UV Raman Spectroscopic Characterization of Catalysts and Catalytic Active Sites

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Abstract UV Raman spectroscopy has been demonstrated to be a powerful technique in catalysis because it can avoid the fluorescence interference occurring in visible Raman spectroscopy and concurrently enhance the Raman scattering intensity owing to the short wavelength of the excitation laser and resonance Raman effect. This article briefly reviews the recent advances in the study on heterogeneous catalysis by UV Raman spectroscopy, including the identification of isolated transition metal ions in molecular sieves, in situ study of zeolite assembly mechanisms and catalytic reaction mechanisms, and the monitoring of the surface phase transformation of metal oxide photocatalysts. UV (resonance) Raman spectroscopy, with the power of resonance enhancement for Raman signal and the advantage of high sensitivity for surface structure, coupling with in situ methodology, can provide the information about the active sites/phase and their assembling mechanisms, which are helpful for the understanding of heterogeneous catalysis and the rational design of highly active and selective catalysts.

Keywords UV Raman · Catalysis · In situ · Mechanism · Surface phase junction

1 Introduction

Heterogeneous catalysis has been playing a great role in chemical processes [1–3]. However, the characterization of catalytic active sites and the understanding of catalytic active sites remain challenging [4, 5]. Over the past decades, numerous techniques have been developed and used for the study of heterogeneous catalysis [6–13]. For example, Weckhuysen et al. [14] have monitored in situ phase changes in a complex iron-based Fisher–Tropsch catalyst and the nature and location of produced carbon species by scanning transmission X-ray microscopy, opening new opportunities for nanometer-resolution imaging of a range of important chemical processes occurring on solids in gaseous or liquid environments; Baiker et al. [15, 16] have systematically examined the catalytic solid/liquid interfaces using attenuated total reflection Fourier transform infrared spectroscopy, the kinetics of complex reactions can be followed by quantifying the concentration of reactants and products simultaneously in a non-destructive way with the in situ technique. With the development of experimental devices for in situ solid state NMR measurements, NMR spectroscopy has been widely used for the study of the adsorption of reactants on active sites, the identification of reaction intermediates and products, and the elucidation of reaction mechanisms of heterogeneous catalysts nowadays [17, 18].

Among the characterization techniques, Raman spectroscopy is considered to be a powerful tool for the study of heterogeneous catalysis. It can provide the chemical structure information about both the solid catalyst and the surface species in a single measurement [19, 20]. The wide spectral range ($50\text{--}4,000\text{ cm}^{-1}$) and high spectral resolution ($\sim 1\text{ cm}^{-1}$) enable Raman spectroscopy to identify the crystalline phase of solid, determine the structure of surface

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amorphous phase and examine the nature of molecular species. In spite of this, conventional Raman spectroscopy with visible laser as the excitation source often fails to work in solid catalyst characterization due to the strong fluorescence interference caused by impurities, organic species and defect sites [21–23].

One efficient way to avoid fluorescence interference could be time-gating methods [24], including either pulsing or optical Kerr-gating. Because the lifetime for Raman process (10^{-11} – 10^{-13} s) is much shorter than that for fluorescence process (usually 10^{-6} – 10^{-9} s), Raman and fluorescence signals can be well separated by the time-gating methods using a picosecond pulsed excitation laser and a synchronized, gated detector (and Kerr-medium for Kerr-gating). However, the drawbacks of these methods are also prominent: the potential for sample destruction caused by the very short pulse laser with high peak power; the limitation to excitation lines in the visible to near IR region [24].

As the fluorescence is produced mainly from the transition from the first excited electronic state to the vibrational states of ground electronic state, fluorescence band primarily appears in the range from 300 to 700 nm or the longer wavelength region, and it doesn't change with the variation of excitation wavelength. However, Raman signal shifts as the excitation line shifts. Therefore, the fluorescence interference could be avoided by shifting the excitation wavelength from the visible region to the IR or UV region [25] as shown in Fig. 1a. In the 1980s, the

development of FT Raman spectroscopy and UV Raman spectroscopy has dramatically increased the utility and applicability of Raman spectroscopy [26–29]. FT Raman spectroscopy using near IR laser as the excitation line has the advantage to increase the spectral S/N with a Michelson interferometer as the light dispersion system. However, FT Raman measurements are problematic with samples at elevated temperatures because of the background arising from sample luminescence [23] and the Raman intensity is relatively low due to the scattering law inversely proportional to the fourth power of excitation wavelength. The shortcomings limit its application in heterogeneous catalysis.

