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X-ray absorption spectroscopy for single-atom catalysts: Critical importance and persistent challenges

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1. Introduction

Advances in characterization techniques, synthesis methods, and theory have provided the growing number of evidence for the presence of single-metal atoms in supported noble metal catalysts [1–10], even in those closely relevant to industrial catalysts (e.g. Au/C [11] and Pt/Al₂O₃ [12]), and their significant roles in catalysis.

As the interest on such single-atom catalysts (supported mononuclear metal complex catalysts) has grown rapidly and been active, X-ray absorption spectroscopy (XAS) [13–15] has become an essential tool to characterize them. XAS is an element-specific technique that provides information about both electronic and structural properties of single-atom catalysts. XAS is one of the few techniques that can probe metal–support interface, which is critical for such catalysts because supports act as ligands [16] and influence their catalytic performance and stability; their electron donating character and geometry of coordination to single-metal atoms influence how reactants become bonded to a metal, enter a catalytic cycle, and converted into products, and how single-metal atoms resist against sintering during reactions at high temperatures [1–5,17,18].

In this perspective, the importance of XAS in the research of single-atom catalysts is described by summarizing its strengths. Then, persistent challenges for characterization using XAS for supported catalysts are presented. Several examples are shown to illustrate how the challenges can be overcome to advance toward the goal of catalyst development through design that is based on the fundamental understanding of structure–performance relationships. Throughout this perspective, the emphasis is placed on the importance of high structural uniformity of active sites and characterization by XAS in concert with other complementary techniques such as infrared (IR) spectroscopy and electron microscopy.

Extended X-ray absorption fine structure (EXAFS) characterized by oscillation above the absorption edge in X-ray absorption spectra provides quantitative information on the average coordination number of nearby backscatterer atoms and the average interatomic distance between the absorber atom

and the backscatterer atoms. X-ray absorption near-edge structure (XANES) characterized by peaks, shoulders, and other features near or on the edge of X-ray absorption spectra provide information on oxidation state of metals and geometry of supported metal species.

In addition, XAS can be performed under reactive atmosphere with realistic conditions [19] to characterize working catalysts in a cell designed to serve as a plug flow reactor [20]. Therefore, the structure of working active sites and oxidation states of metal atoms, which are often different from those *ex situ*, can be probed and correlated with their catalytic performance. In addition, isosbestic points in sets of XANES spectra demonstrate stoichiometrically simple transformation of active metal sites [21,22].

However, a persistent and daunting challenge for characterization of single-atom catalysts by XAS (and more generally characterization of supported catalysts) is the structural nonuniformity of active metal sites in many catalysts. XAS can provide structural information even when catalysts do not possess long-range order. However, it provides information about ensemble average of all species present in catalysts that are both kinetically significant (often minor) and insignificant. Therefore, deep understanding of structure–performance relationship by this technique remains limited for catalysts that are structurally nonuniform.

2. Example of benefits of XAS characterization of structurally uniform active sites

A good example about how the structural uniformity of solid catalysts incorporating metals enables detailed characterization by XAS can be found in the work with metalloenzyme [23] and a metalloenzyme-like catalyst [24]. In the latter work, a metalloenzyme-like catalyst, Sn- β -zeolite [25], which incorporates post-transition metal ions, Sn⁴⁺, in the framework site of crystalline microporous molecular sieves was synthesized, and the structure of active site was characterized by XAS in detail. Light elements like support oxygen atoms scatter photoelectrons at low *k* (wave-vector) values. In addition to this, when

catalyst structure is disordered, it results in quick decay of EXAFS data as the k value increases. These factors often limit the k -range used in analysis and consequently the number of statistically justified free parameters determined by the Nyquist theorem ($n = (2\Delta k\Delta R/\pi) + 2$, where Δk and ΔR are the k (wave-vector) and R (distance) ranges used in the fitting [14]). However, because the metalloenzyme-like catalyst possesses the active site with high structural uniformity, it enabled the collection of excellent EXAFS data, and higher-shell analysis with an R value up to 5 Å to locate the exact site of Sn atoms (Fig. 1). Although this catalyst poses a challenge in characterization by X-ray diffraction technique because of inherent stacking disorder along one-dimension, the crystalline nature of catalyst structure allowed the researchers to examine local structure of active sites by considering various multiple scattering paths in X-ray absorption fine structure (XAFS) analysis (Fig. 1), and successfully determined the exact position of Sn atoms and their coordination environment. This example illustrates the power of XAS and its high potential to characterize single-atom catalysts consisting of noble metal atoms in a similar fashion when structure of active sites is highly uniform.

