Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Structural and electronic properties of V_2O_5 and their tuning by doping with 3*d* elements – Modelling with DFT+*U* method and dispersion correction

A. Jovanović[1,2], A. S. Dobrota[1], L. D. Rafailović[2], S. V. Mentus[1,3], I. A. Pašti[1,4]*, B. Johansson,[4,5] N. V. Skorodumova[4,5]

[1]*University of Belgrade - Faculty of Physical Chemistry, Studentski trg 12-16, 11158 Belgrade, Serbia*

[2]*CEST Center of Electrochemical Surface Technology, Viktor-Kaplan Strasse 2, 2700 Wiener Neustadt, Austria*

[3]*Serbian Academy of Sciences and Arts, Knez Mihajlova 35, 11000 Belgrade, Serbia*

[4]*Department of Materials Science and Engineering, KTH - Royal Institute of Technology, Brinellvägen 23, 100 44 Stockholm, Sweden*

[5]*Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden*

Corresponding author:

Dr. Igor A. Pašti

University of Belgrade – Faculty of Physical Chemistry

Studentski trg 12-16, 11158 Belgrade, Serbia

Phone: +381 11 3336 625

Fax: +381 11 2187 133

E-mail: igor@ffh.bg.ac.rs

The effects of inclusion of +*U* correction on dopant atoms – Cases of Mn- and Co-doped V_2O_5

We present here the overview of the results of the calculations where +*U* correction was applied also onto the dopant 3*d* states. In order to demonstrate the effects we chose the cases of Mn and Co. Following the overview of Capdevila-Cortada *et al*.[S1] a wide range of values of *U* were applied so far for these two elements. For CoO_x compounds *U* was found in the range 3.3 to 6.7 eV, and most frequently was chosen by fitting experimental properties. For MnO_x compounds *U* was found in the range 1 to 6.63 eV. Here we see that the addition of *U* on dopants does not affect overall conclusions regarding the expansion of lattice (Table S1). The changes are much smaller in the case of substitutional doping. Also, an increase of the value of *U* applied onto dopant 3*d* states in general leads to the expansion of the lattice (Table S1).

Table S1. Change of the unit cell volume (ΔV / %)* of Mn- and Co-doped V_2O_5 obtained by PBE+*U*+D2 calculations. The values of *U* applied on dopant 3*d* states was varied while the value of U applied to V 3*d* states was kept to 6 eV.

	Mn-doped V_2O_5		**Co-doped V_2O_5**	
***U*@M / eV**	**substitutional**	**interstitial**	**substitutional**	**interstitial**
0	-0.60	3.48	-0.64	5.01
2	-0.48	4.14	-0.55	5.43
4	-0.11	8.30	-0.52	2.25
6	0.57	8.98	0.67	6.37

*evaluated as $100\times(V_{doped} - V_{pristine})/V_{pristine}$; the volume of pristine 1×1×2 V_2O_5 supercell is 372.7 $Å^3$ using PBE+*U*+D2

Here we also show the electronic structure of Co-doped V_2O_5 (Fig. S1). It can be seen that the effects of addition of *U* on Co 3*d* states (in addition to the V 3*d* states) affects the electronic structure, as expected. The case of interstitial doping is more sensitive to the addition of *U* on dopant states. In the case of substitutional doping we see that the band gap of parental V_2O_5 is

completely lost, irrespectively on the value of *U* applied to the Co 3*d* states. Nevertheless, without proper experimental reference it is difficult to derive a definite conclusion regarding the addition of *U* to dopant states.

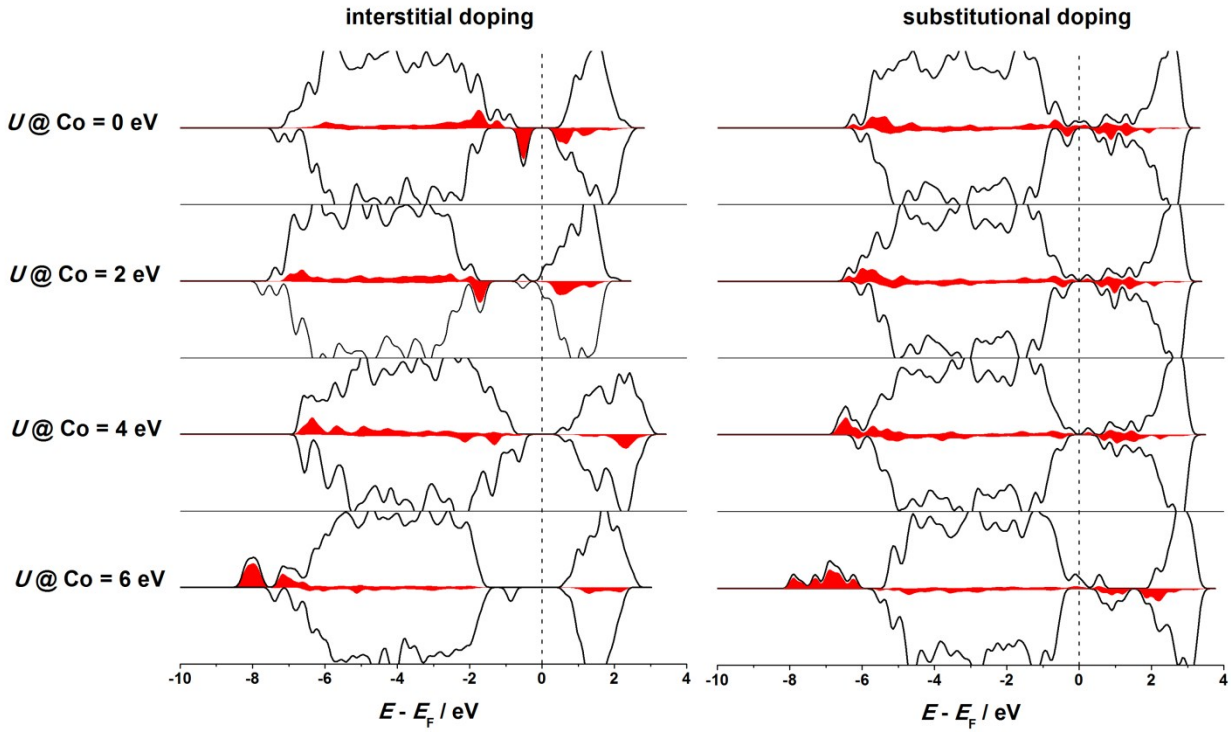

Figure S1. DOS plots for Co-doped V_2O_5 (projected densities of dopant states are shaded) obtained by PBE+*U*+D2 calculations. The values of *U* applied on dopant 3*d* states were varied while the value of U applied to V 3*d* states was kept to 6 eV. Vertical dashed lines denote Fermi levels.

Supplementary references

S1 M. Capdevila-Cortada, Z. Łodziana and N. López, *ACS Catal.*, 2016, **6**, 8370–8379.