectroscopy confirmed formation of alloy with Mo and STEM-EELS data confirmed the elemental composition of Pt particles as Pt-Mo for a series of Pt/Mo₂C/MWCNT catalysts. A linear correlation is obtained between the WGS rate per gram at 120°C and the area covered by Pt-Mo alloy nanoparticles on Mo₂C, estimated using STEM images. Pt is shown to preferentially bind to the Mo₂C domains. The kinetic data in tandem with the characterization techniques suggest that the active sites are formed by Pt-Mo alloy nanoparticles in contact with Mo₂C, not by the formation of the alloy. The water activation on Mo₂C is suggested to be the cause for the higher WGS rate over Pt/Mo₂C.

Keywords

Molybdenum carbide; Platinum; Water-gas shift; MWCNT; STEM-EELS; XAS

1. Introduction

Metal-modified transition metal carbides have been a topic of interest in the field of heterogeneous catalysis, owing to their intriguing catalytic properties [1]. Recent studies have shown that admetals such as Pt and Ni can dramatically affect those properties [2–5]. The source of these effects is the ability of molybdenum carbide surfaces to stabilize the small admetal nanoparticles [6].

It has been shown previously by Schweitzer et al. [2] that platinum/ molybdenum carbide (Mo_2C) has WGS rate per gram of catalyst higher than the commercial $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst at 240°C in presence of 11% CO , 6% CO_2 , 21% H_2O , 43% H_2 and balance N_2 . Platinum supported on Mo_2C was also shown to have WGS rate per total mole of Pt that was higher than that of any oxide supported Pt catalysts [2]. In our previous work [7], we have verified these results, also confirming that the transition metal-modified molybdenum carbide catalysts exhibit water gas shift (WGS) reaction rates that are 4 to 8 times higher than the commercial catalyst when normalized by the surface area of the catalyst. Unlike the oxide supports, Mo_2C exhibits its own WGS activity; hence the WGS rates measured over metal/ Mo_2C are a combination of the rates due to Mo_2C support sites and the rate due to the sites created by the admetal. The combination of metal and carbide, however, produces a catalyst that has a rate much higher than the sum of the two. Additional challenges are that Mo_2C adsorbs chemisorption molecules (such as CO and H_2), which are normally used for determination of the exposed surface area of the admetal particles [2] for normalization of the WGS rate. Bulk Mo_2C also has sufficiently high Z (atomic number) to create poor contrast between admetal particles and the Mo_2C support when imaged in electron microscopy. In short, from the point of view of catalyst

characterization for determination of the active sites, bulk Mo_2C is not an ideal catalyst. In order to overcome the aforementioned limitations, in the present work, we have utilized Multi-Walled Carbon Nanotubes (MWCNT) as the support for the synthesis of $\text{Pt}/\text{Mo}_2\text{C}$, allowing us to de-convolute the importance of Pt or $\text{Pt}-\text{Mo}_2\text{C}$ contact sites towards the WGS reaction rates from the contribution of Mo_2C . We have performed X-ray absorption spectroscopy to observe the working state of the catalysts during the carburization pretreatment and WGS reaction. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) combined with Electron Energy Loss Spectroscopy (EELS) was used to understand the morphology of the catalysts and qualitatively determine the elemental composition of the supported metal particles over Mo_2C . The results indicate that Pt is preferentially bound to the Mo_2C domains forming an alloy. The active sites are shown to be created by the Pt-Mo alloy nanoparticles supported on Mo_2C .

2. Experimental Methods

2.1. Catalyst Preparation. The catalysts prepared for this work were a series of $\text{Pt}/\text{Mo}_2\text{C}/\text{MWCNT}$ samples with varying Pt and Mo weight loadings. The low-Z MWCNTs have been shown to be a good support for catalyst characterization using electron microscopy and X-ray absorption techniques [8]. The MWCNT support was purchased from Cheap Tubes Inc. The as purchased support was treated with 69 wt% HNO_3 for 4 h at 120°C , followed by washing with deionized water. After the support was dried overnight, the metals were added by sequential incipient wetness impregnations. An aqueous solution of ammonium paramolybdate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, Alfa Aesar) was

used as the Mo precursor. After the impregnation of Mo, the material was dried overnight in a static oven at 150°C. The dried material was subjected to temperature programmed reduction in presence of pure hydrogen (ramp rate 3°C min⁻¹, final temp. 600 °C) and was maintained at the final temperature for 4 hours. During this reduction process, the carbon from the support reacted with the Mo to form Mo₂C domains [9]. This material was passivated at RT with 1% O₂/Ar mixture, before Pt was impregnated using the aqueous solution of tetrammineplatinum nitrate (Sigma Aldrich). Two sets of catalysts were prepared: (1) varying the Mo loading (to vary the amount of Mo₂C formed) while keeping the Pt loading fixed and (2) varying the Pt loading (to increase the number of Pt/Mo₂C contact sites) at a fixed Mo loading. For the first series, the Pt loading was kept fixed at 1.5 wt %, while the Mo loading was varied as 2 wt%, 3 wt%, 10 wt% and 20 wt%. For the other series, the Mo loading was fixed at 10%, while the Pt loading was varied as 0 wt% (no Pt), 0.5 wt%, 1.5 wt%, 3 wt% and 5 wt%. A Mo-free sample 4 wt% Pt/MWCNT was also synthesized.

2.2. WGS Kinetic Measurements. The WGS reaction rates and apparent kinetic parameters were measured using a four fixed bed, plug flow reactor system described elsewhere [10]. Appropriate amounts of each catalyst were loaded. The catalysts were reduced in pure H₂ (75 sccm) at 600°C (3°C min⁻¹) for 4 h, in order to remove the oxygen introduced during passivation from the surface of Mo₂C. Following the reduction pretreatment, the catalysts were cooled to 120°C under Ar. The WGS reaction mixture comprised of 7% CO, 22% H₂O, 8.5% CO₂, 37.5% H₂ and balance Ar was introduced as feed to the reactors. Prior to the measurement of apparent kinetic parameters, the catalysts were maintained under the aforementioned WGS conditions for 20 h. In order to

achieve differential conditions, the conversion of CO was kept below 10%. For the measurement of apparent reaction orders, one gas concentration was varied at a time (4–21% CO, 5–25% CO₂, 11–34% H₂O, and 14–55% H₂). The apparent activation energies were measured by varying the temperature over a range of 110 to 140°C, while keeping the gas concentrations fixed at standard conditions. After the measurement of apparent kinetic parameters, the catalysts were passivated at room temperature in 1% O₂ in Ar.

