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Computational insights into reduction of the Phillips CrO_x/SiO_2 catalyst by ethylene and CO

Maciej Gierada, Jarosław Handzlik *

Faculty of Chemical Engineering and Technology, Cracow University of Technology, ul. Warszawska 24, 31-155 Kraków, Poland

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ABSTRACT

The mechanism of the reduction of the Phillips CrO_x/SiO_2 catalyst with ethylene is still not determined. In this work, full reaction pathways for this process, including further transformations of the oxygenated products, are calculated. The mechanism of the CrO_x/SiO_2 reduction with CO is also studied. It is predicted that the most kinetically favored reduction mechanism involves the reaction between ethylene and both oxo ligands of the surface dioxo Cr(VI) species, leading to formation of Cr(II) site and two formaldehyde molecules. We show that formaldehyde oxidation to carbon oxides and water over the dioxo Cr(VI) sites can be kinetically more accessible than conversion to methyl formate over Cr(II) sites. Formaldehyde can also easily generate various surface intermediates. The calculated activation barrier for the reduction of the CrO_x/SiO_2 system with CO is higher than in the case of the reduction with ethylene.

1. Introduction

The Phillips catalyst, composed of Cr oxide species supported on silica, is still one of the most important catalytic systems that is successfully used in the industrial production of high-density polyethylene [1–9]. Despite many years since the discovery [10] of its unique activity in ethylene polymerization, several questions about its nature are still being discussed. Among others, there is no clear picture how ethylene reacts with Cr(VI) surface oxide species to produce reduced Cr sites which are able to initiate ethylene polymerization.

Typical experimental procedure of the Phillips catalyst preparation leads to a system with a surface covered by well-dispersed Cr(VI) oxide species [2,4,9,11–16]. Different structures of such a species were proposed, i.e., monomeric, dimeric and polymeric [2,4,5,11–14,17–32]. However, it is often claimed that monomeric Cr(VI) sites dominates on the silica surface at low chromium loadings [4,12–15,21,23,25,26,28–32]. Our previous computational studies [27] also indicate thermodynamic preference for the monomeric Cr(VI) structures over their dimeric counterparts. Monomeric dioxo Cr(VI) species are commonly postulated [4,12–15,25–27], although some authors also proposed minor monooxo Cr(VI) species [12–14,24–27]. The previous DFT calculations [25] showed that the dioxo Cr(VI) species is thermodynamically much more stable than the monooxo one. *In situ* and *operando* Raman spectroscopy studies suggested that the former species are easier to reduce/activate than the latter [12,14,26].

When the calcinated Phillips catalyst is contacting with ethylene, usually at about 373 K, an induction period of the polymerization process is observed. Cr(VI) species are reduced to Cr(II) and/or Cr(III) [1,2,4,14,32–35]. Several authors postulate formation of various by-products, i.e., formaldehyde [33,34,36], esters [37–39], aldehydes/ketones [37] and oligomers of ethylene [33,34,37] at the initial stage of the reaction. In the past, Baker and Carrick [36] reported formation of carbonyl compounds together with Cr (II) sites when Cr(VI) reacts with various olefins. They also proposed a concerted mechanism of these transformations, involving formation of dioxachromacyclopentane intermediate. Liu et al. [33,34], based on XPS and TPD data, demonstrated that formaldehyde can be formed, together with unsaturated hydrocarbons, mainly propylene and butylene, when the calcinated Phillips catalyst is contacted with ethylene. They postulated that formaldehyde-coordinated Cr(IV) ethylidene site, possibly generated via 1,2-hydrogen transfer of π-bonded ethylene, is responsible for propylene and butylene formation through alkene metathesis

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* Corresponding author.
E-mail address: jhandz@pk.edu.pl (J. Handzlik).

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type mechanism [34]. On the other hand, our recent computational studies on ethylene polymerization over the Phillips catalyst suggest that direct 1,2-hydrogen shift resulting in Cr(IV) ethylidene species is a very unlikely process, at least in the absence of formaldehyde [40], in accordance with other works [41–43]. Zhong et al. [43] theoretically found that bare Cr(II) oxide species strongly interacts with formaldehyde, suggesting that the latter acts as a mild poisoning agent. Such a role of ethylene-oxidized by-products was also postulated elsewhere [1,4,44,45]. Zhong et al. [43] concluded that no reaction can start over Cr(II) site with two formaldehyde ligands coordinated, in contrast to bare Cr(II) site and Cr(II) with one formaldehyde molecule adsorbed. Barzan et al. [38,39] recently proposed that aldehydes react with the reduced Cr sites giving ester species, which would remain in the coordination sphere of Cr and can influence the activity towards ethylene polymerization. Other experimental results suggest that partially oxidized products, formed during the reduction of the CrO_x/SiO_2 system with ethylene, can be converted to CO_2 and H_2O at temperatures much higher than those typical of ethylene polymerization [26,37].

Pre-reduction of the Phillips catalyst with CO results mainly in Cr(II) formation [1,2,4,8,9,16,17,46]. The reduced catalyst shows activity in ethylene polymerization even at room temperature practically without the induction period and the oxygenated by-products are not formed. Hence, many authors investigate ethylene polymerization over the Phillips catalyst starting from the reduced system [3,4,35,41–43,47–53]. However, in the case of the industrial process, the reduction step using CO is usually not carried out [1,4,9].

