

Chemical Bonding in Borides-Based Catalysts

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Geometrical variety and fascinating aesthetics of crystal structures of boron and borides showing sometimes unusual atomic arrangements (cf. e.g., elemental boron) since decades attract attention of research groups around the world, focusing on the understanding of chemical bonding, which creates and enables all these phenomena. New insights in this field were achieved implementing quantum chemical bonding analysis techniques in position space [1]. The development and importance of this approach originate - on the one hand - from the necessity to study and understand atomic interactions in chemical systems, which cannot be described using simple classical valence rules, in particular chemical substances with low number of valence electrons, for which boron and borides are the striking example. On the other hand, the use of quantum chemical techniques in position space is especially attractive for catalytic issues, e.g. for application of site-isolation concept.

A wide spectrum of bonding scenarios was discovered recently for different classes of borides employing the position-space approach [2-4]. In the borosilicide clathrates-I [2] and clathrates-VIII [3], boron plays a role of a typical Zintl anion, carrying even larger effective charge than the silicon one and forming two-center bonds with low level of delocalization [2]. While the bonding picture in main-group metal diborides is closest related to graphite, one with dominant covalent B-B bonding, transition-metal diborides display smaller effective B-B bond order but higher effective TM-B and TM-TM bond orders [4]. In the self-optimizing OER catalyst $\text{Hf}_2\text{B}_{2-2\delta}\text{Ir}_{5+\delta}$, a further delocalization of 2c interactions is found, leading to the appearance of three-atomic Ir-B-Ir bonds within the boron-iridium framework. Their alteration with Ir-Ir interactions results in the unusual catalytic behavior [5].

[1] F. R. Wagner, Yu. Grin, Chemical bonding analysis in position space In: Comprehensive Inorganic Chemistry III (Third Edition) Elsevier, 2023, p. 222-237. [2] W. Jung et al. Dalton Trans.50 (2021) 1274. [3] J. Hübner et al. J. Am. Chem. Soc. 144 (2022) 13456. [4] F. R. Wagner et al. Z. Anorg. Allg. Chem.639 (2013) 2025. [5] A. M. Barrios Jiménez et al. ACS Adv. En. Mat. 3 (2020)11042.