A DFT insight into phenol adsorption on Mn-Ce oxide

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1 Introduction

Phenol, an important precursor for many industrial processes, is a nocive contaminant even at very low concentration because of its high toxicity and stability. Thus, its complete removal from wastewater becomes crucial and drives the search for catalysts that would efficiently adsorb and oxidize phenol molecules.

Recently, Ce-Mn oxides catalytic performance was tested in phenol removal from water at 100 ºC, and atmospheric pressure [1]. The results suggested the participation of MnOx species in this process, while DRIFTS spectra of Mn-Ce oxide sample indicated the formation of surface phenolate groups. However, the role of Ce and Mn cations during phenol adsorption on MnOx-CeO_2 solid solutions is still not fully understood.

Thus, in this work we performed ab-initio total energy calculations to evaluate the interactions of a phenol molecule on the 12.5% Mn-doped CeO_2 (111) surface.

2 Theoretical methodology

The density functional theory (DFT), as implemented in the Vienna Ab-initio Simulation Package [2,3], was applied to perform spin-polarized energy calculations of phenol interactions on Mn-Ce oxide catalyst. We also considered the Hubbard correction (U = 5 eV) to describe the strongly correlated Ce(4f) and Mn(3d) electrons. The Kohn-Sham equations were solved with the PAW_GGA approximation and PBE functionals. In this work, we employed the valence electrons: Ce(5s), (5p), (5d), (4f), (6s), O(2s), (2p), and Mn(3d), (4s), an energy cutoff value of 408 eV, a Gaussian smearing of 0.2 eV, and a 4x3x1 k-points Monkhorst-Pack grid. The tolerance for the total free energy change was set in 10^{-3} eV, and the final results were extrapolated to those of SIGMA = 0 eV.

3 Results and discussion

Mn-Ce oxide was modeled as 12.5% Mn-doped CeO_2 fluorite-type solid solution, with a supercell consisting of 2 x 2 x 2 CeO_2 unit cells. This model reflected the XRD spectra of Mn-Ce oxide with molar ratio 10-90; which was prepared by co-precipitation of manganese and cerium nitrate at pH = 11. This spectra only shows the presence of CeO_2 (fluorite-type structure JCPDS # 43-1002). The absence of diffraction peaks corresponding to MnO_x allows us to say that the Mn cations enter CeO_2 fluorite structure, leading to the formation of Mn-Ce oxide solid solution.

Our 12.5% Mn-doped CeO_2 bulk calculations resulted in a lattice parameter value of 10.926 Å (a = 5.463 Å), and an energy value for the formation of two O-vacancies of -2.23 eV. Thus, the catalytic $Ce_{0.875}Mn_{0.125}O_{1.9375}(111)$ surface, generated by cleaving the optimized bulk superstructure with the ideal (111) plane and retaining an extra O-layer, exposed Ce, Mn and O ions (see Fig. 1, left). Then, we evaluated phenol perpendicular interactions with different surface active sites: O, Ce, Mn and also OH groups.

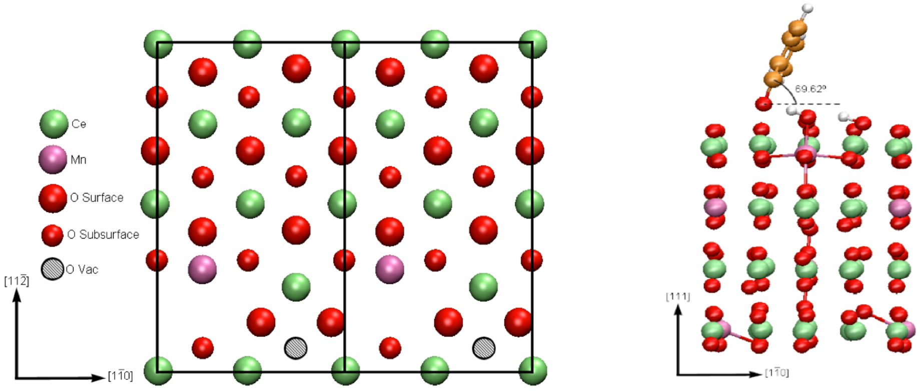

Fig. 1. Left: $Ce_{0.875}Mn_{0.125}O_{1.9375}(111)$ surface. Right: Phenol chemisorption on the hydroxilated surface

