



Investigation of hydrogen occlusion by molybdenum carbide

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ABSTRACT

The incorporation of hydrogen in the bulk of molybdenum carbide is studied by experimental and theoretical methods. The motivation for this study is to explain the features of the deactivation of Mo₂C catalyst during the hydrogenation of benzene when the reaction is performed at atmospheric pressure. In this condition, deactivation occurs for different reaction times depending on reaction temperature. By means of thermal-programmed desorption it was observed that there is an evolution of hydrogen for the deactivated catalyst at temperatures higher than 923 K. In order to verify if during the carburization of MoO₃ to Mo₂C there is hydrogen occlusion in the interior of the carbidic phase, a systematic thermodynamic analysis was performed based on density functional theory (DFT) and the harmonic oscillator-rigid rotor approach to calculate partition functions. Possible diffusion paths of hydrogen atoms in molybdenum carbide were calculated by the nudged-elastic bands method at DFT level. The results of calculations are totally consistent with experimental findings confirming that there is indeed hydrogen occlusion during the synthesis of molybdenum carbide.

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1. Introduction

Transition metal carbides, particularly molybdenum carbide, are highly active for a large number of reactions catalyzed by noble metals based materials [1–5]. Results from literature show that the electron density is transferred from Mo to C atoms and there is a high density of states at Fermi level as expected for a metal [6].

Molybdenum carbide catalysts have been employed in several reactions in which hydrogen is used, such as hydrogenation [7–9], hydrogenolysis [10], Fischer–Tropsch (FT) synthesis [11,12], hydrocracking [13], and hydrotreating [14–16]. These reactions have also been performed on specific metallic catalysts and the hydrogen adsorption has a key role for the adequate activity of the active phase, therefore a high chemisorption capacity is a critical and desirable characteristic.

The performance of molybdenum carbide in the benzene hydrogenation reaction at atmospheric pressure was previously studied and it has been hypothesized that after the synthesis by temperature-programmed carburization of the molybdenum oxide with a mixture of CH₄ and H₂, some amount of hydrogen remained on the carbide surface and was responsible for the activity of the

material [17]. It was observed that an initial conversion of 100% was achieved but after 30 min of reaction, it started to decrease and at approximately 4 h after the beginning of reaction, the conversion was zero. Based on temperature-programmed desorption experiments and theoretical calculations a mechanism for deactivation was proposed. Apparently, deactivation is caused by the strong adsorption of benzene on the carbide surface, preventing further hydrogen adsorption and thus leading to deactivation. In the beginning of the reaction, the surface is covered by hydrogen and hydrogenation of benzene occurred favorably, apparently through Eley–Rideal mechanism. As reaction goes on, benzene molecules will eventually find a spot on surface free of hydrogen. The benzene strongly adsorbs poisoning the surface, which prevents more hydrogen to be adsorbed.

One point not discussed in detail previously is that if only a monolayer of adsorbed hydrogen is available to hydrogenation of benzene, the deactivation would be faster than that observed. Therefore, there must be an additional source of hydrogen. TPD results suggested that hydrogen could diffuse from the bulk of molybdenum carbide toward the surface as soon as the surface hydrogen is consumed. These hydrogen molecules could have been imprisoned in the carbide bulk during the carburization step.

The main objective of this study using both theoretical and experimental results is to investigate if it is possible to have hydrogen occlusion during the carburization step. Accordingly,

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benzene hydrogenation and temperature-programmed desorption experiments have been carried out and systematic theoretical calculations based on density functional theory have been performed.

2. Experimental

2.1. Synthesis and activity of bulk β -Mo₂C

The molybdenum carbide synthesis was described in a previous paper [17]. Briefly, molybdenum oxide (Aldrich) was carburized using a 350 mL min⁻¹ flow of a mixture of 20% (v/v) CH₄/H₂ (Linde UP) up to a temperature of 923 K at a 10 K min⁻¹ heating rate and holding the final temperature for 2 h.

Immediately after the synthesis, at 923 K, the reactor was cooled down to room temperature (RT) under two different conditions: (i) pure helium flow; (ii) pure hydrogen down to RT and then, the gas was changed to helium.

After the synthesis and cooling, a thermal programmed experiment was performed by heating the reactor from RT up to 923 K at a heating rate of 10 K min⁻¹ under flow of pure He (50 mL min⁻¹), and analyzing the gas exiting the reactor in a mass spectrometer (MKS-PPT). The signals were chosen to allow the study of some compounds of interest that were monitored and recorded, i.e., *m/z* values of 2 (hydrogen), 16 (methane), 18 (water), and 28 (carbon monoxide). After the desorption experiment, the system was cooled down to RT and a new heating and monitoring was performed with the objective of eliminating and analyzing all of the hydrogen trapped in the bulk of the molybdenum carbide.