3. An approach for synthesis of supported mononuclear metal complex catalysts with high structural uniformity

One of the excellent approaches to synthesize supported mononuclear complex catalysts with high structural uniformity is to use organometallic precursors (e.g. $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acac})$,

$\text{Rh}(\text{C}_2\text{H}_4)_2(\text{acac})$, $\text{Ir}(\text{CO})_2(\text{acac})$, $\text{Rh}(\text{CO})_2(\text{acac})$, and $\text{Au}(\text{CH}_3)_2(\text{acac})$, etc.) (acac = acetylacetonate, $\text{C}_5\text{H}_7\text{O}_2^-$) on crystalline supports like zeolites [26,27] and metal-organic frameworks (MOFs) [28]. When the synthesis process is precise, it forms coordinatively unsaturated mononuclear metal complexes bonded to the support via metal-oxygen bonds, which are structurally uniform, essentially molecular in nature, and can be considered prototypical. Therefore, investigations of their structure-performance relationships using a series of samples [29] provide the basis of understanding more structurally complex catalysts as well as design principles that can be broadly applicable to the development of new supported catalysts. These samples offer advantages because their structures are simple enough to allow investigations of subtle changes by techniques such as XAFS and IR spectroscopies as well as electron microscopy even when they function under reactive atmospheres. In addition, when oxophilic metals like rhenium are used, it offers stability at high-temperature conditions [30].

The organometallic precursors shown above are simple in structure but provide advantages to achieve the goal. C_2H_4 is an important molecule broadly in catalysis, and π -bonded C_2H_4 on metals can be readily characterized. CO is also an important molecule because it is a common poison for many supported catalysts. Strong ν_{CO} bands of adsorbed CO ligands appear in uncluttered regions of IR spectra. When supported metal species bear high structural uniformity, it gives narrow ν_{CO} bands [31,32], which facilitate characterization. The ν_{CO} frequency

Fig. 1. An example of higher-shell analysis by EXAFS for the Sn- β zeolite. Each row represents one of the three possible families of sites for Sn in the β -zeolite structure. The schematic representations of the atoms included in the model surrounding each of these T-sites are shown in the first column (a–c). The Si atoms are represented by the blue spheres and the Sn atom (at the T-site) by the red, light blue, and green spheres for the T5 (a), T3 (b), or T9 (c) site, respectively. (The O atoms have been omitted for clarity). The T5-site is made up of a four- and a five-membered ring, the T3-site is made up of a single four-membered ring, and the T9 contains several five- and six-membered rings. The real part (d–f) and the magnitude (g–i) of the Fourier transform of the EXAFS data of the Sn- β sample are shown in the middle and final columns (black curve). Note that only the data from 2 to 5 Å are shown in d–i. The best fit data are compared to the model for Sn substitution into each of the different T-sites (red, light blue or green curves). Adapted with permission from Bare et al. [24]. Copyright (2005) American Chemical Society.

provides information about a degree of electron deficiency of a metal center because an extent of π back-donation from the metal to a CO ligand influences CO bond strength. Characterization of metal–CO species by EXAFS spectroscopy is facilitated by analysis of a multiple scattering path. Acac is a bidentate anionic ligand and mimics anchoring sites of concentrated negative charge of metal oxides (e.g. Al centers of zeolites), and it generally allows simple exchange with bidentate oxygen ligands of a support. Therefore, isostructural metal complexes (e.g. $\text{Ir}(\text{C}_2\text{H}_4)_2$ and $\text{Ir}(\text{CO})_2$) can be formed on various supports through this approach and effects of supports as ligands can be investigated by minimizing complications from other effects caused by additional organic ligands and metal nuclearity [33]. Structure-performance relationship of a family of the single-atom catalysts incorporating isostructural metal complexes on different supports can be investigated by performing XAFS and IR spectroscopies under reactive atmospheres as well as test reactions that are simple and yet capture essential features about how support and additional ligands influence the selectivity [29,33,34].

Zeolites are crystalline aluminosilicate and contain well-defined anchoring sites near Al centers to anchor cationic metal complexes with high structural uniformity. MOFs have emerged as prospective catalyst supports to synthesize single-atom catalysts with high structural uniformity although many of them have limitation in thermal stability. Metal oxides nodes [28,35,36] and organic linkers [37] of MOFs have been demonstrated to serve as anchoring sites for metal complexes. MOFs offer advantages of tunable pore size by a choice of the type of nodes and linkers. Anchoring sites present on metal oxide nodes of MOFs can be tailored using modulators in MOF synthesis [35,36].