The situation is different for UV Raman spectroscopy, besides the avoidance of fluorescence interference, the sensitivity is remarkably improved owing to the short wavelength of the excitation laser. Figure 1b shows the Raman spectra of $\text{AlPO}_4\cdot 5$ excited at 532, 325, and 244 nm. The spectrum excited at 532 nm is dominated by fluorescence. When the excitation line shifts to 325 nm, Raman signal with a weak fluorescence background can be collected. Further more, Raman spectrum of $\text{AlPO}_4\cdot 5$ with no fluorescence background and high quality can be obtained with 244 nm excitation. The example clearly reflects the advantages of UV Raman spectroscopy, no fluorescence interference and high sensitivity. Since the electronic transition of chemical compounds are usually located in the UV region, the other advantage of UV Raman spectroscopy is that resonance Raman spectroscopic study can be carried

Fig. 1 **a** UV Raman spectroscopy avoiding fluorescence interference while increasing Raman scattering intensity; **b** Raman spectra of $\text{AlPO}_4\cdot 5$ excited at 532, 325, and 244 nm; **c** A schematic description of UV resonance Raman spectroscopy, the Raman bands attributed to S and T components can be selectively enhanced by shifting the excitation laser lines towards their UV–visible absorption bands

out for many samples. The intensity of Raman scattering is proportional to $|\alpha_{\rho\sigma}|^2$, and the polarizability ($\alpha_{\rho\sigma}$) can be expressed by the Kramers–Heisenberg equation [30],

$$(\alpha_{\rho\sigma})_{fi} = \sum_{r \neq i,f} \left(\frac{\langle f | \hat{p}_\rho | r \rangle \langle r | \hat{p}_\sigma | i \rangle}{\Delta E_{ri} - \hbar\nu_0 - i\Gamma_r} + \frac{\langle f | \hat{p}_\sigma | r \rangle \langle r | \hat{p}_\rho | i \rangle}{\Delta E_{rf} + \hbar\nu_0 + i\Gamma_r} \right)$$

In the equation, ν_0 is the frequency of excitation laser, ΔE_{ri} stands for the energy difference between the two electronic states r and i , while state f is the first excited vibrational energy level. When the laser line ($\hbar\nu_0$) is close to an electronic transition (ΔE_{ri}), the polarizability ($\alpha_{\rho\sigma}$) would be greatly increased. As a result, the cross section of Raman scattering could be considerably enhanced, and Raman intensity can be increased by several orders of magnitude owing to the resonance Raman effect (Fig. 1c). Since Raman bands associated with different components can be selectively enhanced by excitation at different laser lines according to their electronic transitions, UV resonance Raman spectroscopy is particularly powerful in characterizing the complex solid catalysts in heterogeneous catalysis [24, 25].

In the feature article, we briefly review the recent advances in UV Raman spectroscopic characterization of catalysts and catalytic active sites in our group, including the characterization of transition metal-containing catalytic materials, the synthesis mechanism of zeolites, and the study on the phase transformation of metal oxide photocatalysts. The information obtained by UV Raman spectroscopy is beneficial for the understanding of heterogeneous catalysis.

1.1 UV Raman Spectroscopic Characterization of Transition Metal-Containing Catalytic Materials

The isomorphous substitution of the silicon and aluminum in microporous and mesoporous materials with transition metal elements is one of the most effective ways to modify the physicochemical properties of microporous and mesoporous materials [31]. Transition metal-containing microporous and mesoporous materials such as TS-1, Ti-MCM-41 and Fe-ZSM-5 have been successfully used in a number of catalytic oxidation processes [32–35]. The catalytic performance of these transition metal-containing materials depends largely on their composition and structure. A deep understanding of the active sites and the formation mechanism in these materials is helpful for the development of catalysts with high selectivity and activity [36, 37]. However, due to the low concentration of transition metal ions (<2 %), it is difficult to obtain definite information on the transition metal ions in these materials [31], such as their coordination environments and distributions. Since there is usually a UV charge transfer transition between the framework oxygen ion and the framework transition metal

ion, e.g. 220 nm for TS-1, 250 nm for Fe-ZSM-5, and 280 nm for V-MCM-41 (Fig. 2a) [25], UV resonance Raman spectroscopy is considered as a powerful technique for the characterization of transition-metal containing materials. The information about transition metal species can be selectively enhanced and obtained by UV resonance Raman spectroscopy.

