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Highly Active Pt/MoC and Pt/TiC Catalysts for the Low-Temperature Water-gas Shift Reaction: Effects of the Carbide Metal/Carbon Ratio on the Catalyst Performance

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Abstract

Pt/MoC and Pt/TiC(001) are excellent catalysts for the low-temperature water-gas shift (WGS, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) reaction. They exhibit high-activity, stability and selectivity. The highest catalytic activities are seen for small coverages of Pt on the carbide substrates. Synergistic effects at the metal-carbide interface produce an enhancement in chemical activity with respect to pure Pt, MoC and TiC. A clear correlation is found between the ability of the Pt/MoC and Pt/TiC(001) surfaces to partially dissociate water and their catalytic activity for the WGS reaction. An overall comparison of the results for Pt/MoC and Pt/Mo₂C(001) indicates that the metal/carbon ratio in the carbide support can have a strong influence in the stability and selectivity of WGS catalysts and is a parameter that must be taken into consideration when designing these systems.

Keywords: Water; Water-gas shift; Hydrogen production; Platinum; Molybdenum carbide; Titanium carbide.

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1. Introduction

The industrial production of hydrogen as a feedstock usually involves the steam reforming (SR) of methane and other hydrocarbons [1]. New raw materials, such as biomass or waste, also can be used for reforming purposes [1]. The hydrogen produced by the SR process usually contains small amounts (1-5%) of CO as an impurity. The water-gas shift reaction (WGS, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) is a convenient route to remove the CO and produce additional hydrogen [2,3]. Mixtures of Fe-Cr and Zn-Al-Cu oxides are frequently the commercially used catalysts for the WGS reaction at temperatures between 350-500 and 180-250 °C, respectively. However, these oxide catalysts are pyrophoric and frequently require lengthy and complex activation steps before they are used [2,3]. Consequently new catalysts are being sought.

In recent years, it has become clear that metals supported on metal-carbides can be good catalysts for the WGS reaction [4,5,6]. A systematic study has been carried out examining the performance of several metals (Pt, Pd, Ni, Au, Ag and Cu) supported over Mo₂C for the WGS reaction [5]. It was found that the reactivity of the catalysts increased in the sequence: Mo₂C < Ag/Mo₂C < Cu/Mo₂C < Ni/Mo₂C < Pd/Mo₂C < Au/Mo₂C < Pt/Mo₂C [5]. The Pt/Mo₂C catalysts exhibited an activity that was 4-8 times than that found for a commercial Cu/ZnO/Al₂O₃ catalyst [5]. In fact, it was shown that Pt/Mo₂C has an activity higher than that of any Pt/oxide catalyst studied [4,5]. On the other hand, a basic study has shown that Pt(111) has a moderate activity for the water-gas shift reaction and exhibits a tendency to deactivate via carbon deposition by the Boudouard reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$) [7]. This suggests that metal-support interactions may be modifying the intrinsic chemistry of platinum in the Pt/Mo₂C catalysts. It is known that metal

carbides are non-innocent supports and can modify the electronic and chemical properties of admetals [4,8]. Indeed, results of density functional calculations indicate that Pt atoms in contact with a δ -MoC(001) surface have a negative charge [8,9].

An important parameter to check when dealing with the design of metal carbide catalysts is the metal/carbon atomic ratio in the system [10,11,12]. In general, a decrease in the metal/carbon ratio in a carbide usually reduces the reactivity of the system as a consequence of electronic—a raise in the positive charge on the metal centers—and structural effects—a reduction in the number of metal centers exposed on the carbide surface. This drop in reactivity makes the carbide less sensitive to attack by oxygen [6,8]. In principle, the metal/carbon ratio could have an effect in the activity, selectivity and stability of a metal carbide catalyst [10,11,12]. In this study, we move from Mo₂C as a substrate to two carbides that have a 1:1 metal/carbon ratio: MoC and TiC. To the best of our knowledge, powders of these carbides have not been used as a catalyst for the WGS. Au/TiC(001) exhibits catalytic activity and is useful as point of reference.[6] In the Pt/MoC and Pt/TiC systems, we find evidence for synergistic interactions involving the metal and carbide support. These interactions help with the dissociation of water and produce excellent WGS catalysts. Over Pt/MoC and Pt/TiC, there is no production of methane as a side product, as occurs in the case of Pt/Mo₂C, and the catalysts do not deactivate by the formation of an oxycarbide.