Even with single-atom catalysts with high structural uniformity, additional challenges remain for characterization by XAS. Distinguishing light and heavy neighboring atoms is relatively straightforward by EXAFS, but it is not sufficient and requires the direct information from electron microscopy (e.g. scanning transmission electron microscopy, (STEM)) to exclude the presence of small clusters and nanoparticles and to investigate the location of metal sites [2–10]. In addition, it is difficult to distinguish light elements like oxygen, carbon, and

nitrogen atoms, which are critical for single-metal catalysts. Therefore, information from other techniques (IR and NMR spectroscopies, calculation by theory, and X-ray emission spectroscopy) [15,38,39] is necessary to identify the type of neighboring atoms and complement EXAFS data.

In addition to these challenges, generally EXAFS analysis itself is not straightforward and requires a good practice and judgement. Some good books and articles regarding detailed XAFS analysis have been reported with theory and illustrative examples [13,14]. Kistler et al. [40] reported an example of detailed analysis procedures about how candidate structural models are constructed and examined, and a recommended structural model is obtained.

In the following sections, some examples are shown to illustrate benefits of supported mononuclear metal complex catalysts with high structural uniformity and investigation of their structure-performance relationship with XAS in conjunction with complementary techniques.

4. MOF as a support

UiO-66, UiO-67, and NU-1000 consist of Zr_6 -based nodes (Fig. 2), each linked to carboxylate linkers (terephthalate for UiO-66, biphenyl-4,4'-dicarboxylate for UiO-67, and 1,3,6,8-tetrakis(*p*-benzoic-acid)pyrene for NU-1000) and exhibit exceptional thermal stability and well-defined structures, which make these materials attractive as catalyst supports [41, 42]. The Zr_6 -based nodes in the MOFs bears hydroxyl (OH) and aqua (OH_2) groups that function as Brönsted acids like those present on the surfaces of metal oxides and zeolites, and the smallness of metal oxide nodes facilitates structural modeling by theory. UiO-66 and UiO-67 contain many defects because of missing linkers, and these defect sites are occupied by hydroxo ligands. Yang et al. demonstrate that these materials allow precise tuning of anchoring sites using acetic acid or HCl used as the modulator during MOF synthesis [35] or using methanol or ethanol in the post-synthetic step [36], showing prospective opportunities to create tailored and uniform surface sites to anchor single-metal atoms and control its catalytic properties. For example, the synthesis of UiO-66 and UiO-67 using the modulator HCl exclusively forms single and different type of

Fig. 2. $\text{Ir}(\text{CO})_2$ deposited onto the Zr_6 nodes of NU-1000. (a) Location of the iridium complex in a periodic crystal of NU-1000. (b) Expanded view of the iridium complex at the Zr_6 node. (c) Same site in pristine NU-1000 prior to $\text{Ir}(\text{CO})_2$ complexation. Adapted with permission from Yang et al. [28]. Copyright (2015) American Chemical Society.

anchoring sites on them.

Yang et al. [28,35] synthesized supported mononuclear iridium complexes using $\text{Ir}(\text{CO})_2(\text{acac})$ and $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acac})$ as organometallic precursors. In the synthesis, $\text{Ir}(\text{CO})_2(\text{acac})$ or $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acac})$ was slurried with MOF powder in *n*-pentane, and after adsorption of the precursor, the *n*-pentane was removed by evacuation. Then, the samples were characterized by XAFS and IR spectroscopies in concert with theoretical calculations by DFT, and tested for the conversion of ethylene in the presence of hydrogen (hydrogenation and dimerization). The catalytic conversion of ethylene is a convenient test reaction that can be conducted under mild conditions with supported iridium catalysts.

NU-1000 (and UiO-67) bears hydrogen-bonded $\text{H}_2\text{O}/\text{OH}$ groups at the nodes (called as **site 1** in the literature). Yang et al. [28] show that the reaction of NU-1000 with iridium dicarbonyl complex, $\text{Ir}(\text{CO})_2(\text{acac})$ removed the protons in the hydrogen-bonded $\text{H}_2\text{O}/\text{OH}$ groups and formed chemisorbed $\text{Ir}(\text{CO})_2$ complexes that are coordinatively unsaturated. The IR spectroscopy data show the decreased intensity of a band at 2745 cm^{-1} associated with hydrogen-bonded $\text{H}_2\text{O}/\text{OH}$ groups, and appearance of new bands at 2066 and 1990 cm^{-1} that indicates dicarbonyl ligands on a chemisorbed iridium atom. This information facilitated EXAFS analysis, which shows the formation of site-isolated supported iridium complexes with iridium atoms being bonded to the surface via two Ir–O bonds at a distance of 2.05 Å and retaining two CO ligands (Fig. 2).