2.3. Catalyst Characterization. The CO uptake was measured over each catalyst at 35°C using the Micromeritics ASAP 2020 analyzer. A second isotherm was measured after evacuation at 35°C. The difference of CO uptakes between first and second isotherms was extrapolated to zero, in order to estimate the amount of CO strongly (irreversibly) adsorbed. Prior to the chemisorption measurement, the passivated catalysts were reduced in H₂ at 600°C. The CO uptake measurements are used as a measure of the total number of active sites (Mo₂C sites and the sites created by the addition of Pt).

The *in situ* and *ex situ* X-ray absorption (XAS) experiments at the Pt L_{III} edge and the Mo K edge were carried out at the MRCAT 10 BM (bending magnet) beam line at the Advanced Photon Source at Argonne National Laboratory. Due to the low-Z MWCNTs, all the XAS experiments could be carried out in the transmission mode. The XAS experiments were conducted in 1 inch OD quartz tubes connected to welded ball valves with Ultra-Torr fittings (for gas inlet/outlet and sealing) and to Kapton windows. The catalyst samples were pressed into a 6 well sample holder as self-supporting wafers. The sample holder was placed inside a 1 inch OD quartz tube. The catalysts were reduced at 600°C, *in situ* in pure H₂. The scans at Pt L_{III} edge and Mo K edge were collected at RT

in presence of He. The X-ray absorption was also measured for the catalysts with varying Pt loading under WGS conditions at 160°C, following the reduction at 600°C. The catalysts were exposed to a mixture of 6.8% CO, 8.5% CO₂, 22% H₂O, 37.4% H₂ and balance helium.

The XAS data were analyzed using WINXAS 3.1 software. The X-ray absorption data were energy-calibrated by aligning the inflection point of the leading edge of the X-ray absorption near edge spectra (XANES) for Pt and Mo metal foil standards to the known energy positions. The edge energies for the Pt and Mo XANES data for various catalyst samples were determined from the inflection point in the leading edge, i.e., the maximum in the first derivative, of the XANES spectra. The extended X-ray absorption fine structure (EXAFS) data were fitted using experimental standards and references computed using the FEFF6 code. Phase shifts and amplitudes for Pt-Pt and Mo-Mo scatters were obtained from the foil standards of the respective elements. The phase and amplitude for the Pt-Mo bimetallic alloy was obtained using FEFF6. The model parameters e.g., S_0 , $\Delta\sigma^2$ etc., were determined by fitting the Pt and Mo foils. From the least square fits for the first shell, average coordination numbers, bond distances and the Debye-Waller factors were obtained for all the tested catalysts.

STEM and EELS analyses were carried out at 200 kV using a dedicated aberration-corrected STEM Hitachi HD-2700C equipped with a modified Gatan Enfina ER spectrometer and hosted at the Center for Functional Nanomaterials, Brookhaven National Laboratory. The convergence angle and the ADF collection angles were 28 mrad and 64-341 mrad, respectively. The Enfina spectrometer entrance aperture was set to 3 mm resulting in EELS collection angle of 26.7 mrad and an energy resolution of 0.35 eV

as measured from the full width at half maximum (FWHM) of the zero-loss peak. The EELS spectra for Mo, and Pt were collected at the $M_{4,5}$ edges. The EELS dwell time was varied between 0.1–0.3 seconds to avoid beam induced structural changes. The step size for line-scans and mapping was varied between 1-3 Å. The core-loss intensities were extracted by extrapolating the background using a power-law model and subtracting it from the acquired signal. Data processing was carried out using Gatan Digital Micrograph.

The area of the MWCNT support covered by the Mo_2C domains as well as the Pt containing particles was computed using ImageJ software. The average particle size of the Pt containing particles over the catalysts used for WGS was measured using the Adobe Photoshop software.

3. Results

3.1 Interpretation of WGS Kinetics

The method of preparation of Mo_2C /MWCNT was adapted from the published literature [9]. As mentioned, two sets of Pt/ Mo_2C /MWCNT catalysts were prepared: (1) varying the Mo loading (to vary the amount of Mo_2C formed) while keeping the Pt loading fixed (1.5 wt%) and (2) varying the Pt loading (to increase the number of Pt- Mo_2C contact sites) at a fixed Mo loading (10 wt%). The detailed WGS kinetic data over these catalysts are presented in Table 1. Except for the 10 wt% Mo/MWCNT (Pt free) catalyst and the 4 wt% Pt/MWCNT (Mo free) catalyst, all the other catalysts in these two sets were tested at 120°C, so that the WGS kinetic parameters can be objectively compared.

Table 1: WGS Kinetic data measured over Pt/Mo₂C/MWCNT catalysts at 120°C

Catalyst	WGS Rate at 120°C/10 ⁻² mol H ₂ (mol Pt) ⁻¹ s ⁻¹	WGS Rate at 120°C/ 10 ⁻⁶ mol H ₂ (g cat.) ⁻¹ s ⁻¹	Ea /kJ(mol) ⁻¹ (±3)	H ₂ O (±0.04)	CO ₂ (±0.04)	CO (±0.04)	H ₂ (±0.04)
4% Pt/MWCNT ^a	1.1×10 ⁻³	2.3×10 ⁻³	83	0.87	-0.09	0.15	-0.38
0.5% Pt/10%Mo/MCWNT	1.6	0.40	58	0.75	-0.01	-0.04	-0.19
1.5% Pt/10%Mo/MWCNT	1.7	1.3	55	0.70	-0.04	-0.01	-0.24
3% Pt/10%Mo/MWCNT	1.4	2.1	52	0.79	-0.02	-0.09	-0.25
5% Pt/10%Mo/MWCNT	1.2	3.1	48	0.75	0.00	-0.11	-0.30
1.5% Pt/2%Mo/MWCNT	0.90	0.70	49	0.78	0.01	-0.13	-0.30
1.5% Pt/3%Mo/MWCNT	1.3	1.0	51	0.80	-0.01	-0.03	-0.24
1.5% Pt/10%Mo/MWCNT	1.7	1.3	55	0.70	-0.04	-0.01	-0.24
1.5%Pt/20%Mo/MWCNT	1.9	1.5	55	0.72	-0.03	-0.05	-0.32
10%Mo/MWCNT ^b	----	2.0×10 ⁻²	56	0.59	-0.14	0.55	-0.31
1.5% Pt/Mo ₂ C[7]	2.7	1.8	45	0.72	-0.02	0.05	-0.33
Mo ₂ C[7]	----	0.3	87	-0.10	-0.10	0.54	-0.12