Figure 2b shows the Raman spectra of silicalite-1 and TS-1 excited at different laser lines. With the charge transfer transition of TS-1 at 220 nm excited by the 244 nm laser, three new bands at 490, 530, and 1125 cm^{-1} are observed in the UV Raman spectrum of TS-1 excited at 244 nm. None of these bands is clearly observed in the Raman spectra excited at 325 and 488 nm due to the low concentration of titanium ion and non-resonance excitation. There is no doubt that the appearance of these bands are associated with framework titanium but not with silicalite-1 [38]. The three resonance-enhanced Raman bands are attributed to a local unit of $[\text{Ti}(\text{OSi})_4]$ in TS-1, denoted by Ti–O–Si. The bands at 490 and 530 cm^{-1} are assigned to the bending and symmetric stretching vibration of the framework Ti–O–Si species, respectively, while the band at 1,125 cm^{-1} is ascribed to the asymmetric stretching vibration of Ti–O–Si [36, 39]. Similar phenomenon was observed for iron-containing microporous material Fe-ZSM-5 (Fig. 2c). In comparison with ZSM-5, the UV Raman spectrum of Fe-ZSM-5 excited at 244 nm exhibits new bands at 516, 1016, 1115, and 1165 cm^{-1} . The intensities of Raman bands at 516, 1115, and 1165 cm^{-1} become considerably weaker when it is excited at 325 nm and the three Raman bands almost disappear once the excitation line shifts to 532 nm. Notably, the band at 1,016 cm^{-1} is observed regardless of excitation line. Periodic DFT calculation indicates that the resonance-enhanced bands at 516 and 1,115 cm^{-1} are attributed to the symmetric and asymmetric stretching vibrations of the framework Fe–O–Si species in tetrahedral coordination, and the resonance Raman band at 1,165 cm^{-1} is ascribed to the asymmetric stretching vibrations of the framework Fe–O–Si, driven by the stretching of four neighboring framework Si–O–Si bonds, while the non-resonance Raman band at 1,016 cm^{-1} is associated with the vibration of Si–O–Si bond near framework iron [40]. Therefore, the framework titanium and iron species with low content was unambiguously identified by UV resonance Raman spectroscopy [38–41].

Besides the microporous materials, the titanium and iron-containing mesoporous materials were also studied by UV resonance Raman spectroscopy excited at 244 nm [42, 43]. Ti-MCM-41 shows a resonance-enhanced Raman band at 1,110 cm^{-1} , which is 15 cm^{-1} lower than that of TS-1 (Fig. 3). Similarly, the resonance Raman band at 1,090 cm^{-1} for Fe-SBA-15 is also lower than that at 1,115 cm^{-1} for Fe-

Fig. 2 **a** Charge transfer transition between oxygen and transition metal ions in the framework of molecular sieves; **b** Raman spectra of TS-1 and silicalite-1 excited at 244, 325 and 488 nm [38, 39]; **c** Raman spectra of Fe-ZSM-5 and ZSM-5 excited at 244, 325, and 532 nm [40]

ZSM-5 (Fig. 3). The differences in wavenumber indicate the differences in coordination environments of metal ions in the two kinds of materials. The metal ions in microporous materials are fixed in the rigid framework sites, while that in mesoporous materials are relatively flexible. When the coordination environment becomes much more flexible, the resonance Raman band for Ti/SiO₂ shifts to 1,085 cm⁻¹, which is 25 cm⁻¹ lower than that of Ti-MCM-41 (Fig. 3) [44]. Therefore, the wavenumber of resonance-enhanced Raman band can be used as a figure of merit in assessing the coordination environment of metal ion in microporous and mesoporous materials and to discuss the structure-performance relationship [12].

1.2 UV Raman Spectroscopic Study on the Synthesis Mechanism of Zeolites

Although numerous zeolites (*e.g.* Fe-ZSM-5, X zeolite) have been successfully synthesized and used in chemical processes [31, 35], understanding the formation mechanism of zeolite is still all-important for the rational design and synthesis of new zeolites. Several assembly mechanisms have been proposed by scientists since the 1960s [45], including the growth from soluble and pre-assembled units [46–48], the autocatalytic nucleation [49, 50] and solid-liquid interfacial nucleation mechanism [51, 52] etc. However, it's very difficult to study the detailed formation mechanism of zeolite due to the extreme complexity of hydrothermal crystallization [51]. Most studies were carried out by *ex situ* techniques, namely, the hydrothermal reaction is quenched for sample analysis. This may cause dramatic and undeterminable structural changes. *In situ* characterization under working conditions is an ideal method to monitor the entire process of zeolite synthesis. However, the exploration of *in situ* characterization for zeolite synthesis is relatively lacking [53]. Due to the low Raman scattering cross section of water, Raman spectroscopy is considered as a suitable technique to *in situ* study

