Formation of Phenoxy-Type EPFR over Hydrated Pure Alumina and Si-Doped Alumina Surfaces

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Introduction

Phenols and phenolic compounds constitute major precursors for the synthesis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F).[1] Their principle sources are coal conversion plants, petroleum, municipal waste treatment plants, synthetic processing and phenol producing industries.[2] In municipal waste incinerators (MWIs), these species reach concentrations of up to 1000 μg/m^3.[3] In the cool zone of a typical MWI, metal oxides, typically dispersed on alumina and silica, provide catalytic surfaces that facilitate the production of environmentally persistent free radicals (EPFR) from phenol[4] via physisorption and chemisorption processes.

The appreciable concentrations of alumina in MWI enable it to serve as an important surface mediator for the heterogeneous formation of PCDD/F. Its concentration in fly ash can reach up to 25–30 %, by mass.[5] In light of the temperature window of the cooling-down zone of the combustor, which is typically 200-600 ℃,[6] the alumina surface endures a combination of hydrated and dehydrated facets. The interplay of alumina and water has been a thematic topic of a great deal of research.[7] In the course of water interaction with alumina, heating reversibly removes the hydroxyl groups, producing a fully dehydrated surface of alumina at a temperature of 450-600 °C.[8] Hence, the lower and higher temperature ends of the cooling zone involve both the hydrated and dehydrated surfaces of alumina.

In our recent study[9], we investigated the interaction of phenol with the dehydrated alumina (0001) surface. We have found that, the mixed Al/O surface termination along the (0001) facilitates the rupture of the phenol O-H bond, producing phenolate − a species that constitutes a precursor for the formation of persistent surface-bound radicals on the surface. Nonetheless, considering the temperature range of interest, a dehydrated alumina surface represents a limiting case scenario for alumina configurations, for which hydrated and dehydrated entities coexist. Thus, an investigation of all modes of interaction between phenol and alumina necessitates addressing the pathways underlying the generation of EPFR on a hydrated alumina surface. Likewise, in real scenarios, trace loads of elements (Si, Cd, Zn, Fe) in combustion systems could readily be deposited on pure termination of alumina. Thus, it is important to investigate the effect of atomic dopants on the efficiency of hydrated alumina surfaces in producing phenoxy-type EPFR.

To this end, this paper has a three-fold aim: (i) to report the modes of interactions between phenol and hydrated α-Al_2O_3 (0001) surfaces, (ii) to offer some important insights into the Si-Al_2O_3 doping system and its effect on the catalytic activity of the surface, and (iii) to improve our current understanding of chemical phenomena operating in the formation of EPFR over both doped and undoped alumina surfaces.

Materials and methods

We deployed the DMol^3 program[10] to perform structural optimisations, energy computations, and estimation of vibrational frequencies for 2×2 α-Al_2O_3 (0001) surface, using the generalised-gradient-approximation (GGA) Perdew-Burke-Ernzerhof (PBE)[11] exchange-correlation functional, along with the Grimme dispersion correction[12] and a double-polarised numeric basis set of DNP. A vacuum distance of 30 Å separated the slab and its images in the periodic system along the *z*-direction. The energies and total forces converged with tolerances of 1×10^{-6} and 1×10^{-5} Ha, respectively. We fitted the reaction rate constants to the Arrhenius equation (i.e. $k(T) = A \exp(-E_a/RT)$ in the temperature range of 298.15 to 1000 K, according to the classical transition state theory (TST).[13]

Results and discussion

Surface-Mediated Dissociation of Phenol over Undoped hydrated α-Al_2O_3 (001) Surface

Dissociation of phenol molecule over the alumina surface results in the formation of either a phenoxy moiety (i.e. phenolate anion) or a phenyl moiety. In our recent study,[9] we found that the rupture of the aromatic C-H bond over the dehydrated surface causes an OH-phenyl adduct to incur a very high energy barrier of approximately 333 to 390 kJ/mol. Accordingly, we limit our analysis to pathways leading to the formation of a phenoxy moiety.

Two possible pathways are considered, water elimination mechanism and hydrogen elimination corridor. The first mechanism signifies a concerted pathway for the elimination of a surface group along with the phenolic H atom as a water molecule and the attachment of the phenoxy O to a surface Al atom. In the second pathway, a hydrogen molecule is produced upon fission of the phenolic O-H and hydroxyl O-H bonds in a process that forms a peroxy linkage between the phenolic O and the surface hydroxyl O. Figure 1 depicts the energy profiles for the two reaction corridors. Both dissociative pathways initiate from the physisorbed molecule oriented vertically above the surface. The formation of the two products D_1 and D_2 was found to be endothermic. Water elimination via Pathway 1 requires an activation energy of 195 kJ/mol, significantly lower than 432 kJ/mol required for H_2 elimination in Pathway 2. Therefore, the kinetics prefer the formation of a phenoxy moiety via the H_2O elimination mechanism.

