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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.

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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 [4–6]. 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 [10–12]. 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

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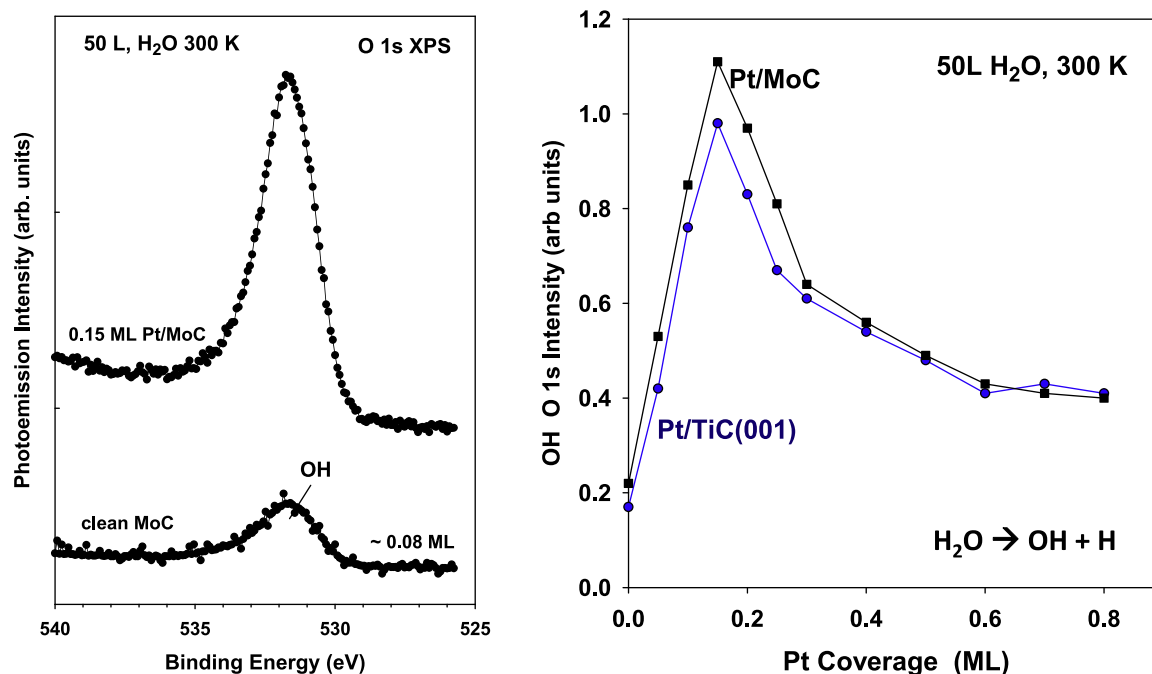


Fig. 1. Left-side: O 1s XPS spectra collected after dosing water to a clean MoC surface and to a carbide surface pre-covered by 0.15 ML of platinum. Right side panel: Variation in the intensity of the OH features in the O 1s XPS region as a function of Pt coverage on MoC. In all the experiments, 50 L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

principle, the metal/carbon ratio could have an effect in the activity, selectivity and stability of a metal carbide catalyst [10–12]. 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 ~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 min 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 Fig. 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 Fig. 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.

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