Editor's choice paper

Theoretical and experimental study of ethanol adsorption and dissociation on β-Mo₂C surfaces

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Nilda Chasvin [a], Alejandra Diez [a], Estela Pronsato [b], Romana Šedivá [c], Viktor Johánek [c], María Alicia Volpe [d,*], Carolina Pistonesi [b]

[a] Departamento de Química, Universidad Nacional del Sur, & INQUISUR(UNS-CONICET), Av. Alem 1253, 8000 Bahía Blanca, Argentina
[b] Instituto de Física del Sur IFISUR, Departamento de Física, Universidad Nacional del Sur, (UNS)-CONICET, Av. Alem 1253, 8000 Bahía Blanca, Argentina
[c] Department of Surface and Plasma Science, Charles University, Prague, Czech Republic
[d] Planta Piloto de Ingeniería Química, UNS-CONICET, Camino Carrindanga Km 7, 8000 Bahía Blanca, Argentina

ABSTRACT

The adsorption and dissociation of ethanol over molybdenum carbide were studied in the context of the production of H_2 from alcohols. A β-Mo_2C catalyst was prepared from char and Mo salts. The sample was characterized by N_2 sorptometry at 77 K, temperature programmed reaction of H_2, X-ray diffraction (applying Rietveld approximation) and X-ray photoelectron spectroscopy for investigating on the catalytic properties of the prepared sample. The catalyst would be active and stable for H_2 dissociation at 500–600 K. The value of ethanol adsorption energy was −0.92 eV, as calculated on β-Mo_2C (001) surface by means of self-consistent density functional calculations. A transfer of electron density from the surface to adsorbed ethanol was concluded from calculations. Plausible reaction pathways corresponding to ethanol dissociation to ethoxy were theoretically studied by using the Climbing Image Nudged Elastic Band (CI-NEB), which shows and activation energy value of 0.57 eV.

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1. Introduction

Alcohols decomposition on heterogeneous catalysts is an important reaction related to H_2 production for fuel cell [1–3]. Pt supported on Al_2O_3 is active for this reaction, however this catalyst produces CO and it becomes easily deactivated [4,5]. Taking into account the technological importance of alcohols decomposition, there exists a great interest to find new catalysts, more efficient, and more stable under reaction conditions than traditional Pt based ones.

Transition metal carbides have been studied as catalysts for different reactions because of their low price and peculiar chemical and physical properties. Levy and Boudart have concluded that tungsten carbide (WC) exhibits similar or even better catalytic behaviour than Pt for several reactions [4]. Later, other works have demonstrated that molybdenum carbide (Mo_2C) is effective for carrying out different reactions, as for example alcohols decomposition [6–9] and CH_4 aromatization [10]. Mo_2C exists in different crystalline phases such as cubic γ-Mo_2C, hexagonal α-Mo_2C, δ-Mo_2C and orthorhombic β-Mo_2C (following Joint Committee on Power Diffraction Pattern). Although in earlier works, the hexagonal α phase was considered to be the active one for alcohols dissociation, at the present, β-Mo_2C is considered to be responsible for developing activity [1].

Theoretical studies, at density functional theory level, focused on the catalytic activity of Mo_2C. Ren et al. have studied the adsorption of O_2, H, CH_2 and C_2H_2 on Mo_2C surfaces, finding stronger adsorptions on the Mo-terminated than on the C-terminated surfaces [11,12]. Water-gas shift reaction over β-Mo_2C(001) surfaces has been studied by Tominaga and Nagai finding a reaction pathway for CO_2 formation [13], they also have analyzed methane reforming on the same surface, modeling the formation of ethylene or ethane [14]. Some of us have obtained theoretical results on CO adsorption [15,16] and also on the dissociation of methyl iodide [17] and methanol [2,18] on β-Mo_2C(001) surface, finding adsorption energies, vibrational frequencies and reaction pathways in agreement with experimental values.

In the present work, the study of the adsorption and the dissociation of ethanol on a β-Mo_2C catalyst is carried out from two different approaches, a theoretical and an experimental one. A model β-Mo_2C catalysts is studied with self-consistent density functional theory (DFT) calculations, to carry out the analysis of the

adsorption and the subsequent dissociation of ethanol. In addition, reaction pathways for the ethanol dissociation on molybdenum carbide were analyzed by using the climbing image nudged elastic band method (CI-NEB). Besides, a β-Mo_2C sample is prepared from commercial carbon and molybdenum salts. The sample is characterized with N_2 sortometry, temperature programmed reaction of H_2, X-ray diffraction (performing a Rietveld refinement) and X-ray photoelectron spectroscopy. An attempt to conclude about the catalytic properties of molybdenum carbide for the ethanol decomposition for producing H_2 is carried out.

2. Methods and materials

2.1. Catalyst preparation and characterization

Mo_2C was prepared from Molybdic acid (Sigma, 98.98%), ammonium molybdate (Sigma, 98.98%), and char (Anedra). 0.22 g of molybdic acid, 0.23 g of ammonium salt and 0.55 g of char were put in a furnace under H_2 flow (5 ml/min) at 650 °C, for 4 h. Finally the material was cooled down to room temperature under H_2 flow, subsequently the H_2 flow was switched to a N_2 flow. The resulting material was characterized by X-ray diffraction (XRD) in a Philips PW1710 BASED instrument with CuKα radiation, within a 2θ range of 20–110°, with a scanning speed of 1.2°/min. The pattern was analysed following Rietveld approximation. Textural characterization of the catalysts was carried out by N_2 adsorption at 77 K in a Quantachrom Nova 1200e sorptometer. The specific surface areas were calculated employing the BET equation and the pore volume by the Dubinin–Radushkevich equation.