2. Experimental

We investigated the performance for the water-gas shift of a series of catalysts generated by the deposition of Pt on TiC(001), polycrystalline δ -MoC, and β -Mo₂C(001)

surfaces. The experimental data were collected in an instrument that combined an ultra-high vacuum (UHV) chamber for surface characterization and a micro-reactor for catalytic tests [6,13]. The UHV chamber was equipped with instrumentation for X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), ion-scattering spectroscopy (ISS), and thermal-desorption mass spectroscopy (TDS) [6,13].

The TiC(001) and β -Mo₂C(001) surfaces were prepared and cleaned as described in previous works [6,14]. The δ -MoC examined in this study is best described as polycrystalline [15]. Surface impurities were removed by Ar⁺ sputtering, and a C/Mo ratio close to 1 was restored by exposing this surface to C₂H₂ or C₂H₄ at 800-900 K [15]. Several attempts were made to prepare well-defined surfaces of δ -MoC oriented along the (001) plane of this carbide. However, it was not possible to prepare an ideal δ -MoC(001) surface. The preparation of this particular surface is very difficult due to the complex phase diagram of MoC [11,15]. Pt was vapor deposited on the metal carbide substrates at 300 K

In the kinetic measurements the sample was transferred to the batch reactor at $\sim$ 300 K, then the reactant gases were introduced (20 Torr of CO and 10 Torr of H₂O) and the sample was rapidly heated to the reaction temperatures investigated (410, 425, 435, 450, 465 K). The amount of molecules produced was normalized by the active area exposed by the sample [6,13]. In our reactor a constant rate for the production of H₂ and CO₂ was reached after 2-3 minutes of reaction time. The kinetic measurements were done at the limit of low conversion (< 5%). The CO gas was cleaned of any metal carbonyl impurity by passing it through purification traps [6,13].

3. Results and Discussions

3.1 Performance and stability of Pt/MoC and Pt/TiC(001) WGS catalysts

The left-side panel in Figure 1 shows O 1s XPS spectra collected after dosing 50 Langmuir (L) of water to clean MoC and a surface pre-covered with 0.15 ML of platinum at 300 K. In both spectra, there is a single peak at a binding energy of ~ 531.6 eV. This binding energy corresponds to OH groups [16] produced by the dissociation of water. Clean MoC is not very reactive and exposure to water produces a small amount of OH groups, ~ 0.08 monolayer (ML), on the surface. Pt(111) also does not interact well with water [7], since the dissociation process of the molecule is hampered by a large activation barrier [7,13]. In contrast, the Pt/MoC system reacts well with the water molecule producing a large amount of adsorbed OH. Thus, there is a synergy at the Pt-carbide interface that helps with the dissociation of water. As shown in the right-side panel of Figure 1, the reactivity of the system depends strongly on the coverage of Pt on the surface. As Pt is added, a maximum in activity is seen at 0.15-0.2 ML. Thus, high activity probably involves small particles of Pt in close contact with MoC. Results of density functional calculations show a substantial negative charge on Pt atoms bonded to a δ -MoC(001) surface [9]. The electronic perturbations on the Pt adatoms probably affect their chemical behavior.

Experiments were also conducted for the reaction of water with Pt/TiC(001) surfaces obtaining results very similar to those shown for Pt/MoC, but the reactivity towards water was a little bit smaller (Figure 1). Water dissociation is a rate limiting step for the WGS reaction on Pt(111) [7,13,17,18] and on many other metal surfaces

[19,20,21]. Over Pt(111), the slow dissociation of water is problematic because the main channel for the WGS eventually cannot compete with the Boudouard reaction and there is deactivation of the catalyst by carbon deposition [7]. This may not be a problem on Pt/MoC and Pt/TiC due to the fast dissociation of water. On these surfaces, there is a relatively large reservoir of OH groups that can react with CO to give an HOCO intermediate [17,19,20] and CO₂ and H₂ as products of the WGS.