When UiO-66 was used instead, the chemistry was similar. However, subtle but important differences were observed [28]. The $\text{Ir}(\text{CO})_2(\text{acac})$ reacted with non-hydrogen-bonded OH groups on the node (**site 2**) in addition to OH groups at **site 1**. The IR data show the disappearance of OH bands 3781 and 3692 cm^{-1} associated with the non-hydrogen-bonded OH groups. The IR data show bands at 2074 and 1996 cm^{-1} , corresponding to CO ligands on the iridium at **site 2**. Because the frequencies of these bands are higher than those for the chemisorbed species on **site 1**, the researchers infer that the iridium center in the chemisorbed species at **site 2** is more electron deficient than that at **site 1**, which indicates higher electron withdrawing property of ligands at **site 2** than those at **site 1**. Conducting IR spectroscopy characterization of the samples in flowing C_2H_4 , Yang et al. [28,35] demonstrated that only one of two CO ligands in $\text{Ir}(\text{CO})_2$ at **site 2** was replaced by C_2H_4 ligand and formed supported $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)$.

To investigate the effects of ligands of the Zr_6 nodes further, Yang et al. [28,35] synthesized MOF-supported catalysts using $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acac})$ precursor that incorporate reactive C_2H_4 ligands, and tested them in the conversion of ethylene in the presence of H_2 , and compared results with isostructural iridium complexes on other metal oxides to investigate effects of supports as ligands (see the next section). The IR and EXAFS data show that $\text{Ir}(\text{C}_2\text{H}_4)_2$ complexes were anchored on the surface via two Ir–O bonds after acac ligands were liberated. The EXAFS data show a Ir–O distance of 2.15 Å , which is longer than that characterizing $\text{Ir}(\text{CO})_2$ supported on the MOFs. Yang et al. [28,35] also recorded EXAFS and IR spectroscopies for samples after they were brought into contact with CO, and the results

show the facile exchange of C_2H_4 ligands with CO ligands, forming supported $\text{Ir}(\text{CO})_2$.

In summary, the results shown here illustrate how characterization of XAS with IR spectroscopy determined the chemistry of reaction of the mononuclear iridium complexes with MOF nodes, and elucidated the nature of supported mononuclear iridium complexes and their interactions with MOF nodes. EXAFS spectroscopy provides quantitative data about the bonding of iridium atoms to the surface. IR spectroscopy under reactive atmosphere provides information about sites at which the iridium metal complexes reacted, additional ligands on iridium atoms, and their reactivity. The results also show prospects of MOFs for synthesis of single-atom catalysts with high structural uniformity with tailored anchoring sites.

5. Zeolite as a support

Although tailoring anchoring sites of zeolites may be more difficult than that of MOFs, zeolites bear anchoring sites that are nearly equivalent and they facilitate the synthesis of highly uniform supported metal complexes [21,36,37,31–34]. The high structural uniformity of these catalysts has been demonstrated by narrowness of ν_{CO} bands in IR spectroscopy data measured using CO as a probe molecule [31,32]. The ν_{CO} bands characterizing $\text{Ir}(\text{CO})_2$ on zeolite HY (FWHM $\approx 5\text{ cm}^{-1}$) are much narrower than those characterizing $\text{Ir}(\text{CO})_2$ on NU-1000 (FWHM $\approx 26\text{ cm}^{-1}$) [32,35], indicating that the iridium complexes on the zeolite are structurally more uniform than those on the MOF. This result may be surprising, considering the high crystallinity of the MOF characterized by powder XRD diffraction technique, and it suggests subtlety that may not be fully captured by a single technique alone.