Ethanol decomposition process was monitored by temperature programmed reaction (TPRx). Experiments were conducted in a custom-built laboratory micro-reactor system. The sample is sandwiched between a resistive heater at the bottom and a silicate glass with two feeding holes and a network of channels for effective gas distribution over the sample surface at the top, forming a small micro-reactor cell volume. Silicon rubber sealing (100 mm thick) is placed around the perimeter of the sample to prevent leakage. The reactor cell is incorporated in a massive metal block with integrated thermocouple (K-type) to assure good thermal stability and spatial homogeneity. All experiments were done at total gas pressure of 1 bar and the sample temperature ranging between 300 and 630 K; the heating rate of the temperature ramps was set to 2 K/min. Ethanol was fed to the reactor in the form of vapor generated by bubbling pure helium (Linde Gas, 4.6, 20 sccm flow rate) through a heated saturator (303 K) filled with liquid ethanol (Penta, 99.5% purity). The He flow was adjusted precisely by Alicat Scientific mass flow controller. All stainless-steel tubing between the saturator and the reaction cell was heated to about 360 K to prevent condensation of ethanol vapor before reaching the sample. The stream of products leaving tinly unreacted ethanol vapor and water) from clogging the metering valve or deteriorating vacuum in the QMS chamber.

The sample was also characterized by X-ray photoelectron spectroscopy (XPS). The sample was previously calcined at different temperatures (250, 400 and 600 °C) *ex-situ*. Another pre-treatment consisted of heating at 250, 400, 600 and 800 °C in the apparatus chamber. For all the cases, binding energy, BE, of $Mo3d_{5/2}$ were measured following charge correction employing C1s peak.

2.2. Computational method and surface model

The density functional theory, implemented by the Vienna *ab initio* simulation package (VASP) [19], which employs a plane-wave basis set and a periodic supercell method [20,21] was applied for studying β-Mo_2C. Potentials within the projector augmented wave method (PAW) [22] and the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional were used [23,24].

For bulk optimization, the lattice parameters for β-Mo_2C were obtained by minimizing the total energy of the unit cell using a conjugated gradient algorithm to relax the ions and considering a set of $7 \times 7 \times 7$ Monkhorst–Pack k-points to sample the Brillouin Zone [25].

Molybdenum terminated and carbon terminated (001) surfaces were modeled with slabs of five layer thicknesses using the DFT lattice parameters, previously obtained from bulk optimization. During optimization the first two layers were allowed to relax, and a set of $3 \times 3 \times 1$ Monkhorst-Pack k-points was used.

The adsorption of the ethanol molecule was investigated on different sites of Mo and C terminated surfaces, with ethanol coordinated *via* the O atom to the substrate. For these calculations, the adsorbed species and the first two surface layers were allowed to relax. A kinetic energy cutoff of 750 eV was employed for all the calculations. Also, for all the geometry optimizations a cut condition of 10^{-3} eV for the total energy of the system between two ionic relaxation steps, was considered. The electronic relaxation convergence criterion was set to 10^{-4} eV. Van der Waals interaction between pairs was included by means of Grimme DFT-D2 method [26].

The ethanol adsorption energy was computed by subtracting the energies of the gas-phase species and the surface from the energy of the adsorbed system as follows:

$$E_{ads}(ethanol) = E(ethanol/slab) - E(ethanol_{gas}) - E(slab)$$

With this definition, negative adsorption energies correspond to energetically favorable adsorption sites on the surface. The more negative the values, the stronger the adsorption bonds.

Ethanol dissociation to ethoxy on both Mo and C terminated surfaces was also investigated. Plausible reaction pathways were modeled using the climbing image nudged elastic band method (CI-NEB) [27]. Eight geometry images for each cycle were considered. The nature of the transition states on the potential energy surface has been tested based on the analysis proposed by Henkelman et al. [28] and its configuration was verified by a vibrational analysis, finding one imaginary frequency.

The electronic charges on atoms were computed using Bader analysis [29]. The net charge of the ethanol/ethoxy molecule was calculated adding the individual charges of the C, H and O atoms.

3. Results and discussion

3.1. Experimental characterization

The Mo_2C sample prepared form molybdenum salts and char was analysed by XRD to confirm the presence of β-phase. The XRD pattern of the sample is shown in Fig. 1, in which the experimental data, as well as the ones calculated from the Rietveld method approximation are shown. The presence of other species than molybdenum carbide could be disregarded since no other peaks than the corresponding to the β-Mo_2C phase was detected. Besides, the position of the diffraction peaks is in line with the β-Mo_2C phase crystalline structure, which has an orthorhombic crystal structure with Mo atoms slightly distorted from their positions in closed-packed planes and carbon atoms occupying one-half of the octahedral interstitial sites.

The agreement between experiment and calculation following Rietveld method is quite high for the low angle diffraction peak. On the other hand, at high 2θ angles, the agreement is rather low. The disagreement would be more likely associated to an instrumental artifact, originated in the fixed slit of the diffractometer.