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Interaction of different poisons with $MgCl_2/TiCl_4$ based Ziegler-Natta catalysts

Naeimeh Bahri-Laleh

Polymerization Engineering Department, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965/115, Tehran, Iran

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ABSTRACT

Adsorption of different poison molecules on activated $MgCl_2$ is investigated within DFT using a cluster model of the $MgCl_2$ surface with $(MgCl_2)_{16}$ formula containing four 4-coordinated and eight 5-coordinated Mg atoms as (110) and (104) surfaces, respectively. Studied poison molecules are chosen as possible impurities in hydrocarbon solvents and monomer feeds and contain water, hydrogensulfide, carbondioxide, molecular oxygen and methanol. First, adsorption of 1–4 molecules of different poisons to the (104) and (110) lateral cuts of $MgCl_2$, as well as their adsorption on $[MgCl_2]/TiCl_2Et$ active center and $AlEt_3$ cocatalyst is considered. Results reveal that poisons strongly stabilize both crystal surfaces, mostly Ti active center relative to the unpoisoned solid. Second, energy barrier (E_{TS}) for ethylene insertion in the presence of different poisons located on the first and second Mg atom relative to the active Ti is calculated. While poison molecule located on the second Mg does not change E_{TS}, coordination of it into the first Mg atom increases E_{TS} by 0.9–1.2 kcal mol^{-1}. In the last part of this manuscript, the stereoselective behavior of active Ti species, with and without poison molecules and external electron donor, is fully explored.

1. Introduction

$MgCl_2$ is the support of choice for the Ziegler–Natta (ZN) catalyst systems currently used in the polyolefin industry [1,2]. It is believed to act as a template for the epitactic chemisorptions of the active Ti species [3]. Ziegler-Natta catalysts of the latest generation allow a morphological control of the polymer particles and require small amounts of titanium and aluminum alkyls ensuring a good control of the various aspects of polymerization [4]. Nevertheless, catalyst deactivation, the loss over time of catalytic activity and/or selectivity, is a problem of great and continuing concern in the practice of industrial ZN catalytic process [5,6].

The mechanisms of solid ZN catalyst deactivation are many; nevertheless, they can be grouped into six intrinsic mechanisms of catalyst decay: (1) poisoning, (2) fouling, (3) thermal degradation, (4) vapor compound formation and/or leaching accompanied by transport from the catalyst surface or particle, (5) vapor–solid and/or solid–solid reactions, and (6) attrition/crushing [7]. Considering these mechanisms, the causes of deactivation are basically threefold: chemical, mechanical, and thermal in which mechanisms 1, 4 and 5 are chemical in nature while 2 and 6 are mechanical.

Among deactivation mechanisms, poisoning is an important concept that has not yet been well understood. It is defined as the strong chemisorption of impurities on sites otherwise available for catalysis. Thus, poisoning has operational meaning; that is, whether a species acts as a poison depends upon its adsorption strength relative to the other species competing for catalytic sites. Catalyst poisons consume catalyst and co-catalyst with the result that operating costs and the residual concentration of the catalysts in the final product increase.

Specifically, in the case of the titanium-based ZN ($TiCl_4/MgCl_2$) polymerization catalysts, such systems are extremely sensitive to some organic compounds, which may act as poison, reducing polymer productivity. Usually, the poisons include mainly carbon monoxide, carbon dioxide, alcohols, sulfide, water, and oxygen, etc [8]. It is well known that, the organoaluminum compounds very rapidly react with most common catalytic poisons, such as water, oxygen and alcohols, and convert them into other compounds, usually aluminum alkoxides R_2AlOR' [9], that are less detrimental to catalyst performance. Some other poisons, e.g., carbon monoxide and carbon dioxide do not interact with organoaluminum compounds. If small quantities of these poisons are deliberately added to the reactor, they immediately halt the polymerization reaction [10].

The introduction of a poison molecule in the catalyst system can influence different aspects of the catalytic process. It can coordinate

E-mail address: n.bahri@ippi.ac.ir

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to the surfaces of $MgCl_2$, to the Ti active center, to the neighborhood of the catalytic active site, or even can coordinate to the Al-alkyl used as cocatalyst influencing the activity and stereo selectivity. Although many computational studies were concentrated on to the first Ti active site formation [11], chain growth [12], support structure and its interaction with electron donors [13], no investigation was considered the interactions between different classes of poison molecules with the $MgCl_2$ support and Ti active center.

This work is aimed to shed light in these issues using molecular simulation by density functional theory studies. After studying possible interactions between poison molecules and different Lewis acidic species (i.e. $MgCl_2$, $Al(Me)_3$ and $TiCl_4$), their influence on catalyst activity and stereospecifity is concerned.

2. Computational details

All the calculations are carried out with density functional theory (DFT), employing the Gaussian 09 software [14]. Geometry optimizations are performed using the Perdew and Ernzerhof (PBEh1PBE) functional [15], which is a hybrid generalized gradient approximation functional, since we have previously shown that for ZN catalyst systems the best performances, in the case of geometry, are achieved by this functional [13]. The electronic configurations of the atoms are described by a triple-ξ basis set augmented by a polarization function (Gaussian basis set TZVP) [16]. After geometry optimizations, single point calculations on B3LYP/TZVP level of theory are performed on the PBEh1PBE/TZVP geometries and energy values obtained by this functional are reported here since as reported before better agreement with the experimental results can be obtained with B3LYP and it is a widely used functional in the molecular simulation of transition metal catalytic systems [17,18].

