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p-Block elements for catalysis

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Renewable energy applications largely rely on transition metal catalysts. Similar to organocatalysts, *p*-block elements exhibit transition-metal-like catalytic performances. Si Zhou and co-workers review the latest advances in *p*-block elements as catalysts for energy conversion to deeply understand the concept of metal-free catalysis and establish the design principles for *p*-block catalysts.

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Catalysts are an engine of human society. Catalysis is a prerequisite for life in biological systems, and is indispensable for the industrial conversion of chemical feedstocks into valuable products, such as pharmaceuticals and agrochemicals. Advances in catalysis are also critical for the realization of carbon neutralization. Traditionally, there are two types of catalysts, namely, metals and enzymes. The metal species with incompletely filled *d* orbitals serve as active sites for reactions to occur. It was not until 2000 that the third type of catalyst called the asymmetric organocatalyst was developed[1,2], which constitutes small organic molecules containing mainly carbon, hydrogen, nitrogen, sulfur, and phosphorus, but no metal species. These catalysts are environmentally friendly, and their production is inexpensive. Moreover, organocatalysts can be used to drive asymmetric catalysis, which is in high demand for the production of pharmaceuticals. Benjamin List and David MacMillan, the scientists who conducted pioneering work in organocatalysis, have been awarded the Nobel Prize in Chemistry 2021. Their seminal work clarified the principles for inducing reactivity and controlling reaction pathways in organocatalysts. Their achievements have opened new avenues in chemistry toward broadening the catalytic application scope of main group species, which are greener and more efficient (Fig. 1).

In parallel, the rapid progress of synthetic technologies has facilitated the fabrication of various inorganic materials. With the development of nanomaterials, tremendous attention has been focused on low-dimensional materials with peculiar geometric and electronic structures, which allow the design of novel catalysts for renewable energy applications. With unique structures and ultrahigh atom utilization, efficient catalysis based on these novel nanostructures may be achieved with reduced consumption of or without transition metals (mostly precious metals such as Pt, Pd, and Ru). Some low-dimensional materials made of *p*-block elements, such as group-IV and group-V monolayers (graphene, silicene, phosphorene, etc.) and carbon nanotubes, also exhibit unexpected capability for catalytic energy conversion. This raises the question of whether *p*-block materials can exhibit both outstanding catalytic performance and practical applicability. As mentioned above, the activity of transition metals stems from their incompletely filled *d* orbitals, endowing tunability of oxidation states and the ability to form complex intermediates with reagents. The *d*-band theory, proposed by Jens K. Nørskov, has been widely adopted to explain the activity trend of transition metals on the basis of the correlation between reactivity and the *d*-band center of a metal[3]. In contrast, *p*-block elements possess limited oxidation states. Thus, the mechanism for triggering the activity and the principles for designing *p*-block catalysts are considerably different from those for transition-metal-based catalysts, but similar to those for organocatalysts to some extent.

In *npj Computational Materials*, Si Zhou and co-workers attempted to address the above question by reviewing the latest advances in experimental and theoretical explorations of *p*-block elements as catalysts for clean energy applications. They focused on the situation wherein *p*-block elements (carbon, silicon, oxygen, boron, and phosphorus) serve as active sites, and endeavored to elucidate the regulation of *p*-orbital-dominated catalysts by a systematic survey of relevant computational results.

Carbon-based materials are the most commonly reported metal-free catalysts for energy conversion. Remarkable electrocatalytic activity has been widely observed in carbon materials such as graphene and carbon nanotubes doped with heteroatoms, incorporating structural defects or encapsulating metals. The activity can be generally explained by the change in charge density and electron affinity for the surface carbon atoms induced by the dopants, defects, or metal fillers. Zhou et al. proposed a concept to understand the *p*-orbital-dominated reactivity in terms of the occupancy and energy level of *p* states[4]. Taking encapsulated graphitic carbon nanospheres and nanotubes as an example, they attributed the catalytic activity to the breaking of the π conjugation of carbon networks, resulting in partially filled p_z orbitals for carbon atoms, thereby rendering them with the ability to withdraw or donate electrons from the reagents[5]. Some parameters such as local charge density, *p*-band center, and work function are demonstrated to be good descriptors for the binding capability and catalytic activity of carbon species.

Similar correlations have also been found for other *p*-block materials[6–8]. The carbon, boron, silicon, and phosphorus atoms, when not in perfect sp^2 or sp^3 hybridization, have their *p*-state electrons activated and exhibit reactivity that is tunable with the occupancy and energy levels of *p* orbitals. Such electronic structure-activity relationships are referred to as the "*p*-band model". This simple concept provides guidance for activating *p*-block species through band structure engineering, according to which some predicted carbon hybrid electrocatalysts have been corroborated with those determined by experiments[9].

Many other materials exhibit a *p*-orbital-dominated reactivity. However, the large discrepancies among different *p*-block elements result in diverse material structures, and each system may follow a unique reaction mechanism. It would be difficult to establish a unified concept for understanding the design

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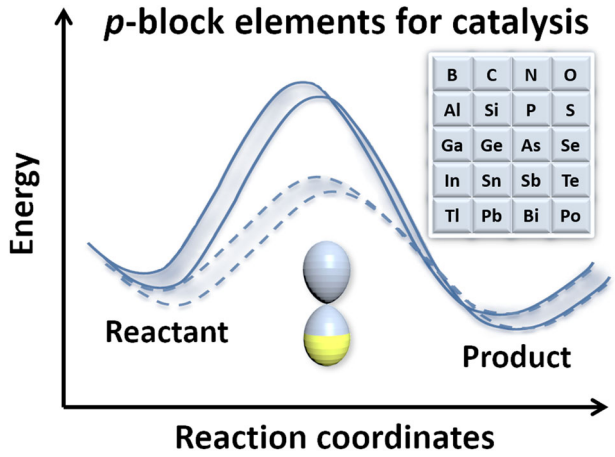

Fig. 1 Catalysts consisting of *p*-block elements. In the table are listed main *p*-block elements; the solid and dashed curves show the reaction procedures without and with catalysts, respectively; the spindle indicates a partially filled orbital.

principles for all types of *p*-block catalysts. Inspired by the achievements in organocatalysis, both experimental and theoretical investigators have been continuously exploring *p*-block-element-mediated reactions to develop inexpensive and eco-friendly catalysts for carbon neutralization.

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COMPETING INTERESTS

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ADDITIONAL INFORMATION

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