In all reported results, we calculated the adsorption energy of an adsorbate A (A: H_2O or phenol), as:

$$\Delta E_{ads,A} = E[A/\ Ce_{0.875}Mn_{0.125}O_{1.9375}(111)] - E[Ce_{0.875}Mn_{0.125}O_{1.9375}(111)] - E[A]$$

The hydroxilated surface was generated by the dissociative adsorption of a water molecule. Our results indicated that OH and H groups preferentially bonded Mn and O ions, respectively. The calculated adsorption energy was $\Delta E_{ads,H\text{-}OH} = -1.22$ eV (see Table 1) with a HO-Mn bond length of 1.89 Å, very similar to bulk Mn-O distances; while H located at 1.01 Å of a surface O.

Table 1. H_2O adsorption energy, on different sites of the bare $Ce_{0,875}Mn_{0,125}O_{1,9375}(111)$ surface

Site	$\Delta E_{ads,H2O}$ (eV)
Mn	-1.22
Ce neighboring an O-defect	-0.68
Ce neighboring Mn	-0.51
Ce neighboring an O-defect and Mn	-0.34
Ce	-0.28

Phenol interactions were evaluated on the bare and hydroxilated $Ce_{0.875}Mn_{0.125}O_{1.9375}(111)$ surface.

Energy calculations for phenol perpendicular adsorption on the clean $Ce_{0.875}Mn_{0.125}O_{1.9375}(111)$ surface indicated weak phenol interactions. Phenol molecule preferentially interacted with a Ce cation first neighbor of Mn-dopant (see Table 2, $\Delta E_{ads,Phenol} = -0.62$ eV). The H_{phenol} formed a $H\text{–}O_{surface}$ bond of 1 Å length and the aromatic ring bonded Ce through the O_{phenol}; which resulted in a O-Ce distance of 2.32 Å, very similar to that in CeO_2 (2.37 Å).

Table 2. Phenol adsorption energy, on different sites of the bare $Ce_{0,875}Mn_{0,125}O_{1,9375}(111)$ surface

Site	$\Delta E_{ads,Phenol}$ (eV)
Ce neighboring Mn	-0.62
Ce neighboring an O-defect and Mn	-0.46
Ce	-0.36
Ce neighboring an O-defect	-0.33
Mn	-0.22

On the other hand, phenol interaction with the hydroxilated $Ce_{0.875}Mn_{0.125}O_{1.9375}(111)$ surface was defined by its chemisorptive character ($\Delta E_{ads,Phenol} = -1.13$ eV). In this interaction, the H of OH_{phenol} fraction bonded a surface O (O-Mn moiety). The remaining C_6H_5-O fraction chemisorbed over a bridge position between Mn and Ce cations, with a tilted angle of 69.62° (see Fig. 1, right). This result could be interpreted as an indication of phenolate-type species formation due to phenol strong interactions on hydroxilated Mn-Ce oxide catalyst surface.

The experimental results of phenol adsorption on Mn-Ce oxide with molar ratio 10-90, could be described with the Langmuir model. Phenol isotherm at 25 °C displayed an L-curve pattern, suggesting a high affinity adsorbent-adsorbate. In addition, the DRIFTS spectra indicated the presence of an aromatic group (1633 and 1494 cm^{-1}) and phenoxy species (1265 cm^{-1}). Thus, our DFT+U calculations, suggesting the formation of phenolate-type species from chemisorptive phenol interactions on the hydroxilated $Ce_{0.875}Mn_{0.125}O_{1.9375}(111)$ surface, were in good agreement with the experimental measurements. Moreover, the theoretical findings showed that phenolate-type species formation involved the participation of Mn and Ce cations.

4 Conclusions

The theoretical calculations performed in this work indicated weak phenol molecule perpendicular interactions on the bare $Ce_{0.875}Mn_{0.125}O_{1.9375}(111)$ surface, involving the participation of a Ce cation neighboring Mn-dopant and the formation of surface OH ($O_{lattice}$-H_{fenol}). On the other hand, the results showed that phenol interactions on the hydroxilated surface were stronger than that on the bare one. The H of OH_{phenol} group bonded to a surface O; while the remaining C_6H_5-O fraction chemisorbed, with a tilted angle of 69.62°, over a bridge position between Mn and Ce cations. Our DFT+U findings were in good agreement with experimental measurements suggesting high affinity adsorbent-adsorbate and the presence of phenoxy species.

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