Lu et al. [43] synthesized zeolite HY- and MgO-supported $\text{Ir}(\text{C}_2\text{H}_4)_2$ complexes by the reaction of $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acac})$ with these supports. The EXAFS data show the formation of $\text{Ir}(\text{C}_2\text{H}_4)_2$ complexes on both supports, which are isostructural to those on the MOFs, and bonding of these complexes to the surface via two Ir–O bonds. Upon exposure of the samples to CO, C_2H_4 ligands were replaced with CO and formed supported $\text{Ir}(\text{CO})_2$ as characterized by IR and EXAFS spectroscopies. The ν_{CO} frequencies characterizing $\text{Ir}(\text{CO})_2$ on the zeolite were 2109 and 2038 cm^{-1} , much higher than those characterizing $\text{Ir}(\text{CO})_2$ on MgO (2051 and 1967 cm^{-1}). The XANES spectra collected at L_{III} edge demonstrated a relationship between normalized white line intensity and the position of the $\nu_{\text{CO,as}}$ peak in the IR data, indicating higher electron deficiency of iridium centers in $\text{Ir}(\text{CO})_2$ complexes on the zeolite than those on MgO [44]. $\text{Ir}(\text{CO})_2$ complexes on MgO are highly stable and resist against ligand exchange even after 2 h of C_2H_4 flow whereas those on the zeolite undergo replacement of one of two CO ligands with C_2H_4 , and able to accommodate additional C_2H_4 , forming species like $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)$ and $\text{Ir}(\text{CO})(\text{C}_2\text{H}_4)_2$. When the family of $\text{Ir}(\text{C}_2\text{H}_4)$ complexes supported on zeolite HY, MgO, the MOFs, and conventional ZrO_2 were tested in the conversion of ethylene in the presence of hydrogen, the turnover frequency (TOF) of ethylene conversion as well as selectivity to dimerized products mostly increased as the iridium complexes becomes

more electron-deficient [35]. The zeolite-supported catalyst exhibited more than one order of magnitude higher TOF than the MgO-supported catalyst [33]. Using IR and EXAFS spectroscopies of working catalysts, Lu et al. [33] show that changing the support from MgO to zeolite altered the rate-determining step of ethylene conversion. These results demonstrate the significant effects of supports as ligands to influence reactivity and catalytic performance of the supported catalysts.

Lu et al. [33] investigated further the zeolite- and MgO-supported $\text{Ir}(\text{C}_2\text{H}_4)_2$ by time-resolved XAS when they were exposed to H_2 flowing at 353 K and 1 bar under flowing hydrogen. The time-resolved XANES data showed a stoichiometric conversion of the supported mononuclear iridium complexes to Ir_4 clusters as indicated by isosbestic points (Fig. 3). The EXAFS data provide the change of metal-support interface upon this transformation by showing that breaking of Ir–O bonds, corresponding to the detachment of the iridium complexes from the support, preceded the formation of Ir–Ir bonds. The stoichiometric conversion of the mononuclear complexes

Fig. 3. Normalized XANES spectra at the Ir L_{III} edge characterizing the sample formed by the chemisorption $\text{Ir}(\text{C}_2\text{H}_4)_2(\text{acac})$ on (a) dealuminated HY zeolite and (b) MgO as cluster formation was occurring at 353 K with the samples in flowing H_2 for 1 h at atmospheric pressure. The isosbestic points indicate the almost stoichiometric conversion of one species to another. The decrease of the white line intensity indicates the reduction of the initially mononuclear iridium species (cluster formation). Adapted with permission from Lu et al. [33]. Copyright (2011) American Chemical Society.

to clusters indicate the retention of high structural uniformity of supported species, which were confirmed directly by characterization using STEM. Such high structural uniformity provided the authors with the opportunity to investigate the structure-performance relationship of the supported metal catalysts by resolving effects of ligands and metal nuclearity (single atom vs. cluster) [33].

Combination of XAFS and IR spectroscopies as well as STEM provides information about atomic-scale changes of the structure of working catalysts including the locations of supported single-metal sites as demonstrated by Fierro-Gonzalez et al. [45] and Lu et al. [46]. The authors synthesized supported mononuclear gold complex catalysts by the reaction of $\text{Au}(\text{CH}_3)_2(\text{acac})$ with zeolite NaY in *n*-pentane solution, characterized the catalysts by XAFS and IR spectroscopies and STEM, and tested them for CO oxidation.

The EXAFS and IR data show that the gold species in the initially prepared sample is physisorbed $\text{Au}(\text{CH}_3)_2(\text{acac})$ complexes near Al site with the gold retaining its +3 formal oxidation state (Fig. 4(a)) [45,46]. Characterization of the sample by STEM showed that the gold complexes were mononuclear, and they were present in two crystallographically distinct sites, T5 and T6, of the zeolite with approximately 36% of the gold complexes residing at T6 site [46].