a. Measured at 270°C

b. Measured at 190°C

As shown in Table 1 and Figure S1, the apparent WGS reaction orders over Pt/Mo₂C/MWCNT catalysts are independent of both Pt and Mo loading. The apparent orders observed are H₂O (0.75 ± 0.04), CO (-0.05 ± 0.04), CO₂ (-0.02 ± 0.02), and H₂ (-0.26 ± 0.05). This suggests that the chemical nature of the active sites over these catalysts is similar across the two sets of samples tested for WGS. More importantly, the apparent reaction orders over Pt/Mo₂C/MWCNT catalysts are similar to the apparent reaction orders, apparent activation energies (49-56 kJ mol⁻¹), and the rates per total mole of Pt ($1-2 \times 10^{-2}$ s⁻¹) measured over Pt/bulk Mo₂C [7]. While it is possible that the agreement of these apparent kinetic parameters could be the coincidental overlap of different detailed kinetic mechanisms, the agreement, together, with chemical similarity of the catalytic materials supplied by the detailed characterization analysis, provide strong evidence that such a scenario is unlikely. Thus, the MWCNT supported catalysts are used as ‘surrogates’ for the characterization of Pt/Mo₂C systems, based on the conclusion that they possess the active sites of similar chemical nature.

The central idea is to de-convolute the importance of Pt sites (Pt-Mo₂C contact sites) from the Mo₂C sites, towards the WGS reaction, as Mo₂C has significant reactivity for WGS at 120 °C. As all the catalysts in the two sets possess the active sites of similar nature, the difference in the WGS rates (normalized by the amount of catalyst) is caused only by the difference in the absolute number of active sites over these catalysts.

As shown in Figure 1, for a constant amount of Pt (1.5%), the WGS rate per gram of catalyst at 120 °C increases by a factor of 2.1, with a change in Mo weight loading from 2 wt% to 20 wt%. This amounts to an increase in the area covered by Mo from 5% to 52% of the MWCNT surface, if it is assumed to be dispersed in a single layer (assuming $1 \times$

10^{19} sites m^{-2}). On the other hand, for a constant amount of Mo (10% wt or 26% of MWCNT area covered theoretically), the WGS rate per gram increases by a factor of 8.2 with a change in the Pt weight loading from 0.5 wt% to 5 wt% (Figure 1). This change in the Pt loading translates into the change from 0.6% to 6.4% in the area covered by Pt on the MWCNT surface, assuming full dispersion. The shape of the curve for varying Mo loading suggests that the WGS rate per gram of catalyst at 120 °C levels off after a certain amount of Mo. However, there is a linear increase in the WGS rate per gram when Pt loading is increased, while the Mo loading is fixed.

Figure 1: WGS rate per gram at 120°C versus % Pt loading at a fixed (10%) Mo loading (green circles with solid line, linked to the top x-right y axes) and WGS rate per gram at 120°C versus % Mo loading at a fixed (1.5%) Pt loading (blue squares with dashed curve, linked to the bottom x-left y axes).

3.2 Catalyst Characterization

Carbon monoxide uptake experiments were performed to count the total number of sites that adsorb CO. The catalysts were reduced at 600 °C (to mimic the pretreatment

performed before the WGS kinetic measurement) prior to CO adsorption at 35 °C. As shown in Figure 2 the moles of CO adsorbed per gram of catalyst increased linearly with the Mo loading, suggesting the creation of identical Mo₂C sites with increasing amount of Mo. However, for the set of catalysts with increasing Pt loading, the amount of CO adsorbed remained constant with the amount of Pt, implying that the presence of Pt had a negligible effect on creating additional adsorption sites on these catalysts.

Figure 2: Moles of CO adsorbed at 35°C vs. % Pt loading at 10% Mo loading (squares with solid line) and moles of CO adsorbed at 35°C vs. % Mo loading at 1.5% Pt loading (circles with dashed line) for the Pt/Mo₂C/MWCNT catalysts

In Figure 3, the nominal turnover frequency (TOF) i.e. the WGS rate per gram normalized by the moles of CO chemisorbed per gram of catalyst is plotted against the Mo and Pt loadings. For the increasing Mo series, the nominal TOF at 120°C decreases with the increasing Mo loading, while for the increasing Pt series, the nominal TOF increases linearly with the Pt loading.

Figure 3: Nominal WGS TOF at 120 °C vs. % Pt loading at 10% Mo loading (squares with solid line) and nominal WGS TOF at 120 °C vs. % Mo loading at 1.5% Pt loading (circles with dotted curve) for the Pt/Mo₂C/MWCNT catalysts.

In situ and *ex situ* X-ray absorption was performed on all the Pt/Mo₂C/MWCNT catalysts to study the structure and oxidation state of the Pt clusters after the 600°C reduction treatment. Figure 4 (a) depicts the representative Pt L_{III} XANES spectrum measured under He atmosphere for 1.5 wt% Pt/ 2 wt% Mo/ MWCNT after reduction at 600°C. As compared to the Pt foil, there are observable differences exhibited. There is a shift in the leading edge towards higher energy. However, the edge energies (obtained from the energy of the first inflection point) are similar for the Pt foil (11.5640 keV) and the catalyst (11.5652 keV), suggesting that Pt is fully reduced. The observed differences are attributed to the formation of Pt-Mo bimetallic nanoparticles [11]. The Fourier transforms of Pt L_{III} edge EXAFS spectra are shown in Figure 4 (b). Differences in the magnitudes of the peaks between the foil and the catalyst indicate scattering from elements other than

Pt. The fit parameters (Table S1 in the supplementary information) show the Pt-Pt contribution with coordination number 4.1 (after reduction) with inter-atomic distance of 2.74 Å. The peak at 2.73 Å is attributed to Pt-Mo bonds, with the inter-atomic distance consistent with metallic Mo atoms directly bonded to Pt. Thus, Pt L_{III} EXAFS also indicates the formation of Pt-Mo bimetallic particles. Table S1 shows that before reduction, the Pt is oxidized (evident from Pt-O coordination) at all Mo loadings. After reduction, the Pt-Pt coordination numbers (~ 4) and Pt-Mo coordination numbers (~ 4.6) are similar for all the catalysts and are independent of the Mo loading.