the synthesis mechanism of zeolite under hydrothermal condition. Raman spectroscopy can provide the information on the nucleation and crystal growth in the synthesis process, especially the information about the evolution of species in the early stage, which is crucial for the understanding of zeolite assembly mechanism [54, 55]. The power of *in situ* visible Raman spectroscopy has been demonstrated by Weckhuysen and co-workers in studying the synthesis mechanism of aluminophosphate molecular sieves [56, 57]. However, visible Raman spectroscopy often fails to work due to the strong fluorescence interference caused by template decomposition under hydrothermal condition. As mention above, UV Raman spectroscopy can address this problem very well, and the sensitivity can be obviously improved, especially under the condition of resonance excitation. These advantages make UV Raman spectroscopy an excellent technique to *in situ* study the synthesis mechanism of molecular sieves [58–61] and investigate the assembly mechanism of transition metal-containing zeolites [62] since the information about transition metal ion is hard to obtain due to the low concentration of transition metal ion incorporated into zeolite framework [63, 64].

UV Raman spectroscopy with the excitation lines at 325 and 244 nm were used to study the synthesis mechanism of Fe-ZSM-5 (Fig. 4a, b). As for the initial precursor, the Raman bands assigned to five-, six-membered silicate rings and Fe(OSi)₄ species are observed in the UV Raman spectra. Upon hydrothermal treatment, a weaker Raman band at 378 cm⁻¹ attributed to the MFI structure is detected in the 325 nm excited Raman spectra of the sample hydrothermalized for 6 h. Such a band appears much later when the excitation line is at 244 nm. Beside, the Raman band at 983 cm⁻¹ associated with the Fe(OSi)₄ species in flexible coordination gradually becomes sharp and shifts to a higher frequency with the synthesis time increasing. However, the hypsochromic shift rate of the band at 983 cm⁻¹ becomes much slower when the

Fig. 3 Characteristic Raman frequencies in UV Raman spectra of titanium and iron-containing microporous and mesoporous materials and the schematic description of the coordination environments of metal ions

Fig. 4 UV Raman spectra of Fe-ZSM-5 (Si/Fe = 152) at different crystallization stages excited at 325 nm (a) and 244 nm (b); c A proposed scheme for the formation mechanism of Fe-ZSM-5 [62]

excitation line shifts from 325 to 244 nm. Since all the samples at various crystallization stages show strong absorption below 300 nm, UV Raman spectroscopy excited with 244 nm laser provides the information mainly from the surface region while that excited with 325 nm laser provides the information mainly from the bulk of sample particles (Fig. 4c). These results definitely suggest that the formation of Fe-ZSM-5 structure is initiated at the core of sample particles, then the crystallization develops from inside to outside, which was also confirmed by HRTEM.

Therefore, we proposed the synthesis mechanism of Fe-ZSM-5 shown in Fig. 4c [62].

Although the assembly mechanism of faujasite zeolite from ring units has been studied by numerous techniques, such as NMR and Raman spectroscopy [65, 66], the detailed chemical connection of the ring units remains unclear. Besides, the relevance between the species in solution and the nature of solid phases should be further addressed. To gain a deeper understanding of the formation mechanisms of zeolite X and other molecular sieves, we

Fig. 5 **a** A schematic diagram of the experimental apparatus used for in situ UV Raman spectroscopic studies of hydrothermal reactions (1); In situ UV Raman cell for liquid (2) and solid (3) phase study; **b** In situ UV Raman spectra of solid phase of zeolite X synthesis at 373 K (λ_{ex} : 325 nm); **c** Plots of intensities of the bands at 380, 514, 575, and 774 cm^{-1} as a function of time; **d** A proposed scheme for the formation mechanism of zeolite X [58]

have developed in situ UV Raman spectroscopy to observe the hydrothermal reactions directly [58–60].

With the home-made in situ UV Raman cells with different depth (Fig. 5a) [58], both the solid and liquid phase under hydrothermal conditions were investigated. The liquid phase during the synthesis process of zeolite X is dominated by monomeric silicate species with the characteristic Raman bands at 774 and 920 cm^{-1} [65]. While the initial gel is composed of four-membered rings and a small amount of branched derivatives, with the featured Raman bands at 500 and 575 cm^{-1} [58, 67], respectively (Fig. 5b). These bands show very different behaviors in the intensity as a function of time (Fig. 5c). In the early stage of hydrothermal process, the band at 774 cm^{-1} becomes strong due to the depolymerization of amorphous precursors into monomeric silicate species. While the intensity of the band continuously decreases in the late stage due to the continuous consumption of monomeric silicate species for the construction of zeolite X framework. As for the band at 500 cm^{-1} , with the hydrothermal synthesis proceeding, it gradually becomes prominent and gradually shifts to a higher wavenumber at 514 cm^{-1} . Different from the band at 500 cm^{-1} , the band at 575 cm^{-1} becomes weak with increasing crystallization. Interestingly, the band disappears when the characteristic bands at 298, 380 and 514 cm^{-1} associated with the framework of zeolite X appear [54]. These results indicate that four-membered rings and a small amount of branched derivatives are the

main species in the early stage of nucleation and the branched derivative is a key intermediate for the formation of zeolite X.