Figure 2 shows the WGS catalytic activity for a series of Pt/MoC catalysts at 450 K. Clean MoC has a limited activity for catalyzing the reaction. A clear improvement is seen upon the addition of Pt. The trends in Figure 2 match the trends in Figure 1 for the dissociation of water. At Pt coverages of 0.15-0.2 ML a maximum in the rate of water dissociation and in the production of H₂ and CO₂ is seen. The chemical and catalytic activity of the Pt/MoC system decrease when the Pt coverage is large probably due to the formation of large three-dimensional (3D) particles of the admetal in which the atoms are not part of the Pt-carbide interface. Small platinum particles in close contact with the carbide are the best catalysts. An identical result was obtained for the deposition of Pt on the TiC(001) substrate. Again a maximum in catalytic activity was seen at 0.15-0.2 ML and there was a strong correlation with the ability displayed by the Pt/TiC(001) surface to dissociate water.

Figure 3 displays Arrhenius plots for the WGS reaction on Pt/MoC and Pt/TiC(001) catalysts ($\theta_{\text{Pt}} = 0.15$ ML). Since Cu-based catalysts are frequently employed in the WGS process [2,3,19,20,22], we also include for comparison data for a Cu/TiC(001) catalyst [22]. In agreement with a previous study comparing the activity of Pt/Mo₂C and Cu/Mo₂C powder catalysts [5], we find that the Pt/MoC and Pt/TiC(001)

systems have a better performance than the Cu/TiC(001) catalyst. On the platinum-based systems, the apparent activation energies are -9.1 {Pt/MoC} and -9.4 kcal/mol {Pt/TiC(001)}. These values are much smaller than the apparent activation energy of 22.9 kcal/mol reported on a Pt(111) single crystal [7]. The synergistic interactions at the Pt-carbide interface that favor dissociation of water are probably responsible for this large drop in the apparent activation energy. Apparent activation energies of 11.5 and 12.7 kcal/mol have been reported for Pt/Mo₂C powder catalyst [4,5].

From the data in Figure 3, we calculated turnover frequencies (TOFs) for Pt/MoC and Pt/TiC(001), Figure 4, on the assumption that all platinum atoms in the catalytic surfaces were involved in the WGS process. Since the Pt coverage was small, 0.15 ML, this assumption is probably a very good approximation. The TOFs in Figure 4 indicate that our Pt/MoC and Pt/TiC(001) catalysts have a higher activity than the best catalysts reported in the literature for the low-temperature WGS reaction [3,4,5], although a quantitative comparison of the performance is difficult due to differences in morphology and in the reaction conditions.

Figure 5 compares estimated TOFs for Pt/MoC, Pt/TiC(001) and Cu/TiC(001) with those reported for well-defined catalysts such as Cu(111), Pt(111), and Cu/ZnO(000 $\bar{1}$) [7,22,23,24,25]. This set of catalysts has a very poor performance at temperatures below 500 K [7,22,23,24,25]. At 612 K, Cu(111), Pt(111), and Cu/ZnO(000 $\bar{1}$) have TOFs which are 5-10 times smaller than those of Pt/MoC and Pt/TiC(001) at a much lower temperature of 450 K. In terms of net activity, Cu/ZnO(000 $\bar{1}$) [25], which is a model for an industrial Cu/ZnO catalyst [2,3], does not

compete well with Pt/MoC and Pt/TiC(001). These catalysts are also better than the Au/TiC(001) system examined in a previous study [6].

An important issue when dealing with the use of metal carbides as possible catalysts for the WGS is stability. Reaction of the carbide with water can lead to the formation of an oxycarbide and a reduction in catalytic activity [11,26]. We found that the Pt/MoC and Pt/TiC(001) systems were stable under WGS reaction conditions at temperatures below 470 K. Under these conditions the amount of oxygen or oxygen-containing species deposited on the surface of the carbide was small and did not change with time (Figure 6). A different behavior was seen at temperatures above 500 K: The uptake of oxygen was larger and increased with time (Figure 6). Two phenomena may contribute to this change in stability. On one hand, the formation of oxycarbides from water may have to overcome an activation barrier to rearrange the structure of the MoC or TiC. On the other hand, at elevated temperatures there may be a rupture in the catalytic cycle and the oxygen or OH groups deposited by water dissociation are not removed in an efficient way by reaction with CO. Instead of forming CO₂ gas, the oxygen or OH groups react with the carbide substrate.