Figure 4: (a) Pt L_{III} edge XANES spectrum for the 1.5%Pt/ 2% Mo/MWCNT catalyst after the 600 °C reduction (b) Pt L_{III} edge FT EXAFS spectrum for the 1.5%Pt/ 2% Mo/MWCNT catalyst after the 600 °C reduction (nor corrected for phase shift). The scans were taken under He at RT.

The Mo K edge XANES spectrum for the 1.5 wt% Pt/ 20 wt% Mo/ MWCNT, recorded after 600 °C reduction, is shown in Figure S2 (a). This spectrum is identical to the bulk Mo₂C standard that was treated in 15% H₂/CH₄, which confirms the formation of Mo₂C domains on the MWCNT support. Figure S2 (b) shows the Mo K edge XANES after 600 °C reduction, for the catalysts with varying Mo loading. While there are systematic changes observed in the post-edge features (past the inflection point of the edge), the pre-edge features remain unchanged with the Mo loading. Additionally, the Mo edge energies are also the same for the catalysts with increasing Mo loading. Figure S3 (a) shows the FT magnitude of the Mo K edge EXAFS spectra for the Mo₂C standard and the 1.5 wt% Pt/ 20 wt% Mo/ MWCNT after the pretreatment. The shapes and the positions of the peaks (assigned to Mo-C and Mo-Mo) for the 1.5 wt% Pt/ 20 wt% Mo/ MWCNT catalyst match with the peaks for Mo₂C. The smaller intensity of the peaks for the 1.5 wt% Pt/ 20 wt% Mo/MWCNT catalyst indicates the formation of Mo₂C domains that are smaller in size as compared to those of the bulk carbide. As shown in Figure S3 (b) (the Mo K edge EXAFS for catalysts with increasing Mo loading), the intensity of the Mo-Mo peak increases with increasing Mo loading, suggesting that addition of more Mo leads to the formation of larger Mo₂C domains, consistent with the CO uptake results discussed above. It has been reported by Lee and Boudart [12] that when the size of the Mo₂C domain changes (from bulk Mo₂C to Mo₂C/Al₂O₃), there is a more significant change observed in the Mo-Mo coordination number estimated using EXAFS, as compared to the Mo-C coordination number. In Figure S3 (b), Mo-Mo peak is also affected more strongly with the change in the Mo loading. No evidence for Mo-Pt bonds was obtained in the Mo K edge EXAFS, probably due to the excess amount of Mo as compared to Pt.

Even for the catalyst with 1.5 wt% Pt and 2 wt% Mo (lowest Mo loading), the molar ratio of Pt:Mo is 0.36. This ratio further decreases to 0.036 with 20% wt Mo loading.

Table S2 shows the details of the EXAFS fits for the Pt/Mo₂C/MWCNT catalysts with varying Pt loading at a fixed Mo loading. The X-ray absorption over these catalysts was performed at two different stages, at room temperature after the 600 °C reduction and during the course of WGS reaction at 160°C. The average Pt-Pt and Pt-Mo coordination numbers and the Pt L_{III} edge energies are similar for all the catalysts in this set. These parameters obtained after the 600°C reduction are in turn similar to the parameters obtained for 1.5 wt% Pt/ 2 wt% Mo/ MWCNT (from the varying Mo series), suggesting that Pt was in a similar chemical state and similar coordination environment. Thus, after the 600°C reduction, all the catalysts with varying Pt loading possess Pt-Mo bimetallic particles, where Pt is in a fully reduced state. The Mo K edge FT EXAFS spectra confirm the formation of Mo₂C (even in absence of Pt) as shown in Figure 5. The first shell (Mo-C) is the same for all catalysts with varying Pt loadings. However, the intensity of the Mo-Mo peak at the second shell changes significantly with the addition of Pt. With higher amount of Pt, the intensity of Mo-Mo peak becomes smaller, marking a decrease in the size of the Mo₂C domains. The size of the Mo₂C domains could not be estimated from XAS analyses because we do not have an experimentally determined correlation between the Mo-Mo coordination numbers and the size of the clusters.

Figure 5: Mo K edge FT EXAFS spectrum for the Pt/ Mo₂C/MWCNT catalysts with varying Pt loading (at fixed Mo loading) after the 600 °C reduction, scanned in He at RT (uncorrected for phase shift)

The edge energies at both edges (Mo K edge and Pt L_{III} edge) and the average coordination numbers (Pt-Pt, Pt-Mo, Mo-C and Mo-Mo) do not change significantly when the catalysts are exposed to the WGS reaction mixture at 160 °C (Table S2). This suggests that Pt stays in a fully reduced state, and alloyed with Mo during WGS reaction. No evidence of the Mo₂C surface being oxidized under WGS was obtained from the Mo K edge spectra. In summary, the XAS data indicate that Pt-Mo bimetallic particles are formed over all the Pt/Mo₂C/MWCNT catalysts. The coordination environment of Pt (the average coordination number) does not depend either on the Pt loading or the Mo loading.

Figure 6: Representative HAADF-STEM micrographs obtained for the used 5% Pt/ 10% Mo/MWCNT catalyst. The brightest domains are the Pt-Mo bimetallic particles surrounded by the Mo₂C domains with a relatively lower brightness against the carbon nanotube surface.

Figure 6 (a) shows a HAADF-STEM image of the 5 wt% Pt/10 wt% Mo/MWCNT catalyst. A magnified image of the carbon nanotube region exhibits features with two different contrast levels (Figure 6 (b)). The contrast on HAADF-STEM images stems from differences in mass-thickness, where the intensity scales roughly with the atomic number squared ($\approx Z^2$). Thus based on the contrast difference, the bright features are assigned as Pt particles, whereas regions of lower contrast are designated as patches of Mo₂C in Figure 6 (c). The chemistry of the observed particles was investigated with EELS at both Pt and Mo edges and the particles are confirmed to contain both Pt and Mo, as shown in Figure 7. The particles are predominantly found to be well-mixed Pt-Mo alloys. Additional EELS data for a particle located on a Mo₂C island can be found in Figure S4, which confirm the formation of Pt-Mo alloy.

Figure 7: Typical high resolution HAADF-STEM micrograph of the used 5% Pt/ 10% Mo/MWCNT catalyst used to assess the composition of the observed particles. The EELS signal profile (intensity vs. distance) along the dotted line through the particle shows the presence of well-mixed Pt-Mo alloy.