The transient XAFS data of the sample collected at Au L_{III} edge in a flow-through cell as it catalyzed CO oxidation show the decrease of the Au–O coordination number from 2.0 to approximately one, accompanied by a slight increase in Au–O distance from 2.08 to approximately 2.2 Å [45]. In addition, the

Fig. 4. Structural models of (a) physisorbed $\text{Au}(\text{CH}_3)_2(\text{acac})$ on the zeolite surface and (b) $\text{Au}(\text{CO})$ complex bonded to the zeolite framework. The structures were inferred from the STEM images and EXAFS and IR data. Adapted with permission from Lu et al. [46]. Copyright (2012) Wiley.

IR and XAFS data indicate the chemisorption of the gold complexes at Al sites by detachment of acac ligands from gold atoms, the replacement of CH₃ ligands by CO, and these changes were accompanied by the change of formal oxidation state from +3 to +1 (Fig. 4(b)) [46]. The STEM data show further that some of the gold complexes moved from T5 to T6 site during CO oxidation, and the value of the gold complexes residing at T6 site increased to 76%. However, the EXAFS data show no Au–Au contribution, indicating that the supported gold remained mononuclear throughout these changes.

The results shown in this section demonstrate the importance of conducting XAS in concert with complementary techniques. In addition, the results illustrate the benefit of conducting a systematic work using isostructural metal complexes anchored on various supports to investigate differences in their electronic structure, their reactivity and catalytic performance. The results also illustrate the importance of XAFS characterization of working catalysts to track changes in structures of supported species as well as their location.

6. Summary

XAS is one of the few techniques that provides crucial information about metal–support interface, which is critical for single-atom catalysts because supports act as ligands and influence their reactivity and catalytic performance. High structural uniformity of catalysts synthesized using highly crystalline materials like zeolites and MOFs allows collection of high-quality EXAFS data and precise determination of structure of supported metal species by XAS. The XAFS and IR spectroscopy data characterizing the zeolite- and MOF-supported mononuclear iridium complexes illustrate the determination of detailed chemistry of the reaction of iridium complexes with Al centers of zeolites and MOF nodes, nature of supported iridium

species, and interactions of iridium species with the surface of these supports. The XAFS and IR data characterizing the zeolite-supported iridium catalysts under reactive atmosphere illustrates the determination of reactivity of surface species and a stoichiometric transformation of one surface species to another. The transient XAFS and IR spectroscopy data with STEM data characterizing the zeolite-supported gold sample illustrate the determination of changes of structure of supported gold complexes including metal–support interface and their crystallographic locations in the zeolite. These examples as well as the work with the metalloenzyme-like catalyst demonstrate the power of XAS, and indicate the prospective opportunity for single-atom catalysts with high structural uniformity to advance research work further toward the goal of catalyst development by design through fundamental understanding of structure–performance relationship.

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Graphical Abstract

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X-ray absorption spectroscopy for single-atom catalysts: Critical importance and persistent challenges

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X-ray absorption spectroscopy is an essential technique to investigate the structure–performance relationship of single-atom catalysts. To benefit most from this powerful technique and perform high-level analysis, structural uniformity of active sites is highly desirable.

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采用X射线吸收光谱表征单原子催化剂：至关重要与持久挑战

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摘要: X射线吸收光谱(XAS)可为负载型单中心(单原子或单核金属络合物)催化剂的结构和电子特性提供重要信息. 虽然XAS技术可表征真实反应条件下、无需长程有序结构的催化剂, 并且可提供对于负载型单中心催化剂非常重要的金属-载

体界面信息;但是它给出的信息是包括与催化有关或无关的所有负载型金属物种的平均信息.负载型催化剂的准确表征具有长期挑战性,也限制了我们准确地理解催化剂的构效关系.为了更好地利用XAS表征技术,深入研究催化剂的构效关系,并最终用其指导设计开发出高效的催化剂,制备具有均一结构活性位的负载型单中心催化剂,并采用XAS及相关技术对其表征至关重要.

本文列举了一些实例以说明XAS在表征具有均一结构活性位的负载型单中心催化剂方面的能力,以及XAS如何与其他技术(如扫描透射电子显微镜和红外光谱)互补,为以分子筛和金属-有机骨架材料为载体而制得的具有均一结构活性位的负载型单中心催化剂提供原子尺度的信息.

关键词: 负载型催化剂; X射线吸收光谱; 分子筛; 金属-有机骨架材料; 加氢; 二聚; 红外光谱; 扫描透射电子显微镜

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