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Corrigendum

Corrigendum to “The hydrogenation and direct desulfurization reaction pathway in thiophene hydrodesulfurization over MoS_2 catalysts at realistic conditions: A density functional study” [J. Catal. 248 (2007) 188]

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In this corrigendum, we report a correction to a reaction barrier in the hydrogenation pathway at the Mo edge (Fig. 3 in Ref. [1]). More accurate calculations of the reaction barriers have revealed that the correct reaction barrier for S–C scission of 2.5-dihydrothiophene for the HYD reaction at the Mo edge (reaction III in Fig. 3 of Ref. [1]) is 2.03 eV (in contrast to the incorrect value of 1.13 eV, which we reported in [1]). Thus, Fig. 3 in [1] has to be replaced by Fig. 1, in which the barrier height has been corrected.

In the original paper [1], all reaction barriers were determined using the nudged elastic band (NEB) [2] method and a subsequent refinement using the adaptive nudged elastic band (ANEB) algorithm [3] combined with cubic spline fits to the energies and forces of the images in the reaction pathway. The reaction barrier was then determined as the highest point in the cubic spline fit along the reaction pathway. In the course of additional calculations on the HYD pathway on the Mo edge, we have discovered that the cubic spline fit obtained from NEB calculations did not give the S–C scission of 2,5-dihydrothiophene barrier (reaction III in Ref. [1]) at the Mo edge correctly, but underestimated the barrier considerably. To find the correct reaction barrier, we have performed new NEB calculations with an increased number of images around the transition state. Subsequently, we have used a quasi-Newton algorithm [4] as implemented in the CamposASE software [5] to unambiguously locate the transition state. We verified the nature of the transition state by a vibrational

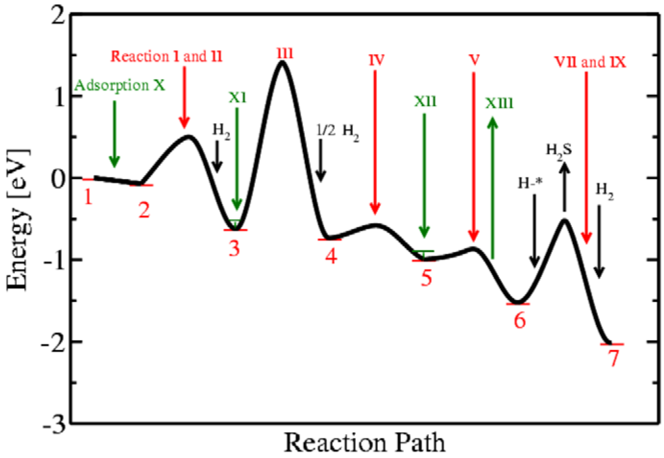

Fig. 1. The Mo edge HYD pathway. The barrier has been changed for reaction III to 2.03 eV. This figure replaces Fig. 3 in the original article [1].

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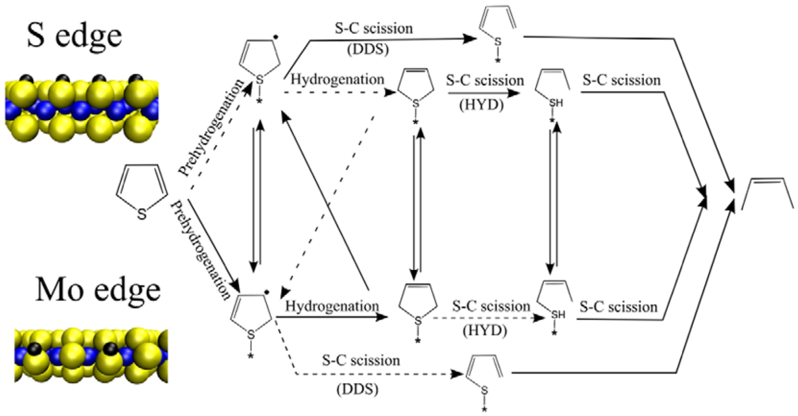

Fig. 2. General scheme of the reaction pathways at the two edges. This figure replaces Fig. 8 in the original article [1].

frequency analysis, which yielded exactly one imaginary frequency. For these calculations, we used a displacement of 0.02 Å to determine the force derivatives by centered differences. We have extensively tested the effect of varying the size of the displacement. We find that increasing the displacement introduces noise into the Hessian matrix but still gives a mode corresponding to the reaction coordinate.

We have checked all the other reaction barriers and could confirm that only the S–C scission barrier at the Mo edge was affected, so all other barriers remain correct. In hindsight, we can rationalize this as follows. The thorough testing of the reaction barriers revealed that the reaction corrected here, i.e. the S–C scission reaction (reaction III) at the Mo edge, has a later transition state than the corresponding reaction III at the S edge. This means that at the S edge the transition state occurs during S–C scission prior to H transfer, and hence the reaction path is rather simple and was estimated correctly. In contrast, at the Mo edge the transition state is on the reaction pathway of the concerted H transfer and S–C scission. Here, the reaction pathway is much more complicated, and this is probably the reason why this reaction requires a much finer sampling of the reaction coordinate.

The much higher corrected barrier for S–C scission in the HYD pathway at the Mo edge necessitates a correction of the general reaction scheme (Fig. 8 in [1]), which is replaced by the corrected scheme depicted in Fig. 2. The HYD pathway at the Mo edge becomes much less favorable due to the increased barrier of reaction III. We can conclude that while hydrogenation of thiophene can occur easily at the Mo edge, S–C bond scission has a very high barrier of 2.03 eV and is therefore not likely to happen at this edge. Furthermore, the increased barrier of reaction III increases the importance of the DDS pathway relative to the HYD pathway. The corrected results also put increased focus on the interaction between the Mo edge and the S edge. As hydrogenation is most facile on the Mo edge and S–C scission only can occur on the S edge, one can easily imagine that thiophene moves from the Mo edge to the S edge after the hydrogenation to complete the S–C scission step there.

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