Using the HAADF-STEM images, the surface area of the Pt-Mo bimetallic particles was quantified and normalized by the surface area of the observed MWCNT surface, as shown in Figure 6 (c). The fractions of the surface area covered by the Pt-Mo bimetallic particles for various catalysts are listed in Table 2. The particle size distribution of these catalysts measured after the reaction is also listed in Table 2.

Table 2: Estimation of the fraction of the support surface area covered by the Pt-Mo bimetallic particles for the Pt/Mo₂C/MWCNT catalysts with varying Pt loading.

Catalyst	MWCNT area scanned (nm ²)	Number of Pt-Mo objects counted	Mo ₂ C area measured (nm ²)	Pt-Mo area measured (nm ²)	% Area covered by Pt-Mo	Average Pt-Mo particle size (nm)
0.5% Pt/ 10% Mo/MWCNT	6425	24	874	33.4	0.5	2.1 ± 0.8
3% Pt/ 10% Mo/MWCNT	5673	66	573	100.1	1.8	2.2 ± 0.8
5% Pt/ 10% Mo/MWCNT	3272	33	347	123.6	3.8	2.5 ± 1.0

Based on the HAADF-STEM intensity data, the thicknesses of a Mo₂C island and a Pt containing particle was estimated for a particle observed over the 5 wt% Pt/10wt% Mo/MWCNT catalyst (see Figure S5 and S6 for details). The observed intensity in HAADF-STEM scales with thickness $\times$ atomic mass², ($t \times Z^2$). The estimated thickness of the Mo₂C island is about 3 to 5 layers, while for the Pt containing particle, assuming the formation of Pt-Mo 1:1 alloy, the thickness ranges from 5 to 8 layers.

4. Discussion

4.1 Description of the Catalyst Structure

Preparation of Pt/Mo₂C catalysts using MWCNT support offers multiple advantages from the standpoint of establishing structure-activity relationships. The MWCNTs provide an

ease of characterization. For example, the X-ray absorption spectroscopy for the bulk Mo₂C catalysts was carried out in the fluorescence mode, as the bulk Mo₂C phase absorbs all the incident X-rays. The MWCNT supports are practically transparent to the incident X-rays since carbon is a low-Z material. This enabled us to perform the *in situ* XAS experiments in transmission mode and with a greater throughput, i.e. 6 samples could be tested per batch. Also, bulk Mo₂C offers a poor contrast between admetal particles and the support for electron microscopy. On the other hand, due to the high transparency and low density of the carbon, STEM micrographs with clear contrast between the admetal and the Mo₂C domains could be obtained for Mo₂C/MWCNT supported catalysts.

The CO uptake measurements for the series with fixed Mo loading and increasing Pt loading were independent of Pt loading. Even though the Pt containing particles are shown to partially cover the Mo₂C domains (using the STEM micrographs), the CO uptake does not change appreciably with increasing amount of Pt. This can be explained if the uptake of Pt containing particles was similar to the Mo₂C underneath. It would also require Pt to be co-located over the Mo₂C domains; so that the total number of sites does not increase by addition of Pt (i.e. sites over Mo₂C that are blocked by a Pt containing particle are compensated for by the sites over the same Pt containing particle). The location of Pt containing particles is discussed later. For the series with increasing Mo loading and fixed Pt loading, the CO uptake increases linearly with increasing amount of Mo. This suggests that the number of the same type of sites per Mo₂C domain is increased with the addition of Mo. However, the linear trend for this series (Figure 2) exhibits a non-zero y-intercept, suggesting that CO uptake will not be zero at 0 wt% Mo

loading. This could be due to the presence of Pt along with Mo i.e. Pt would still exhibit CO uptake in absence of Mo. The linear trend of CO uptake with increasing Mo would require the size of Pt containing particles to remain more or less constant with increasing Mo loading. The EXAFS data obtained over these catalysts after reduction shows that the average Pt-Pt and Pt-Mo coordination numbers are independent of Mo loading, suggesting that the average size of the Pt containing particles does not change appreciably with Mo loading. Hence, the linear trend of CO uptake with increasing Mo loading can be explained.

For the two series of the catalysts that were synthesized, the maximum Mo loading was 20 wt%. Theoretically, even at 20 wt% Mo loading, the maximum coverage is 52% of the MWCNT surface (BET surface area: $240 \text{ m}^2 \text{ g}^{-1}$) if Mo_2C forms monolayer domains. Thus, if Pt deposition were random during Pt impregnation on $\text{Mo}_2\text{C}/\text{MWCNT}$, a sizable fraction of the Pt would be likely to deposit on the MWCNT surface, as opposed to the Mo_2C domains. In this scenario, the likelihood of Pt contacting the MWCNT surface would increase with decreasing Mo loading. As elaborated below, the data are not consistent with this picture, and imply, on the contrary, that Pt interacts preferentially with the Mo_2C domains probably moving during the reduction step from the MWCNT to the Mo_2C .

To determine the fraction of Pt in contact with the Mo_2C domains, we have used the XAS data obtained over these systems. As shown before, after the 600°C reduction, the Pt-Pt and Pt-Mo average coordination numbers obtained at the Pt L_{III} edge for these catalysts were independent of the Mo and Pt loading. This suggests that the coordination environment of Pt was independent of the amount of Mo over these catalysts. In the

random deposition model, at fixed Pt loading, the amount of Pt in contact with the Mo₂C domain should increase with the Mo loading and the average Pt-Mo coordination number should have increased correspondingly since XAS takes an average over the entire sample. No such trend was observed, however. Thus, the EXAFS data show that a significant fraction of the Pt is in intimate contact with Mo₂C, i.e. Pt preferentially binds to the Mo₂C domains. Additional quantitative evidence for this claim was obtained from the XANES spectra obtained after the 600°C reduction pretreatment. It was shown, from XANES data at the Pt L_{III} edge for the Pt/bulk Mo₂C, that there is an observable shift in the leading edge towards higher energy [7], which is attributed to the effect of alloying with Mo [11]. Thus, by modeling the XANES spectra for the Pt/Mo₂C/MWCNT systems as the linear combinations of the XANES spectra of Pt/bulk Mo₂C and the Pt/MWCNT (no Mo), we have quantified the fraction of Pt in contact with the Mo₂C domains. From the spectra in Figure 8, the analysis shows that every catalyst has close to 100% Pt in contact with Mo₂C, except for the samples with 2 wt% and 3 wt% Mo loadings, which had 27% and 18% Pt in contact with the MWCNT respectively (Table S3).