Based on the in situ Raman results, we proposed the assembly mechanism of zeolite X with new intermediate species [58], and the assembly mechanism is schematically shown in Fig. 5d.

1.3 In situ (UV) Raman Spectroscopic Characterization of Catalytic Active Sites and Study of Reaction Mechanisms

As a highly active and selective catalyst, TS-1 has been widely used in a number of oxidation reactions with H_2O_2 as oxidant under mild conditions [32, 33, 37]. However, there are still many issues under debate, such as what's the exact nature of the active site [36, 37, 68, 69] and the reaction pathways [70–73]. Recently, we have conducted a thorough investigation of the active titanium species in TS-1 zeolite [74]. Besides the framework titanium species identified by UV Raman spectroscopy excited at 244 nm, another titanium species with octahedral coordination (TiO_6) was confirmed by UV Raman spectroscopy with the excitation line at 266 nm (Fig. 6a). And the roles of two titanium species in the propylene epoxidation reaction were studied by in situ UV Raman spectroscopy excited at 325 nm (Fig. 6b). Both two kinds of titanium species can react with H_2O_2 to form the η^2 side-on Ti-peroxo species

Fig. 6 **a** Two kinds of titanium species characterized by UV resonance Raman spectroscopy; **b** In situ UV Raman cell for characterizing the propylene epoxidation reaction; **c** The proposed pathway during the propylene oxidation on the two kinds of active centers [74]

with the characteristic band at 615 cm^{-1} , which is the active intermediate for the epoxidation of propylene [75]. Propylene oxide was detected after interaction with propylene, however, the 1,2-propanediol byproduct was also observed for the catalyst with “ TiO_6 ” species. Notably, the Raman band at $1,125\text{ cm}^{-1}$ attributed to “ TiO_4 ” species recovers after the catalytic cycle, while the Raman band at 695 cm^{-1} attributed to “ TiO_6 ” species is not recovered. This can be explained that the “ TiO_6 ” species could be deactivated by the diol byproduct. Therefore, we proposed the possible pathway during the propylene oxidation on the two kinds of active centers (Fig. 6c) [74]. The finding of TiO_6 species is significant not only for the reveal of the mechanism of side reaction, but also for the improvement of framework titanium amount. Recently, we have increased the concentration of the framework titanium in TS-1 zeolite by a factor of 1.5 by lowering the pH value of the synthesis gel [76].

Fe/ZSM-5 catalysts have attracted much attention because of their unique properties in oxidative dehydrogenation of alkanes [77], selective catalytic reduction of NO_x with ammonia [78] and direct catalytic N_2O decomposition [35, 79]. More interestingly, with N_2O as the oxidant, the “ α -oxygen” species can be formed on the Fe/ZSM-5 catalysts, which shows high activity and selectivity in the hydroxylation of methane to methanol and benzene to phenol at room temperature [80]. However, due to the complexity of iron species in Fe/ZSM-5, there are still many controversies in the peculiar active sites and the property of α -oxygen. Different iron species (e.g., mononuclear [81, 82], binuclear Fe sites [83, 84], oligo-nuclear Fe clusters [85, 86]) have been proposed to be the active sites for N_2O decomposition and different transition states of oxygen species (e.g., peroxide [87, 88], superoxides [87, 88], O^*-O species [89]) during N_2O decomposition on

Fe/ZSM-5 have been proposed based on kinetic and calculation methods. Although Mössbauer and ESR spectroscopy have been used for the study of peculiar active sites [90, 91], direct spectroscopic evidence about the nature of the active sites and the transition-state oxygen species during N_2O decomposition are absent, especially under working conditions. Over the past years, in situ resonance Raman spectroscopy has been used to study the peculiar active sites and the property of α -oxygen in iron containing zeolites and the catalytic mechanisms by our group (Fig. 7a) [92].