A previous study using density-functional calculations found that Pt atoms in contact with TiC(001) and δ -MoC(001) are electronically perturbed.[8,9] They receive electrons from the carbide substrates.[9] The extra charge on the admetal atoms favors interactions with CO and water,[12,13] making the Pt/TiC and Pt/MoC systems more reactive than Pt(111). Furthermore, corner and edge atoms present in Pt nanoparticles have a tendency to make them more active for O-H bond cleavage than Pt(111).[13] The

WGS chemistry also could occur at the Pt-carbide interface with the water molecule dissociating on the carbide side and CO bound to the Pt metal.[6]

3.1 Performance and stability of Pt/Mo₂C(001) WGS catalysts

The left-side panel in Figure 7 shows an O 1s XPS spectrum recorded after dosing 50 L of water to a β -Mo₂C(001) surface at 300K. A broad peak is observed which can be separated in two features. The feature near 530 eV matches the binding energy seen in our instrument after depositing atomic O on the β -Mo₂C(001) surface. This feature is probably the product of the full decomposition of water ($\text{H}_2\text{O} \rightarrow \text{O} + 2\text{H}$) on the carbide substrate. A second feature is seen near 531.5 eV which probably corresponds to OH groups [16] generated by the partial dissociation of water. Under the same reaction conditions only a small amount of OH is detected on a MoC surface. From the uptake curves in the right-side panel of Figure 7, it is clear that β -Mo₂C(001) is much more reactive towards water than MoC. This is probably a consequence of ligand (electronic) and ensemble (structural) effects [26]. In MoC, the positive charge on the Mo centers is larger than in β -Mo₂C(001) [14,26] and the number of Mo atoms exposed in the surfaces of the 1:1 carbide is smaller. These two factors moderate the reactivity of MoC towards water.

The large affinity that β -Mo₂C(001) has for water can be problematic since these surface binds OH and O strongly [11,27]. In fact, theoretical calculations predict that this surface is not stable under WGS reaction conditions [26]. The active phase should contain a layer of atomic oxygen on top of the carbide surface [26]. We investigated the stability of a catalyst generated by depositing 0.15 ML of Pt on a clean β -Mo₂C(001)

substrate. Figure 8 shows how the content of $\{O + OH\}$ on the Pt/Mo₂C(001) surface changes as a function of time under WGS reaction conditions at 450 K. The coverage of $\{O + OH\}$ on Pt/Mo₂C(001) is much larger than on Pt/MoC and increases continuously with time leading to problems of catalyst stability. Our results for Pt/Mo₂C(001), and those obtained for a Pt/Mo₂C powder catalyst [5], point to an active phase in which nanoparticles of Pt are dispersed on the surface of an oxycarbide.

In many industrial operations, the WGS process is carried out under hydrogen-rich conditions with mixtures of CO/H₂O/H₂ originated by the reforming of hydrocarbons [1-3,4,28]. The dissociation of CO on MoC and TiC(001) is an uphill process [6,14], but the β -Mo₂C(001) surface can dissociate the molecule [14,27]. Under hydrogen-rich conditions, β -Mo₂C(001) can transform CO into methane [14,27]. This is problematic for the selectivity towards hydrogen production through the WGS process. Figure 9 compares the product distribution after exposing fresh Pt/MoC and Pt/Mo₂C(001) catalysts to a mixture of CO (20 Torr) and H₂O (10 Torr) at 435 K. The amount of CO₂ produced on both catalysts is comparable but on Pt/Mo₂C(001) there is also methane production.

An overall comparison of the results for Pt/MoC and Pt/Mo₂C(001) indicates that the metal/carbon ratio in the carbide support can have a strong influence in the stability and selectivity of WGS catalysts and is a parameter that must be taken into consideration when designing these systems.