For the adsorption of poison molecules, different surfaces of α-$MgCl_2$ are selected taking into account the previous literature experimental and theoretical: the surface (104) with 5-coordinated Mg, and (110) with 4-coordinated Mg atoms. Different coverages by 1–4 poison molecules of both the (104) and the (110) surfaces are studied. The poison adsorption energy, E_{ad}, is calculated according to Eq. (1):

$$E_{ad} = E_{Mg/P} - E_{Mg} - E_P \quad (1)$$

And, the average adsorption energy per poison molecule, E_{av}, is calculated as in Eq. (2).

$$E_{av} = \frac{E_{Mg/P} - E_{Mg} - n_P \cdot E_P}{n_P} \quad (2)$$

Where, $E_{Mg/P}$ is the energy of the system composed of a poison molecule adsorbed on the $MgCl_2$ surface, E_{Mg} and E_P are the energies of the uncovered $MgCl_2$ system and of the free poison, respectively, and n_P is the number of poison molecules adsorbed.

Vibrational analysis is carried out under standard conditions (P = 1 Atm and T = 298 K) to calculate enthalpy (H_{ad}) and the Gibbs free energy (G_{ad}) of adsorption using the same formula of Eq. (1). The only difference is that instead of zero point energies, H and G were used in the calculations.

It should be noted that, when using Eqs. (1) and (2) to calculate the adsorption energies, since no intermediate is contemplated, the use of infinitely separated species could bring an overestimated stabilization for the overall result.

The transition state for each insertion pathway is approximated by the structure obtained at 2.15 Å of the distance between the ethylene/propene C1 carbon and the C1 carbon of a methyl/isobutyl group (in ethylene/propene polymerizations) bound to the Ti center. The stereospecificity (E_{re-si}) is given as differential activation energies of two propene 1,2-insertion pathways with *re* and *si* prochiral faces.

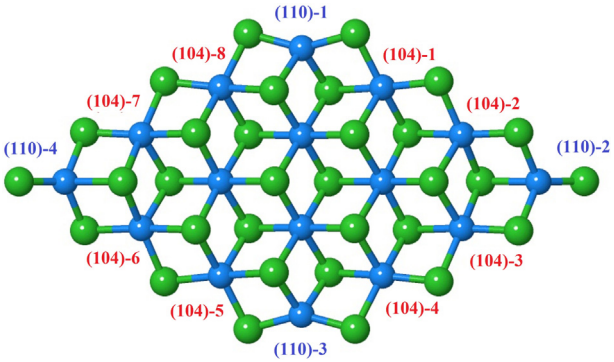

Fig. 1. Model of a $MgCl_2$ monolayer employed for Mg-poison interactions, with indication of the (110) and (104) planes.

In case of Ti^{III} species and those containing O_2 molecule, unrestricted calculations with triplet and quintet spin states, respectively are performed, since Ti^{III} has one unpaired electron, while for O_2 containing systems it is found that a multiple electronic state with unpaired electrons is favored relative to the singlet electronic state.

In all cases, fully relaxed system (containing all species i.e. $MgCl_2$ support, Ti active center, poison molecules, electron donors ...) is optimized. Characterization of the located stationary points as minima or transition state is performed by frequency calculations. Total frequencies and geometries are provided in the Supporting Information.

3. Results and discussions

Considering the chemical species in the polymerization medium, three principal different paths can be envisaged for the possible interaction between poison molecules with these species i.e. Mg-poison, Al-poison and Ti-poison interactions. Here, the coordination stability of poison molecules on the acidic species in the polymerization medium is discussed.

3.1. Interaction of poisons with neat $MgCl_2$ (poison-Mg interaction)

The modeling of the poison species on a $MgCl_2$ support is done using a cluster model that was proposed by Gupta group [19]. This model has the advantage of having features that compares favorably to experimentally observed $MgCl_2$ surfaces, as discussed in the work of Cavallo and co-workers [20]. These features mainly include the co-presence of the two most accepted lateral cuts in $MgCl_2$ crystallites, i.e. (104) and (110) lateral cuts that was deduced from optical microscopy and high resolution TEM observation of $MgCl_2$ microcrystals. The structure of the cluster model of $MgCl_2$ support is shown in Fig. 1.

The proposed model with 16-$MgCl_2$ units, has 4 Mg atoms in (110) surface and 8 Mg atoms in (104) surface. The adsorption of poison molecules as water, hydrogen sulfide, carbon dioxide, molecular oxygen and methanol is considered on selected $MgCl_2$ surface containing (110) and (104) lateral cuts. As mentioned before, these poisons are chosen as possible impurities in hydrocarbon solvents and monomer feeds [10]. The adsorption energy of the 1–4 molecules of different poisons to the (104) and (110) lateral cuts of $MgCl_2$ is reported in Table 1. Also, Gibbs free energy and enthalpy of adsorption are depicted in Table 2. Adsorption sites are labeled as (110)-1, (110)-2, (110-3), (110)-4, (104)-1, (104)-3, (104)-5 and (104)-7 in the $MgCl_2$ model depicted in Fig. 1. Of course, it is not claimed that the adsorption models proposed here corresponds to real active species. Rather, it is believed that in low