From the information given above it is seen that the mechanistic aspects of ethylene transformations over Cr(VI) oxide species on silica are not established, despite their particular importance. Reduction from Cr(VI) to Cr(II) and consecutive reactions involving oxygenated by-products can account for most of the induction period. As the polymerization process might start rapidly after formation of reduced Cr species, experimental discrimination between the reduction of the Cr(VI) species and ethylene polymerization is a challenging task. Additionally, unambiguous determination of partially oxidized products is difficult, because of coinciding signals coming from different organic species [37].

In this computational work, for the first time full reaction pathways of the Phillips catalyst reduction with ethylene are investigated. We propose several reduction mechanisms involving the most commonly postulated dioxo Cr(VI) species. In particular, the path proposed by Baker and Carrick [36] is studied in detail. Additionally, we investigate reduction of the monooxo Cr(VI) species with ethylene. This enables us to explain different behavior of the monooxo and dioxo Cr(VI) species towards ethylene, recently observed experimentally [26]. Moreover, we also consider further transformations of oxygenated by-products. Among others, possible oxidation of formaldehyde to CO/CO_2 and H_2O, as well as, ester formation, are studied in detail. Additionally, calculated vibrational frequencies for the adsorbed oxygenated organic species are discussed. A mechanism of reduction of the Cr(VI) species by CO is also investigated. To the best of our knowledge, such comprehensive theoretical studies on the reduction of the Phillips CrO_x/SiO_2 catalyst and other related transformations involving the oxygenated by-products have never been reported before.

2. Computational models and methods

Cluster models of the chromium surface species used in this work were developed based on the β-cristobalite framework [54] and they were fully relaxed to allow for the amorphous nature of the support. Fig. 1 presents the optimized structures of the dioxo (**^{1}A**) and monooxo (**^{1}B**) Cr(VI) oxide species. The models, containing 9 and 7 Si atoms, respectively, are larger or comparable to other proposed cluster models of the supported CrO_x/SiO_2 catalyst [41–43,49,50,52,55]. Analogous models were previously successfully applied in the studies of the mechanism of ethylene polymerization over the Phillips catalyst [26,40] and olefin metathesis catalyzed by molybdena-silica system [56,57]. Additionally, to account for possible interactions between Cr(II) site and surface groups, another cluster model was also developed (Fig. S1, Supplementary Data).

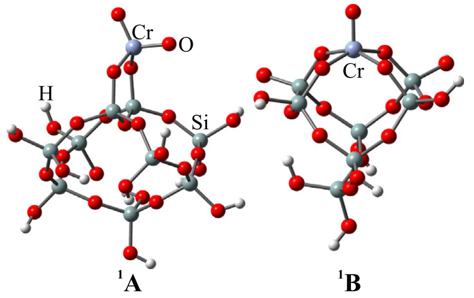

Fig. 1. Models of isolated surface Cr(VI) species: **^{1}A** – dioxo, **^{1}B** – monooxo.

Geometry optimization was carried out using the hybrid PBE0 functional [58], known to be accurate in predicting geometries of transition metal complexes [59–61], combined with the def2-SVP basis set [62]. Harmonic vibrational frequencies were calculated to confirm local minima or first-order saddle points, and, to determine Gibbs energy corrections at T = 373 K (typical catalyst operation temperature) and p = 1 atm (if not stated otherwise). The transition states were additionally verified applying the IRC method [63,64]. The presented ν(CH), ν(CO) and δ(CH) frequencies are scaled by 0.9569, 0.9274 and 0.9835, respectively. The scaling factors were obtained through a least-square approach, based on the experimental and theoretical frequencies for methyl formate and formaldehyde in gas phase. Although a common practice is to use a generic scaling factor for a given theory level, the ratios of the observed frequencies to the calculated harmonic frequencies are not constant for different vibrational modes [65,66].

In order to obtain better estimation of energy, further single point calculations were performed for each optimized structure using the PBE0 functional and the def2-TZVPP basis set [62]. The reaction pathways are discussed in terms of Gibbs energies (if not stated otherwise) estimated by adding the Gibbs energy corrections and the DFT-D3(BJ) dispersion corrections [67,68] to the PBE0/def2-TZVPP single point energies. The computational methodology is the same as in our previous papers on the Phillips catalyst [26,40]. By performing test calculations, we have recently shown [40] that this methodology is adequate for studying the properties and reactivity of the CrO_x/SiO_2 system.

The minimum energy crossing points (MECP) between two potential energy surfaces of different spin states were localized using the method developed by Harvey and co-workers [69]. Spin-unrestricted calculations were performed for the open-shell systems. The ground state for each structure was verified. High-spin ground states for the reduced Cr species were always found, whereas for the Cr(VI) species the ground state is singlet.

Gaussian 09 package [70] was used to perform all calculations. GaussView 5.0 software [71] was applied for the graphic presentation of the structures.

3. Results and discussion

3.1. Nomenclature

The nomenclature of the models studied in this work is based on the capital letters, numbers and numbers in superscript. Capital