Figure 8: Pt L_{III} XANES spectra for (a) catalysts with varying Mo loading (b) catalysts with varying Pt loading plotted with the XANES spectra for the 1.5% Pt/Mo₂C and the 4% Pt/MWCNT catalysts used for linear combination XANES analysis, scanned in He at RT after the 600°C reduction in H₂

Images supporting the claim that most of the Pt is in contact with Mo₂C were obtained from the HAADF-STEM. It was observed that all the noticeable Pt-Mo bimetallic particles had Mo₂C around them, confirming the preferential binding of Pt to the Mo₂C (Figure S7). Such preferential binding of Pt to Mo₂C domains has been reported before

for Pt supported over $\text{Mo}_2\text{C}/\text{Al}_2\text{O}_3$ [13]. We assume that even though some Pt may deposit in the MWCNT surface during synthesis, it migrates to the Mo_2C domains during the 600°C reduction pretreatment. At 600°C , Pt particles can have enough mobility to move around on the support surface. These Pt particles form an alloy with the reduced Mo phase and are surrounded by the Mo_2C domains. The alloy formation is likely to be achieved by the incorporation of Mo into the Pt particles once Pt migrates to the Mo_2C domains during the reduction process. This is evident from the decrease in the intensity of Mo-Mo peak of the Mo K edge EXAFS spectra with increase in the Pt loading (Figure 5). The preferential binding of Pt to the Mo_2C domains highlights the strong adhesive interaction between the admetal particles and the carbide surface.

As shown in the STEM micrographs (Figure S8 and S9), uniformly distributed domains of Mo_2C are formed over the MWCNT surface after the 600°C reduction. Once Pt is deposited and the catalyst is reduced again at 600°C , Pt-Mo alloy nanoparticles are formed, which is confirmed from the EELS data. The structure of the particles deduced from the XAS and STEM-EELS characterization differs from what was proposed before by Schweitzer et al. [2]. It was suggested that Pt forms a flat raft-like particles which are two layers thick on the surface of Mo_2C . The alloy formation was ruled out on account of maximum observed Pt-Mo coordination number of 1.5, which can be satisfied by flat raft-like Pt particles. However, the Pt-Mo coordination numbers observed for our catalysts was ~ 4.6 , suggesting the incorporation of Mo into Pt particles to form the alloy. The difference in the observed morphology for our particles and the data reported by Schweitzer et al. could be due to the differences in the synthesis techniques. In the case of our catalysts the Pt was deposited over passivated form of the Mo_2C domains, while

Schweitzer et al. synthesized the catalysts by directly contacting the Pt precursor solution with the native (carburized) surface of Mo₂C. Additionally, the intensity analysis performed using the HAADF-STEM images (Figures S5 and S6) suggests that the thickness of the alloy nanoparticles ranges from 5 to 8 layers. This further suggests that the particles formed over our catalysts are Pt-Mo alloys which are not raft-like (flat).

Various methods are utilized to gauge the thickness of the Mo₂C domains. One of the methods was to use the HAADF intensity of the STEM micrographs to estimate the Mo₂C thickness based on the relationship between HAADF intensity and the atomic number of the observed structures. A detailed description of these results can be found in the supporting information. This analysis performed on Mo₂C regions suggests that the domains of Mo₂C are up to 3-5 layers thick for a catalyst with 10% Mo in the carbide form. To check the validity of this assessment, the theoretical Mo₂C coverage is compared with that of calculated based on STEM micrographs. If a 3-layer thick raft of Mo₂C is assumed, then 33% of Mo atoms would be exposed on the surface. For this sample, the percentage of MWCNT area covered by the Mo₂C domains was ~ 10% (Table 2). If a monolayer of Mo₂C was assumed to be formed, theoretically, 26% of the MWCNT area would have been covered. The average thickness of the Mo₂C domains estimated by dividing the theoretical coverage with the actual coverage would be ~ 2.6 layers. Thus, the thickness estimated from the intensity analysis is consistent with the thickness estimated from the coverage of Mo₂C measured using the STEM images. It is interesting to note that the CO chemisorption uptake for this Mo₂C configuration with a CO:Mo stoichiometry of 1:3 is about four times lower than expected.

In short, the catalyst structure can be summarized as Pt-Mo alloy nanoparticles (5-8 layers thick) preferentially bound to the Mo₂C domains that are 3-5 layers thick.

4.2 Interpretation of WGS Kinetic Data

From the standpoint of kinetic analysis, the advantage of the Pt/Mo₂C/MWCNT catalysts is that the importance of Pt-Mo₂C sites towards the WGS reaction rates could be deconvoluted from the contribution of Mo₂C sites. Of critical importance, the similarity of apparent kinetic parameters for Pt/bulk Mo₂C and Pt/Mo₂C/MWCNT ensures that the active sites are similar in chemical nature. The chemical similarity has enabled us to use these catalysts to probe the active sites of Pt/bulk Mo₂C catalysts. The orders cannot be compared between 10%Mo/MWCNT and Mo₂C in Table 1 because they were tested at different temperatures but the rate at 120°C normalized per exposed carbide surface area (note that the MWCNT was covered only by about 10% of the area with Mo₂C) are within a factor of 1.5.

As described before, the apparent kinetic parameters measured at 120°C for the Pt/Mo₂C/MWCNT systems were independent of the Pt or Mo loading. This implies that all the Pt/Mo₂C/MWCNT catalysts tested for WGS have active sites of similar chemical nature. Thus, the differences in the WGS reaction rate per gram, observed over these catalysts were due to the difference in the absolute number of dominant active sites. The more prominent increase in the WGS reaction rate per gram at 120°C, with creation of more Pt-Mo₂C sites, as compared to the increase in the rates with increasing Mo₂C sites suggests that the dominant active sites are formed by the contact sites of Pt and Mo₂C domains. The monotonic decrease in the nominal TOF (defined by normalizing the WGS rate per gram by the total number of CO molecules chemisorbed) with increasing Mo

loading suggests that inherently ‘less active’ sites are created with increasing amount of Mo_2C . However, the linear increase in the nominal TOF at 120°C with increasing Pt loading suggests that inherently ‘more active’ sites are created with increase in the number of Pt- Mo_2C contact sites (Fig. 3). The linear increase in the TOF with addition of Pt, coupled with the relatively small change in metal particle size, also supports the claim that all the active sites are of similar chemical nature. Such a linear increase in the WGS rate with increasing Pt weight loading has been reported by Kalamaras et al.[14,15], wherein the interface between Pt particles and the underlying oxide supports was suggested to be the location of the active sites. Based on these observations, we conclude that the dominant active sites for WGS at 120°C are formed by the contact between Pt and Mo_2C domains.

