Thermal degradation of poly (vinyl chloride) over magnetite (111) surface

Oday H. Ahmed1,2, Mohammednoor Altarawneh1, Zhong-Tao Jiang1 and Bogdan. Z. Dlugogorski1

1 School of Engineering and Information Technology, Murdoch University, Murdoch, WA 6150, Australia
2 Department of Physics, College of Education, Al-Iraqia University, Baghdad, Iraq

Introduction

Crude steel manufacturing operations are accompanied by emission of a large amount of hazardous electric arc furnace dust (EAFD) (around 20 kg of dust per each ton of produced steel). Global production of polyvinyl chloride (PVC) plastics is projected to grow to about 180 million tons in 2021. Combined treatment of both EAFD and PVC is a promising technique for extracting valuable metals from EAFD as it is a solution to minimize their environmental harmfulness.

However, despite of many detailed experimental studies over the last few years; the specific underlying mechanism of the reactions between EAFD and PVC remain largely poorly understood.

This contribution provides a systematic theoretical thermo-kinetic study of the initial reactions between (Fe3O4(111) surface, as a representative model for metal oxides in EAFD with HCl and selected chlorinated hydrocarbons, as major products from thermal degradation of PVC.

Computational Methodology

All structural and energetic calculations were performed using the Vienna ab-initio simulation package (VASP) based on density functional theory (DFT) under the generalised gradient approximation (GGA) with the exchange-correlation functional proposed by Perdew and Wang (PW91).

Molecular adsorption energy was calculated from the total energy difference: 

\[ E = E_{\text{molecule}} + E_{\text{surface}} - E_{\text{molecule+surface}} \]

The magnetite (111) surface and the adsorption systems were modeled using an eight-layer 2 × 2 periodically repeatable slab with a vacuum thickness of 15 Å.

Transition states (TS) for the prescribed reaction pathways were carried out by employing the “climbing images” nudged elastic band (CI-NEB) algorithm. Typically, sixteen images were produced between the states of reactant and product in each elementary process as the initial guesses for the reaction coordinates.

Acknowledgement

This study was supported by the National Computational Infrastructure (NCI), Australia and the Pawsey Supercomputing Centre in Perth, as well as funds from the Australian Research Council (ARC). O.A thanks the Higher Committee for education-development in Iraq (HCIED) for the award of a postgraduate scholarship.

Results

Dissociative Adsorption of HCl

Fig. 2-4 present energies and structures for the dissociative adsorption of HCl molecule over the magnetite surface. The following remarks summarise the reaction steps:

- As illustrated in Fig.2, the first step of this reaction characterises weak molecular physisorption states of the HCl molecule evidenced by marginal binding energies of only 1.2 kcal mol⁻¹.
- Dissociation of the H-Cl bonds in the second step produces M2 structure.
- The catalytic capacity of magnetite toward uptake of gas phase HCl becomes evident when contrasting the low energy barriers (i.e. 25.4 kcal mol⁻¹) with the energy requirements for the uncatalysed bond fission of CH bonds at 103.2 kcal mol⁻¹.
- Conversion of FeO₂ into FeCl₂ occurs through two subsequent steps, further dissociative adsorption of HCl molecules on O-Fe linkages and the release of water molecules. Fig. 3 and 4 map out these two chemical events.
- Decomposition of HCl on a neighboring O-Fe bond demands an activation energy of 22.8 kcal mol⁻¹ and forms the structure of M4. In a subsequent step, the formation of M5 structure occurs through a slightly endothermic reaction of 2.6 kcal mol⁻¹ and it necessitates a barrier of 12.1 kcal mol⁻¹ characterized by TS3. This process produces adsorbed H₂O molecule via an intramolecular hydrogen transfer between the two hydroxyl groups.
- Elimination of water in the barrierless reaction marks the formation of the experimentally observed iron oxychloride.

Decomposition of Chlorinated Alkanes And Alkenes

On the basis of the energies reported in Fig. 5–8, the dissociative addition channel either requires a very low barrier (chloroethene and 1-chloropropane) or proceeds without encountering a barrier (chloroethene and 2-chloropropane)

The dissociative addition route assume competing importance in formation of acetylene from vinyl chloride. As a result can switch oxidation states, it will be insightful to assess the kinetic feasibility of iron oxides to act as catalysts in hydrogenation reactions of olefins, i.e., similarly to the well established functionality of transition metal oxides and rare earth metal oxides.

References