Morphology of Ru nanoparticles at titania-water-interface – A computational study

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Introduction

Biomass conversion is one of the key ways forward in solving the problem of dwindling resources. This requires the ability to transform highly oxidized molecules into value added molecules, often requires hydrogenation. One commonly used catalyst for the hydrogenation of biomass molecules is Ru supported over TiO_2. The difficulty in studying the catalyst is that it is used in water, making its surface state hard to determine.

Prior research into the surface state of the Ru-water interface[1] has shown that in the presence of water and under realistic reaction conditions (500K), adsorbed water molecules fully dissociate. This paves the way for investigating more realistic systems, in particular subnanometric (~10 atoms) Ru nanoparticles adsorbed on titania.

Materials and Methods

Global optimization was performed by using the PGOPT[2] program to generate numerous and varied nanoparticle morphologies (Ru_{10} supported on TiO_2 anatase 101) with different combinations of water molecules and varying degrees of splitting of these water molecules. Several thousand structures were thus generated and optimized using the CP2K software (PBE functional), allowing for the free energy of the system to be studied according to different structural parameters. A typical structure obtained through this method is shown in Fig. 1.

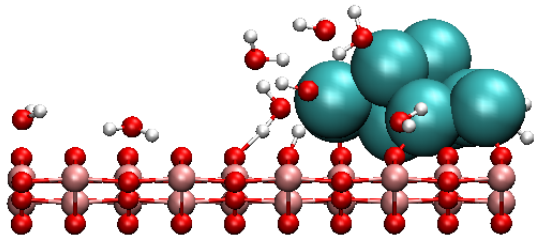

Figure 1. Ru_{10} supported on TiO_2 (anatase 101)

Results and Discussion

The stability of nanoparticles can be analyzed according to the number of water molecules adsorbed, the potential splitting of these water molecules into H + OH or 2H + O, and a variety of morphological parameters.

Fig. 2 shows the free energy of the most stable configuration obtained for different numbers of water molecules adsorbed on the nanoparticle and differing degrees of water dissociation.

z	0	1	2	3	4	5	6	7	8
0	0,00	-1,78	-3,44	-4,12	-7,03	-6,14	-7,46	-9,38	-10,47
1		-1,92	-3,44	-4,74	-4,81	-6,34	-7,29	-9,40	-9,97
2		-1,56	-3,30	-4,00	-5,21	-6,35	-7,90	-9,46	-10,24
3			-1,86	-4,50	-6,64	-6,36	-9,69	-7,44	-10,69
4			-0,41	-3,79	-4,74	-9,40	-8,49	-10,55	-9,89
5				-2,52	-5,73	-9,10	-9,10	-8,81	-8,25
6				-1,65	-4,02	-6,81	-8,40	-8,82	-7,49
7					-2,25	-4,97	-7,15	-9,62	-10,46
8					-0,80				

Figure 2. Free energy (eV, at 500K and water saturation pressure) of the most stable configuration obtained according to the number of water molecules adsorbed on the nanoparticle (horizontal axis) and the number of broken bonds on the water molecules (vertical axis), i.e. the degree of water dissociation.

This establishes the presence of OH adsorbed on the nanoparticles, a key species used to explain reaction mechanisms on Ru nanoparticles but for which there has been no direct of evidence of its presence up until this point.

Significance

This computational study into the surface state of Ru nanoparticles at the titania-water interface allows for a better understanding the *in situ* behavior of a common biomass conversion catalyst, the surface state of which, was, until now, poorly characterized. In particular this work shows evidence for the presence of key OH species adsorbed on Ru nanoparticles.

References

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