The analysis of the XANES data (described in the previous section) to obtain the fraction of Pt in contact with the Mo_2C domains can further explain the trends observed in Figure 1. For the catalysts with increasing Pt loading at a fixed Mo loading, almost all the Pt is preferentially bound to Mo_2C . If the active sites are formed by the contact of Pt and Mo_2C , the linear increase in the WGS rate per gram with increasing Pt loading is expected. For the series with fixed Pt loading, it was shown that sizable fractions of Pt are not in contact with Mo_2C , when the Mo loading is 2 wt% and 3 wt% i.e. sizable fraction of Pt is present over these two catalysts that does not contribute towards formation of the dominant active sites. Thus, the WGS rate per gram is lower by a factor of 2 for the catalyst with 2 wt% Mo as compared to the catalysts with 10 and 20 wt% Mo.

The inability of the Pt that is not in contact with Mo_2C towards formation of dominant active sites can be explained. There is a significant difference in the WGS rate for the Pt

supported on the MWCNT surface and that for Pt deposited on the Mo₂C domains. To show this difference, we compare the WGS rate per surface mole of metal (TOF) for the 4 wt% Pt/MWCNT (no Mo or Mo₂C) with that of the 1.5 wt% Pt/ 10 wt% Mo/MWCNT (with Mo in the carbide form) catalyst at 120°C (Table 3). The WGS TOF for the catalyst with 10% Mo in carbide form is three orders of magnitude higher than the Pt/MWCNT catalyst. The estimation of TOF for the 1.5 wt% Pt/10 wt% Mo/MWCNT catalyst is explained in detail later. In fact, the Pt/MWCNT catalyst was tested at 270°C, and the rate was extrapolated to 120°C using the Arrhenius dependence ($E_{app} = 83 \text{ kJ mol}^{-1}$) since there would be no measurable conversion obtained over this catalyst at 120°C because of its low rate. Based on this observation, it can be assumed that for the Pt/Mo₂C/MWCNT catalysts, the Pt that is in contact with the MWCNT surface is inactive for WGS at 120°C. Thus, the location of Pt is critically important before any quantitative implications are drawn from the WGS kinetic data. Additionally, it should be noted that for the 10 wt% Mo/MWCNT (Mo in carbide form) catalyst with no Pt, the WGS rate per gram at 120°C ($2 \times 10^{-8} \text{ mol H}_2 (\text{g}_{cat})^{-1} \text{ s}^{-1}$) is two orders of magnitude lower than the 1.5 wt% Pt/10 wt% Mo/MWCNT catalyst ($1.7 \times 10^{-6} \text{ mol H}_2 (\text{g}_{cat})^{-1} \text{ s}^{-1}$). In short, the fractions of Pt in contact with the Mo₂C domains obtained from the linear combination XANES analysis can be termed as the ‘active Pt’. The WGS rates at 120°C normalized by this ‘active Pt’ for all the eight Pt/Mo/MWCNT catalysts (Table 1) are of the order of $\sim 1 \times 10^{-2} \text{ mol H}_2 (\text{mol Pt in contact with Mo}_2\text{C})^{-1} \text{ s}^{-1}$ and are all within a factor of 1.6 of each other.

In order to further confirm that the active sites are formed by Pt containing particles in contact with Mo₂C domains, we have used the HAADF-STEM data. As described before, the Pt is located in close proximity of Mo₂C domains in form of Pt-Mo alloy

nanoparticles. The HAADF-STEM images were used to quantify the fraction of the support surface area covered by the observable Pt-Mo bimetallic particles (see Table 2). As shown in Figure 9, there is a linear correlation between the WGS rate per gram at 120°C and the fraction of the surface area of the support occupied by the Pt-Mo bimetallic particles. Based on this correlation, we conclude that the dominant active sites for WGS on the Pt/Mo₂C/MWCNT systems are located either on the Pt-Mo bimetallic particles or the interface between Pt-Mo particles and the Mo₂C domains. We emphasize, however, that the Pt-Mo alloy nanoparticles need be in intimate contact with the Mo₂C domains to generate the high WGS rates. In other words, the high WGS rates are not solely due to the formation of the alloy. To support this argument, we compare the WGS rates over a Pt-Mo bimetallic catalyst supported on Al₂O₃, from the work of Williams et al. [16], where formation of Pt-Mo alloy was confirmed with X-ray absorption. Williams et al. [16] prepared a series of Pt-Mo/Al₂O₃ with increasing amount of Mo. From their series, the highest WGS rate per total moles of Pt was $7 \times 10^{-2} \text{ mol H}_2 (\text{mol Pt})^{-1} \text{ s}^{-1}$ at 270°C. This rate extrapolated to 120°C using the apparent activation energy of 47 kJ mol⁻¹, is about $1 \times 10^{-3} \text{ mol H}_2 (\text{mol Pt})^{-1} \text{ s}^{-1}$, which is about an order of magnitude lower compared to the Pt/Mo₂C/MWCNT catalysts. This suggests that formation of Pt-Mo alloy alone is not responsible for the high WGS rates exhibited by the Pt/Mo₂C/MWCNT catalysts.

Figure 9: WGS rate per gram of catalyst at 120°C for the Pt/Mo₂C/MWCNT catalysts, plotted against the fraction of the support surface area covered by the Pt-Mo bimetallic nanoparticles for the catalysts with varying Pt loading.

The purpose of increasing the Pt loading at a constant Mo loading was to bring about a variation in the average particle size of Pt containing particles. This could help in differentiating the rate dependence on the area sites from the dependence on the perimeter sites. However, regardless of the Pt loading, the catalysts with fixed Mo loading have similar particle sizes, with average particle sizes of 2.2 ± 0.8 nm, 2.2 ± 0.8 nm, and 2.5 ± 1.0 nm for the used catalysts with 0.5 wt%, 3 wt% and 5 wt% Pt at fixed (10 wt%) Mo loading. This suggests that even when the amount of Pt was increased by a factor of 10 there were sufficient nucleation centers available on the Mo₂C domains for the formation of new Pt-containing particles. The WGS rates were normalized by the dispersion (1/average particle size in nm) of the Pt-Mo particles for these catalysts. These

normalized rates are independent of the amount of Pt on each catalyst and are of the order of $\sim (3.1 \pm 0.1) \times 10^{-2}$ mol H₂ (mole surface metal in Pt-Mo particles)⁻¹ s⁻¹ at 120°C. Thus, this rate can be termed as the apparent WGS turnover frequency. However, since the Pt-containing particles were all similar in size, we cannot differentiate the rate dependence on the area of the particles from its dependence on the perimeter, based on that data alone. The enhancement in WGS reaction rate due to addition of Pt could be due to electronic perturbations induced in the Pt by the underlying Mo₂C surface. Based on DFT calculations, it has been shown that there could be a transfer of electron density from Mo₂C to Pt [17], which could affect the interaction of Pt with the adsorbates. Such electron density transfer has been reported for other carbide supports [6]. An alternative explanation for the higher rate may be that water dissociation, or adsorption, occurs on the Mo₂C sites (note the -0.1 water order on Mo₂C and 0.5 order on CO, Table 1), which migrate onto the Pt-Mo particles and react with CO at the particle/support interface (note the 0.7 water order on Pt/Mo₂C/MWCNT and 0 order on CO, Table 1).