As for the Fe/ZSM-5 catalyst, after the high-temperature pretreated sample exposed to N_2O at 523 K, the Raman band at 867 cm^{-1} assigned to the peroxo species bridged on a binuclear iron site [92–94] is observed in the resonance Raman spectrum excited at 605 nm. The active oxygen species can react with benzene at room temperature, with three characteristic Raman bands at 643, 896, and $1,228\text{ cm}^{-1}$ associated with Fe(III)-phenolate [95, 96] observed. Based on these results, we proposed a possible reaction pathway of N_2O decomposition and benzene to phenol shown in Fig. 7b [88]. Besides, the effect of extra-framework aluminum/gallium [97–99], the promotional effect of NO [100] and the inhibiting effect of H_2O on N_2O decomposition over Fe/ZSM-5 catalyst [101] were well studied by our group with the in situ resonance Raman spectroscopy.

Recently, we have further investigated the structure of active iron site and active oxygen species in Fe/ZSM-35 material by in situ resonance Raman spectroscopy combined with Mössbauer spectroscopy and DFT calculations [102]. The active iron site in Fe/ZSM-35 for N_2O decomposition is an $\text{Fe}_2(\mu\text{-O})$ site, characterized by a Raman band at 875 cm^{-1} [102]. Different from the peroxo species formed on Fe/ZSM-5 catalyst, the $\text{Fe}_2(\mu\text{-O})_2$ site with the

Fig. 7 **a** In situ Raman cell for gas–solid reaction; **b** A schematic description of the reaction pathway of N_2O decomposition and benzene to phenol on Fe/ZSM-5 at room temperature; **c** The structure and corresponding Raman band of active oxygen species on Fe/ZSM-5 and Fe/ZSM-35 [92, 102]

featured Raman band at 730 cm^{-1} is formed on Fe/ZSM-35 catalyst upon N_2O reacting with the $\text{Fe}_2(\mu\text{-O})$ site (Fig. 7c) [61, 102]. The result indicates that the topology of iron containing zeolite has a great influence on the active center and then affects the catalytic performance.

1.4 UV Raman Spectroscopic Study on the Phase Transformation of Metal Oxides

It's known that polymorphism is a common phenomenon for most metal oxides. Due to the difference in microstructure, different crystalline phases show the large differences in the physical and chemical properties, such as the catalytic performance [103–105]. As catalytic reactions take place on the surface of metal oxide catalysts, catalytic performance is closely related to the surface phase structure of catalyst. However, it's difficult to characterize their surface phase structures clearly since most techniques are bulk region sensitive. For example, XRD is a bulk sensitive technique due to the long-ranged characteristic of diffraction. HRTEM can provide the structural information from the surface region, but it has the limitations of inconvenience and one-sidedness. In the study of phase transformation of ZrO_2 material, we have found that UV Raman

spectroscopy is a surface region sensitive technique for the system with strong absorption in the UV region [106, 107]. Over the past years, we have studied the phase transformation of TiO_2 and Ga_2O_3 photocatalytic materials by UV Raman spectroscopy and investigated the relationship between the surface phase and photocatalytic performance [104, 108–112].

Compared with visible Raman spectroscopy excited with 532 nm laser, UV Raman spectroscopy excited with 325 nm laser mainly provides the information from the surface region of TiO_2 material due to the strong absorption of anatase and rutile TiO_2 at 325 nm (Fig. 8a). Visible Raman spectroscopic characterization indicates that a small amount of anatase phase is transformed into rutile phase when the sample is calcined at 823 K and the phase transformation is accomplished when the calcination temperature is at or above 1,023 K (Fig. 8b). However, UV Raman spectroscopic characterization indicates that no rutile phase is formed until the calcined temperature is elevated to 973 K and the anatase phase is completely transformed into rutile phase only for the sample calcined at 1,073 K (Fig. 8c). The disagreements between UV and visible Raman spectroscopy suggest that the crystalline phase in the surface region is usually different from that in

Fig. 8 **a** UV–visible diffuse reflectance spectra of anatase and rutile TiO_2 ; **b** Visible Raman spectra of TiO_2 calcined at different temperatures excited at 532 nm; **c** UV Raman spectra of TiO_2 calcined at different temperatures excited at 325 nm; **d** A proposed scheme for the phase transformation of TiO_2 with increasing calcination temperature [108]

the bulk during the phase transformation of TiO_2 material. Based on the above results, we proposed that the phase transformation of agglomerated TiO_2 with the size in 15–40 nm from anatase to rutile starts in the bulk and then develops to the surface of agglomerated particles (Fig. 8d) [108].