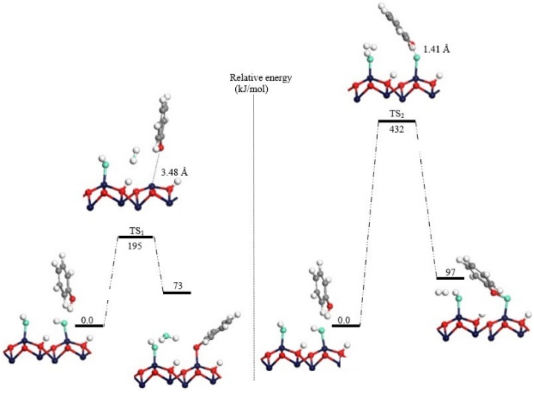

Fig. 1 Relative energy describing the dissociated structures of phenol over the hydrated surface of α-Al_2O_3 (0001). Pathway 1 (TS_1) and Pathway 2 (TS_2). Energy values (in kJ/mol) at 0 K are in reference to physisorbed reactants.

Our recent study investigated the interaction of phenol with the dehydrated alumina surface. We found that, the dehydrated alumina produces surface-bound phenolate through an energy barrier of only 48 kJ/mol.[9] In reference to the energy barrier of Pathway 1 (195 kJ/mol), hydroxyls attached to surface Al atoms substantially increase the energy requirement for the appearance of phenolate adducts on the surface. For the dehydrated surface, the underlying mechanism comprises the direct fission of the phenolic O-H over the Al-O bond on the surface. However, over the hydrated alumina, surface-bound phenolate moieties arise via water elimination; this process typically requires a higher energy barrier.

Doping α-Al_2O_3 (0001) Surface with Silicon

We now investigate the dissociative adsorption of a phenol molecule over a Si-α-Al_2O_3 (0001) doped surface. The underlying aim is to assess to what extent the doping of alumina, either hydrated or dehydrated, modifies its catalytic activity in producing phenoxy-type EPFR.

Figure 2 displays the energy profile for the interaction of a phenol molecule with the Si-α-Al_2O_3 (0001) surface. The reaction proceeds via the physisorption of the phenol molecule on the surface at a binding distance of 1.62 Å above the surface. The phenol molecule dissociates on the surface through a trivial energy barrier of only 31 kJ/mol, where the phenoxy moiety attaches to the Si atom and the hydrogen atom binds to a nearby O atom. This leads to the dissociated structure M_{sd} with a binding energy of -108 kJ/mol. The Si dopant increases the catalytic activity of the dehydrated alumina surface in producing a phenolate adduct, in which the required energy barrier for the formation of phenoxy moiety decreases by 17 kJ/mol compared to an undoped surface (i.e., 48 kJ/mol[9]). A possible explanation for this trend originates from the high coordination number of the Si atom compared to the Al surface atom. The Si atom is saturated due to its attachment to a phenolic oxygen atom.

In an analysis of the catalytic effect of silica on the surface-mediated reactions, Pan et al.[14] reported that, the silica surface mediates formation of polychlorinated dibenzo-*p*-dioxins (PCDD) from the oxidation of 2-chlorophenol molecules (2-CP). The authors examined theoretically the interaction of 2-CP over both hydrated and dehydrated silica clusters. They found that, dehydrated silica clusters produce 2-chlorophenolate from the 2-CP molecule through energy barriers of 27 and 49 kJ/mol over bridge and defect (i.e., double-bonded) sites, respectively. Similarly, in our recent study on the formation of PCDD/F from 2-CP over neat SiO_2 clusters,[15] we investigated the formation of pre-PCDD/F intermediates. In line with the previous finding of Pan et al.,[14] we revealed that, silica facilitates the synthesis of pre-PCDD and pre-PCDF intermediates via the Eley−Rideal mechanism through two different channels that eliminate HCl and Cl_2, demanding energy barriers of 61 and 82 kJ/mol, in that order.

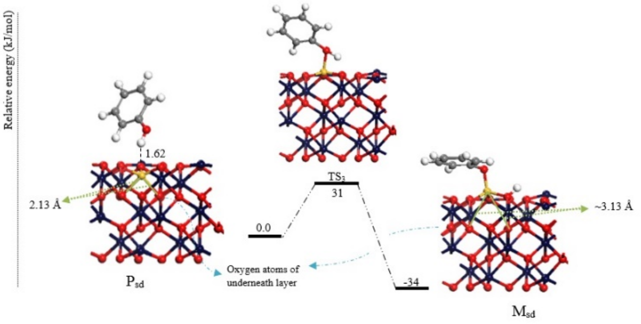

Fig. 2 Relative energy for the formation of desorbed phenolate over the Si-α-Al_2O_3 (0001) substituted surface via dissociative Pathway 3 (TS_3). Energy values (in kJ/mol) at 0 K are in reference to physisorbed reactants.