Benzene hydrogenation was carried out at atmospheric pressure, under a 30 mL min⁻¹ of hydrogen saturated with benzene vapor at 296 K (*p_v* = 11.3 Pa) at 323 and 363 K reaction temperature. Experiments were performed immediately after in situ carbide synthesis with 0.375 g of bulk carbide followed by cooling with pure hydrogen (120 mL min⁻¹). Reaction products were analyzed on-line by a Finnigan 9001 gas chromatograph equipped with a flame-ionization detector and a methyl siloxane capillary column (30.0 m × 250 μm × 1.0 μm). Under the employed conditions, cyclohexane was the only product formed and detected by gas chromatography.

2.2. Theoretical calculations

In order to verify the possibility of hydrogen adsorption on the Mo₂C surface during the cooling step under flow of CH₄/H₂ gas mixture and its concomitant incorporation in the bulk during the carburization step, several models have been constructed containing different amounts of hydrogen for a given Mo₂C unit cell. The unit cells for molybdenum carbide used in this study are of orthorhombic type. The calculated cell constants are *a* = 4.73 Å, *b* = 6.06 Å, and *c* = 5.25 Å [17], which should be compared to experimental values of *a* = 4.729 Å, *b* = 6.028 Å, and *c* = 5.197 Å [18]. We will refer to this unit cell as model cell 1 (MC1), to which different amounts of hydrogen were incorporated. Calculation with this unit cell provided an initial exploratory study of incorporation of hydrogen.

A second type of unit cell, which we will refer as model cell 2 (MC2), was constructed by propagating the MC1 cell one time in the *z* direction, i.e. a (1 × 1 × 2) supercell, and by establishing a vacuum layer of 17 Å, in order to provide a model to surface studies. This supercell was used to study the concomitant adsorption of hydrogen with its imprisoning in its bulk.

In both model cells, atomic positions were optimized but cell constants were kept fixed, since no expansion is experimentally observed when hydrogen is incorporated into molybdenum

carbide, i.e., when molybdenum carbide is prepared by carburization of the oxide.

A detailed thermodynamic analysis was done concerning the process of adsorption and occlusion of hydrogen in molybdenum carbide from gas phase, and the diffusion of hydrogen atoms from the bulk to surface was also investigated. Some diffusion paths have been calculated by the Nudged Elastic Band [19] method, which is commonly used to calculate the minimum energy path. In this method several intermediate images can be generated along the path connecting two minima (reactants and products) and each image is optimized defining the minimum energy path.

Although not very large, these unit cells provide a clear understanding of the problem we are facing. Larger unit cell could be a better choice but there is a computational limitation, especially in what concerns the calculation of phonon frequencies as discussed later.

Calculations were done at spin unpolarized Density Functional Theory (DFT) level with periodic boundary condition, plane wave basis set and ultrasoft pseudo-potentials [20]. The exchange and correlation functional developed by Perdew et al. [21] was used. Occupation was treated by the cold smearing technique of Marzari et al. [22], with smearing parameter of 0.02 Ry for structural optimization. All calculations have been done with Quantum Espresso suite of programs [23].

For thermodynamic analysis, the Fermi-Dirac distribution has been used to determine the occupation of electronic levels and consequently for the calculation of the electronic partition function as discussed below. For the present case though, it will be shown that results are essentially the same if the cold smearing distribution is used in the calculation of the electronic partition function.

The kinetic energy cutoff was 30 Ry. Phonon frequencies have been calculated at Density Functional Perturbation Theory (DFPT) [24] level and the obtained values were used to validate the optimized geometries as real minima. The vibrational data were also used to calculate thermodynamic functions.

For thermodynamic analysis, partition functions were constructed by considering the harmonic oscillator-rigid rotor approximation for molecules in the gas phase, and harmonic oscillator for condensed phases.

The Gibbs free energy is written as:

$$G = H - TS \quad (1)$$

which combined with enthalpy and Helmholtz free energy expressions:

$$H = U + PV \quad (2)$$

$$F = U - TS \quad (3)$$

results in:

$$G = F + PV \quad (4)$$

In the canonical ensemble, the Helmholtz free energy is written as:

$$F = -RT \ln Q \quad (5)$$

Consequently, the Gibbs free energy can be written as:

$$G = -RT \ln Q + PV \quad (6)$$

Using the ideal gas approximation, the Gibbs free energy becomes:

$$G = -RT(\ln Q - 1) \quad (7)$$

For the gas phase, the partition function has electronic, vibrational, translational and rotational contribution. The electronic

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