Besides, we have investigated the effect of nanoparticle size on the outer/inner phase transformation of TiO_2 material by UV Raman spectroscopy [109]. Particle size is found to be the critical parameter determining the onset transition temperature and nucleation performance. The transformation temperature increases with the increase of initial particle size. Rutile nucleates at the interfaces of contacting anatase grains with the size smaller than 60 nm, while the free surface, interface, and bulk are all likely to work as rutile nucleation sites for particles larger than 60 nm.

Due to the excellent photocatalytic performance of TiO_2 material, photocatalytic H_2 evolution reaction were performed on the above-mentioned TiO_2 samples with different bulk and surface crystalline phases [104]. Interestingly, the TiO_2 samples calcined at 973–1,023 K with both phases exposed on the surface exhibit the highest photocatalytic activity no matter the activity is normalized by specific surface area or not (Fig. 9a). Thus, the highest photocatalytic activity of the samples calcined at 973–1,023 K may be attributed to the formation of the surface phase junctions between anatase nanoparticles and rutile particles.

The opinion was demonstrated by fabrication of the surface anatase–rutile phase junction on rutile TiO_2 particles with a wet-impregnation method. Figure 9b shows the UV Raman spectra of $\text{TiO}_2(\text{A})/\text{TiO}_2(\text{R})$ -n samples excited at 325 nm. With a small amount of anatase loaded on the surface of rutile TiO_2 , the $\text{TiO}_2(\text{A})/\text{TiO}_2(\text{R})$ -1 and -2 samples show much higher photocatalytic activities than pure rutile TiO_2 (Fig. 9c). And the photocatalytic activity of $\text{TiO}_2(\text{A})/\text{TiO}_2(\text{R})$ -3 sample is about four times greater than that of pure rutile TiO_2 . This enormous increase in photocatalytic activity can be attributed to the formation of the surface anatase–rutile phase junction. As the amount of loaded anatase further increases, the photocatalytic activity of $\text{TiO}_2(\text{A})/\text{TiO}_2(\text{R})$ -4 sample is decreased somewhat because the surface of rutile TiO_2 may be fully covered by anatase nanoparticles, which decreases the amount of anatase–rutile phase junction exposed on the surface of TiO_2 particle. Therefore, we proposed the concept that the photocatalytic activity can be enhanced by the surface phase junction of semiconductor catalysts [104]. Recently, our time-resolved IR spectroscopic study indicates that the electron is transferred from anatase to rutile in the TiO_2 sample with the surface anatase–rutile phase junction [113], which may be responsible for the enhancement of photocatalytic activity.

Besides in photocatalytic H_2 evolution, such a concept was further confirmed in photocatalytic overall water splitting over Ga_2O_3 photocatalysts [112]. Ga_2O_3 is a polymorphous material with five kinds of crystalline phases

Fig. 9 **a** Photocatalytic H_2 evolution activity on TiO_2 samples calcined at different temperatures normalized by specific surface area; **b** UV Raman spectra of $TiO_2(A)/TiO_2(R)-n$ samples excited at 325 nm; **c** Photocatalytic H_2 evolution activity on $TiO_2(A)/TiO_2(R)-n$ samples with increasing amount of anatase phase on the surface of rutile TiO_2 . The anatase contents estimated from XRD and UV Raman spectroscopy for $TiO_2(A)/TiO_2(R)-n$ samples are also displayed [104]

(α , β , γ , δ , and ϵ phases) [114] and has been reported to exhibit the photocatalytic activity on overall water splitting [115]. We investigated the α to β phase transformation of Ga_2O_3 material by UV Raman spectroscopy with the excitation lines at 266 and 325 nm (Fig. 10a, b) and XRD technique [111]. Different from that of TiO_2 , the phase transformation of Ga_2O_3 from α phase to β phase starts at the surface and then develops to the bulk of single particles. Photocatalytic overall water splitting reaction was performed on the different phase-structured Ga_2O_3 -based photocatalysts, and the photocatalytic activities are shown in Fig. 10c. All of the photocatalysts can stoichiometrically split water into H_2 and O_2 . The Ga_2O_3 sample calcined at 863 K with both α and β phases exposed on the surface shows the highest photocatalytic overall water splitting activity, which is three or seven-fold greater than that of α - Ga_2O_3 or β - Ga_2O_3 alone, respectively. While the photocatalytic activity of mechanically mixed α - Ga_2O_3 and β - Ga_2O_3 samples is nearly equal to the simple sum of the activities of α - Ga_2O_3 and β - Ga_2O_3 alone. Thus, it is only the surface α - β phase junction formed between two different phases that is responsible for the remarkable enhancement in the photocatalytic activity for overall water splitting.