The WGS TOF over the 1.5 wt% Pt/10 wt% Mo/MWCNT catalyst at 120°C, estimated from the dispersion based on the average particles size (3×10^{-2} mol H₂ (mole surface metal in Pt-Mo particles)⁻¹ s⁻¹) is compared with other catalysts in Table 3. The 10 wt% Mo/MWCNT (7×10^{-4} mol H₂ (mol CO ads.)⁻¹ s⁻¹) and the unsupported Mo₂C (8×10^{-4} mol H₂ (mol CO ads.)⁻¹ s⁻¹) [7] have WGS TOFs that are two orders of magnitude lower compared to the 1.5 wt% Pt/10 wt% Mo/MWCNT catalyst. As mentioned before, the TOF for the Mo-free Pt/MWCNT catalyst is 3 orders of magnitude lower. For the catalyst with Pt-Mo alloy supported on Al₂O₃ [16], the TOF is 10 times lower at 120°C compared to the 1.5 wt%Pt/10 wt%Mo/MWCNT catalyst. These comparisons highlight the

indispensability of the contact between Pt-Mo alloy and the Mo₂C. In fact, Williams et al. [16] also suggested that even for Pt-Mo/Al₂O₃ catalysts, the reason for promotion was the presence of non-reducible Mo-oxide, and not merely the Pt-Mo alloy formation.

Table 3: Comparison of WGS TOF over 1.5% Pt/10% Mo/MWCNT catalyst with 10%Mo/MWCNT, unsupported Mo₂C, Pt/MWCNT and Pt-Mo/Al₂O₃

Catalyst	WGS Turnover Frequency at 120°C/ 10 ⁻² mol H ₂ (mole surface sites) ⁻¹ s ⁻¹
1.5 wt% Pt/10 wt% Mo/MWCNT (Mo in carbide form) ^a	3
10 wt% Mo/MWCNT (Mo in carbide form) ^b	7 × 10 ⁻²
Unsupported Mo ₂ C ^c [7]	8 × 10 ⁻²
4 wt% Pt/MWCNT ^d	4 × 10 ⁻³
2.1 wt% Pt/1.4 wt% Mo/Al ₂ O ₃ ^e [16]	3 × 10 ⁻¹

- Rate normalized by the dispersion of Pt-Mo particles estimated from STEM images. The dispersion is estimated as 1/average Pt-Mo particle size in nm. The total Pt moles are multiplied by the dispersion to obtain the moles of surface sites for Pt-Mo particles.
- Rate extrapolated to 120°C (E_a = 56 kJ mol⁻¹) and normalized by moles of CO chemisorbed.
- Rate normalized by moles of CO chemisorbed.
- Rate extrapolated to 120°C (E_a = 83 kJ mol⁻¹) and normalized by moles of CO chemisorbed.
- Rate extrapolated to 120°C (E_a = 47 kJ mol⁻¹) and normalized by moles of CO chemisorbed.

The roles of Pt (or the Pt-Mo) particles and Mo₂C in the WGS mechanism have been elucidated before [7]. The apparent reaction orders with respect to H₂O and CO for the unsupported Mo₂C measured at 120°C are -0.1 and 0.5 respectively. This suggests that water generated intermediates have a relatively higher coverage compared to CO due to the high reactivity of Mo₂C towards water dissociation. These orders are significantly different for Pt/Mo₂C (0.75 and 0.05), suggesting that Pt provides a reservoir of CO and

decreases the extent of competitive adsorption between CO and the water-generated species.

Based on these results, we suggest that it is the synergy between the Pt-Mo alloy and the Mo₂C that leads to the WGS rates that are higher than any other oxide supported Pt catalysts.

5. Conclusions

Two different series of catalysts with varying amounts of Mo (at fixed amount of Pt) and varying amount of Pt (at fixed amount of Mo) were prepared. The number of Mo₂C sites and the number of admetal-Mo₂C contact sites were individually varied. The more prominent increase in the WGS reaction rate per gram at 120°C with creation of more Pt-Mo₂C sites, as compared to the relatively small increase in the rates with increasing Mo₂C sites suggests that the dominant active sites are formed by the contact sites of Pt with Mo₂C domain. This observation was ascertained with normalization the WGS rates per gram by the number of moles of CO chemisorbed on each Pt/Mo₂C/MWCNT catalyst (CO titrates Mo₂C as well as the admetal sites). A linear increase in the nominal TOF was observed with increasing Pt loading while the Mo loading was fixed, whereas a progressive decrease in the nominal TOF was observed with increasing Mo loading while the amount of Pt was fixed. Characterizations of these catalysts performed using XAS and the HAADF-STEM micrographs, indicate that the Pt preferentially binds to the Mo₂C domains after the 600°C reduction and during the course of WGS reaction and forms Pt-Mo bimetallic nanoparticles. This highlights the strong adhesive interaction between the admetal and the Mo₂C domains. The similarity of the kinetics between Pt/bulk Mo₂C and Pt/Mo₂C/MWCNT enabled us to use the latter to probe the active sites

for WGS over Pt supported on Mo₂C. A linear correlation between WGS reaction rate per gram at 120 °C and the fraction of the surface area covered by the Pt-Mo particles was obtained. The location of active sites was determined to be the Pt-Mo particle surface in combination with the interface between the Pt-Mo particles and the Mo₂C domains. The synergy between the Pt-Mo alloy nanoparticles (CO activation) and Mo₂C (water dissociation) is suggested as the cause for the WGS rates per total mole Pt that are higher than any other oxide supported Pt catalysts.

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