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


# Reaction Mechanism for the SCR Process on monomer $V^{5+}$ sites and Effect of Modified Brønsted Acidity

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## Supporting Information

1. Cartesian coordinates of initial state structure $VO_3H/TiO2(001)$

Positions:

| | | | |
|---|---|---|---|
| 0 Ti | 1.8700 | 1.8777 | 12.9420 |
| 1 Ti | 0.0000 | 1.9050 | 10.5954 |
| 2 Ti | 1.7298 | -0.0137 | 15.2908 |
| 3 O | 0.0000 | 0.0000 | 10.0838 |
| 4 O | 1.4437 | 1.8918 | 14.8298 |
| 5 O | -0.0267 | 1.8938 | 12.5224 |
| 6 O | 1.9485 | -0.0246 | 13.3449 |
| 7 O | 1.9050 | 1.9050 | 10.9977 |
| 8 O | 0.0480 | -0.1779 | 16.0255 |
| 9 Ti | 1.9165 | 5.6888 | 12.9490 |
| 10 Ti | 0.0000 | 5.7150 | 10.5954 |
| 11 Ti | 1.7920 | 3.7635 | 15.2970 |
| 12 O | 0.0000 | 3.8100 | 10.0838 |
| 13 O | 2.0050 | 5.6918 | 14.9574 |
| 14 O | 0.0020 | 5.7010 | 12.5596 |
| 15 O | 1.9801 | 3.7951 | 13.3593 |
| 16 O | 1.9050 | 5.7150 | 10.9977 |
| 17 O | 0.0404 | 3.9646 | 15.9645 |
| 18 Ti | 5.6920 | 1.8661 | 13.0703 |
| 19 Ti | 3.8100 | 1.9050 | 10.5954 |
| 20 Ti | 5.9313 | 0.0036 | 15.6751 |
| 21 O | 3.8100 | 0.0000 | 10.0838 |
| 22 O | 5.6908 | 1.9098 | 15.0310 |
| 23 O | 3.8288 | 1.8911 | 12.5730 |
| 24 O | 5.7618 | -0.0388 | 13.5282 |
| 25 O | 5.7150 | 1.9050 | 10.9977 |
| 26 O | 3.1475 | 0.4714 | 16.2517 |
| 27 Ti | 5.6974 | 5.7375 | 12.9966 |
| 28 Ti | 3.8100 | 5.7150 | 10.5954 |
| 29 Ti | 5.9410 | 3.8996 | 15.5387 |
| 30 O | 3.8100 | 3.8100 | 10.0838 |
| 31 O | 5.4961 | 5.7364 | 15.2634 |
| 32 O | 3.8286 | 5.7106 | 12.5335 |
| 33 O | 5.7765 | 3.8668 | 13.5521 |
| 34 O | 5.7150 | 5.7150 | 10.9977 |
| 35 O | 3.2714 | 3.2738 | 16.1955 |
| 36 V | 4.0198 | 1.8241 | 17.2781 |
| 37 O | -2.1998 | 0.5962 | 17.3505 |
| 38 O | 10.8847 | 1.8372 | 18.7441 |
| 39 O | 5.4353 | 3.3261 | 17.4048 |
| 40 H | 6.2035 | 3.0655 | 17.9415 |

2. Frequencies (given in $cm^{-1}$) used to calculate the Gibbs free energy. The frequencies were calculated for atoms marked in black.

$VO_3H* + NH_3(g) \rightarrow NH_4^+ VO_3^- *$
H: [491.5,806.6,3647.8]

$NH_4^+$:
[90.5,119.0,187.7,254.4,304.3,426.8,1410.2,1486.0,1508.9,1699.1,1722.9,3012.0,3073.8,3426.4,3525.5]
$NH_4^+ VO_3^- * + NO(g) \rightarrow NO\ NH_3\ VO_3H *$

NO $NH_3$:
[95.0,135.4,192.2,236.9,416.1,576.7,1042.5,1603.4,1634.4,3386.5,3538.8,3585.0,25.2,65.0,90.3,107.4,347.4,1834.0,491.5,806.6,3647.8]

$NO\ NH_3\ VO_3H * \rightarrow (ONNH_2 \cdots H \cdots VO_3H *) \rightarrow H_2NNO\ VO_3H_2 *$

$ONNH_2 \cdots H$ H:
[491.5,806.6,3647.8,14.1,35.9,73.1,83.0,145.1,384.6,423.5,476.6,629.6,970.2,1054.2,1425.4,1467.9,1556.8,1609.6,3405.0,3518.2]

$H_2NNO$ H:
[27.0,57.7,66.8,85.5,150.4,522.3,624.8,665.4,750.5,850.6,1073.5,1217.3,1524.5,1598.4,3326.0,3485.7,3646.8,491.5,806.6,3647.8]

$H_2NNO\ VO_3H_2 * \rightarrow VO_3H_2 * + N_2(g) + H_2O(g)$

$H_2$: [391.1,796.1,3646.3,491.5,806.6,3647.8]

3. PDOS for V, Mo and W as substitutional dopants.

When V is substitutional doped at the Brønsted acid site (Figure 1 a)-d)) it is reduced to oxidation state +4 and it is the V atom in the active site that is redox active as it changes oxidation state from +5 to +4 during the reduction.

When Mo and W are substitutional doped at Brønsted acid site (Figure 1 e)-h) and i)-l) respectively) they become the redox active sites changes oxidation states whereas the V atom in the active site remains in the same oxidation state.