4. Conclusions

Pt/MoC and Pt/TiC(001) are excellent catalysts for the low-temperature water-gas shift reaction. They exhibit high-activity, stability and selectivity. In terms of performance at low temperature, they are orders of magnitude better than the typical industrial Cu/ZnO catalyst.

The highest catalytic activities are seen for small coverages of Pt on the carbide substrates. Synergistic effects at the metal-carbide interface produce an enhancement in chemical activity with respect to pure Pt, MoC and TiC. A clear correlation is found between the ability of the Pt/MoC and Pt/TiC(001) surfaces to partially dissociate water and their catalytic activity for the WGS reaction.

The metal/carbon ratio in the carbides has a strong effect in the stability and selectivity of Pt/MoC and Pt/TiC(001). In this 1:1 carbides, the positive charge on the metal centers is larger than in a Mo₂C carbide and the number of metal atoms exposed in their reactive surfaces is limited. These two factors moderate the reactivity of MoC and TiC leading to a very good performance in the WGS process.

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Figure captions:

Figure 1: Left-side: O 1s XPS spectra collected after dosing water to a clean MoC surface and to a carbide surface pre-covered by 0.15 ML of platinum. Right side panel: Variation in the intensity of the OH features in the O 1s XPS region as a function of Pt coverage on MoC. In all the experiments, 50 L of water were dosed at 300 K.

Figure 2: Water-gas shift activity of Pt/MoC as a function of Pt coverage. The reported values for the production of H₂ and CO₂ were obtained under steady-state after exposing the catalysts to a mixture of CO (20 Torr) and H₂O (10 Torr) at 450 K.

Figure 3: Arrhenius plots for the WGS reaction on Pt/MoC, Pt/TiC(001) and Cu/TiC(001) catalysts. The data for Cu/TiC(001) was taken from ref. [22]. In the Pt/MoC and Pt/TiC(001) surfaces the platinum coverage was 0.15 ML. The reaction rates for each temperature (410, 425, 435, 450, and 465 K) correspond to steady-state measurements after exposing the catalysts to a mixture of CO (20 Torr) and H₂O (10 Torr).

Figure 4: Estimated TOFs for the WGS on Pt/MoC and Pt/TiC(001) at different temperatures. The values correspond to steady-state measurements after exposing the catalysts to a mixture of CO (20 Torr) and H₂O (10 Torr).

Figure 5: TOFs for the WGS on Pt/MoC, Pt/TiC(001), Cu/TiC(001) [22], Pt(111) [7], Cu(111) [7,23] and Cu/ZnO(000 $\bar{1}$) [25]. The systems containing carbides are low-temperature WGS catalysts.

Figure 6: Coverage of O/OH on the surface of a Pt/MoC ($\theta_{\text{Pt}} = 0.15$ ML) catalyst as a function of time and temperature. Post-reaction O 1s XPS was used to measure the O/OH coverage. The values correspond to XPS measurements performed after exposing the catalyst to a mixture of CO (20 Torr) and H₂O (10 Torr) at 450 or 600 K.

Figure 7: Left-side: O 1s XPS spectra collected after dosing 50 L of water to MoC and β -Mo₂C(001) surfaces at 300 K. Right side panel: Variation in the intensity of the {OH + O} features in the O 1s XPS region as a function of water exposure at 300 K.

Figure 8: Coverage of O/OH on the surface of Pt/MoC and Pt/Mo₂C(001) catalysts ($\theta_{\text{Pt}} = 0.15$ ML) as a function of time. Post-reaction O 1s XPS was used to measure the O/OH coverage. The values correspond to XPS measurements performed after exposing the catalyst to a mixture of CO (20 Torr) and H₂O (10 Torr) at 450 K.

Figure 9: Product distribution after exposing fresh Pt/MoC and Pt/Mo₂C(001) catalysts to a mixture of CO (20 Torr) and H₂O (10 Torr) at 435 K. For comparison are also included the activities of plain MoC and plain β -Mo₂C(001).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9