Next, we describe the effect of Si doping on the catalytic activity of the hydrated α-Al_2O_3 (0001) surface. The mechanistic details of the interaction are similar to those pertinent to the behaviour of undoped hydrated α-Al_2O_3 (001) surface. Two reaction pathways have been considered, namely Pathways 4 and 5, characterising the H_2O and H_2 elimination mechanisms, respectively. Figure 3 displays the energy profile for the interaction of a phenol molecule with the hydrated Si-α-Al_2O_3 (0001) surface. Both pathways display sizable energy barriers of 247 and 418 kJ/mol. By considering the water elimination pathway, the Si-OH-site results in a noticeable increase in the reaction barrier for the formation of phenolate over the Al-OH site (195 kJ/mol versus 247 kJ/mol). This is clearly in contrast to the case of the dehydrated alumina surface, in which dopants reduce the energy barrier for the water elimination from 48 kJ/mol to 31 kJ/mol. Nonetheless, doping the hydrated surface does not modify significantly the energy barrier for the hydrogen elimination channel; cf. 418 kJ/mol with 432 kJ/mol.

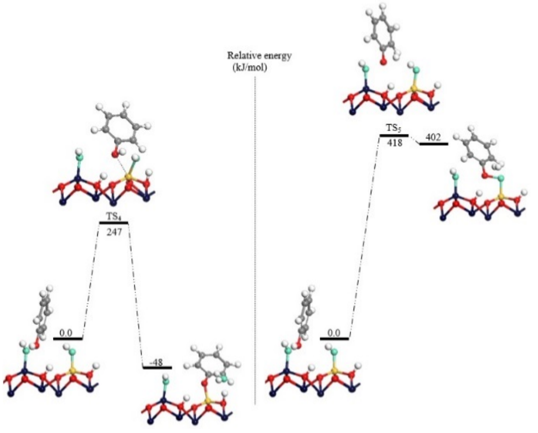

Fig. 3 Relative energy describing the dissociated structures of phenol over Si-α-Al_2O_3 (0001) surface via dissociation Pathway 4 (TS_4) and 5 (TS_5). Energy values (in kJ/mol) are in reference to physisorbed reactants.

A positive correlation exists between the calculated energy barriers for the H_2O elimination mechanism, for both doped and undoped surfaces, and the O-Si/Al bond dissociative energies. For instance, the calculated bond dissociation energies for O-Si and O-Al amount to 798 kJ/mol[16] and 512 kJ/mol,[16] respectively. The difference in the bond dissociation energies of O-Al/Si correlates with the difference in the energy barriers for the water elimination corridors for the Si(O) and Al(O) sites at 247 and 195 kJ/mol, respectively.

Furthermore, desorption of the phenolate moiety into vacuum, from both Si-doped alumina surfaces, is highly endothermic by 300 kJ/mol. This finding accords with those reported in our studies for the interaction of phenol[9] and chlorophenol[15] molecules with alumina surface and a silica cluster of 394 kJ/mol and 379 kJ/mol, in that order. These high energy values make the desorption corridor largely inaccessible. As discussed in the literature,[15] the profound stability of the phenolate species over alumina and silica surfaces enable these adducts to yield PCDD/F by the so-called LH and LR mechanisms.

Kinetic Considerations

Herein, we report the reaction rate constants for all investigated pathways. The search of the transition state involved synchronous and quadratic synchronous transit approaches (LST/QST). Calculated reaction rate constants were fitted to the Arrhenius equation. Figure 4 represents the Arrhenius plots. Pathway 3, corresponding to water elimination over the Si-doped dehydrated alumina surface, incurs the lowest activation energy and displays weak dependence on temperature, in reference to reaction pathways that characterise the hydrated system.

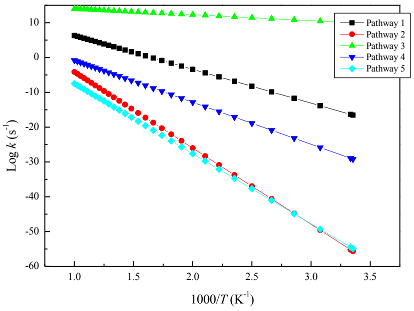

Fig. 4 Arrhenius plots for the studied reactions.

In conclusion, this paper set out to determine the catalytic potential of the hydrated α-Al_2O_3 (0001) surface and the Si modified α-Al_2O_3 (0001) surface in producing phenoxy-type EPFR. Our results, based on the estimated activation energies, show that, the hydroxyl layers attached to the hydrated surface form a shield against attack of the phenol molecules on the surface. A major finding to emerge from this paper is that dehydrated alumina surface doped with Si atoms enhances the catalytic activity of the surface in reference to Al sites by ~36% (based on the difference in analogous activation energies). On the contrary, this effect does not operate for the hydrated alumina surface owing to the presence of the OH layer.

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