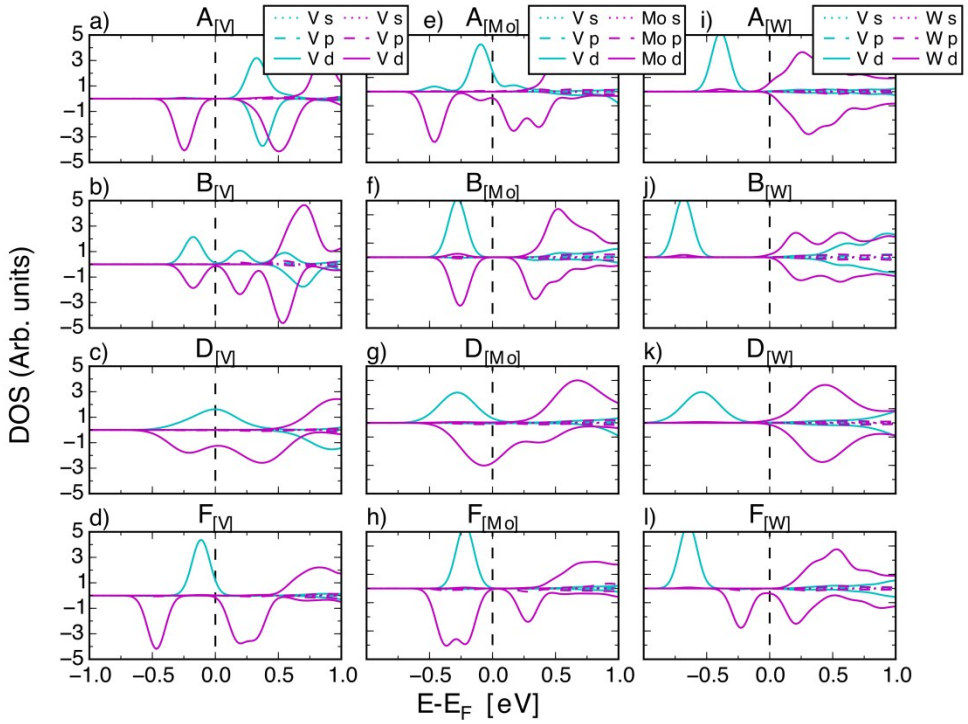


Figure 1: PDOS for s, p and d orbitals of V in the active site (blue) and a)-d)V , e)-h)Mo and i)-l) W as substitution for states A, B, D and F (purple).

When V is substitutional doped at the H accepting site (Figure 2 a)-d)) both V atoms are partially reduced in states A,B and D. In the reduced state the V atom of the active site is reduced to +4 and the V atom in the $TiO_2$ lattice aswell.

When Mo and W are substitutional doped at H accepting site (Figure 2 e)-h) and i)-l) respectively) they become the redox active sites changes oxidation states whereas the V atom in the active site remains in the same oxidation state

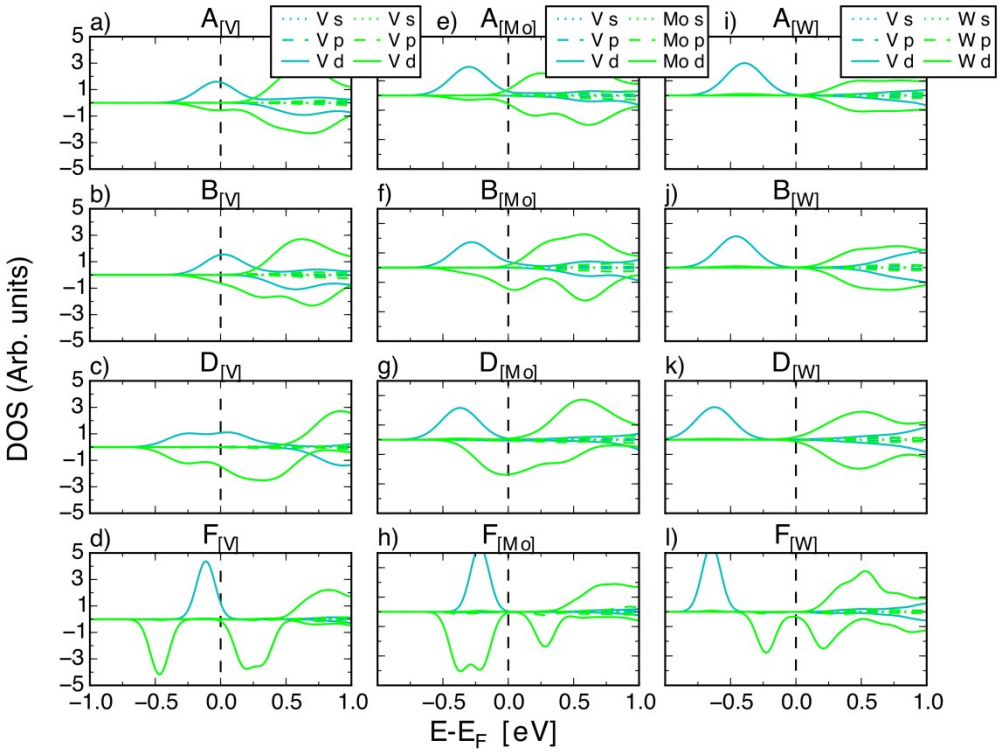


Figure 2: PDOS for s, p and d orbitals of V in the active site (blue) and a)-d)V , e)-h)Mo and i)-l) W as substitution for states A, B, D and F (green).