Notably, although the α - β phase junction is formed for Ga_2O_3 sample calcined at 903 K, it shows photocatalytic activity nearly as low as that of β - Ga_2O_3 . This can be

explained by the situation that only the β phase is exposed on the surface of Ga_2O_3 sample calcined at 903 K with the α/β core/shell structure and the α - β phase junction doesn't work. The results suggest that the presence of the α - β phase junction and the exposure of both phases on the surface are essential for the enhancement of photocatalytic activity, which is also demonstrated by our recent study on the $ZnGa_2O_4$ - β - Ga_2O_3 heterojunction [116]. The analysis of band structure indicates that the α - β phase junction exhibits type-II band alignment, which is favorable for charge separation. An ultrafast transfer at approximately 3 ps is detected for the Ga_2O_3 sample with the surface α - β phase junction by transient absorption spectroscopy, which means a much more efficient charge separation due to the existence of surface α - β phase junction [112]. In a word, the surface phase structure of metal oxide can be well determined by UV Raman spectroscopy and the proposed concept that the photocatalytic activity can be enhanced by surface phase-junction will open new strategies for the development of efficient photocatalysts for overall water splitting, as well as photoelectronic devices.

As the above examples demonstrated, UV Raman spectroscopy is indeed a very powerful technique for the characterization of catalysts and catalytic active sites. Nowadays, UV Raman spectroscopy with the excitation line continuously-tunable in the UV region and deep UV Raman spectroscopy with the excitation line down to

Fig. 10 **a** UV Raman spectra of Ga_2O_3 calcined at different temperatures excited at 325 nm; **b** UV Raman spectra of Ga_2O_3 calcined at different temperatures excited at 266 nm; **c** Photocatalytic overall water splitting activities on Ga_2O_3 samples calcined at different temperatures, also on the mechanically mixed sample with a 1:1 ratio of α - Ga_2O_3 / β - Ga_2O_3 [111, 112]

177.3 nm have been developed by Peter Stair et al. [24, 117] and our group [118, 119], which is necessary for UV and deep UV resonance Raman spectroscopic study in catalysis. And the primary results show the advantages of these techniques. Since the active centers in catalysis often possess the dimension feature of nanometer to atomic scale, imaging catalysts at working condition has attracted much attention nowadays [120, 121]. As a powerful technique, Raman imaging has been used for the preparation and characterization of catalysts [122–124]. However, the spatial resolution is still too low owing to the diffraction limit. One way to overcome this limit is to use an apertureless near-field scanning optical microscope (ANSOM), for which the spatial resolution can be down to several tens of nanometers [125]. Since the sensitivity of UV Raman

spectroscopy is much higher than that of visible Raman spectroscopy, it would be better to develop UV-ANSOM-Raman spectroscopy for catalyst imaging. To establish the structure–activity/selectivity relationship, *operando* spectroscopy based on Raman spectroscopy has been developed, allowing monitoring of catalytic systems with simultaneous on-line product analysis under actual reaction conditions [126–131]. However, the excitation line mostly in the visible region limits its applications due to the fluorescence interference and low sensitivity. As mentioned above, these problems can be well addressed by UV Raman spectroscopy. Therefore, it's significant to develop *operando* spectroscopy based on UV Raman spectroscopy, which may make great breakthroughs in the study of heterogeneous catalysis.

2 Conclusion

Due to the avoidance of fluorescence interference and the improvement of sensitivity, UV Raman spectroscopy has greatly broadened the application of Raman spectroscopy in heterogeneous catalysis. Isolated transition metal species in the framework of molecular sieves can be identified by UV resonance Raman spectroscopy, even at very low concentration. The coordination surroundings of framework transition metal ions in microporous and mesoporous materials can be sensitively detected by UV resonance Raman spectroscopy. The crystallization process of zeolite has been successfully studied by in situ UV Raman spectroscopy, which can sensitively monitor the evolution of precursors and intermediates during the synthesis under working conditions. The reaction mechanisms have been well studied by in situ (UV) Raman spectroscopy, with the interaction information between catalyst and reactant provided. Besides, the surface phase structure of metal oxides can be clearly determined by UV Raman spectroscopy, on this basis, the concept that photocatalytic activity can be enhanced by surface phase junction of semiconductor catalysts was proposed. Undoubtedly, the knowledge obtained from UV Raman spectroscopy will deepen our understanding of catalysis and guide the rational design and synthesis of novel catalytic materials.

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References

- Armor JN (2011) *Catal Today* 163:3–9
- Fechete I, Wang Y, Védrine JC (2012) *Catal Today* 189:2–27
- Descorme C, Gallezot P, Geantet C, George C (2012) *ChemCatChem* 4:1897–1906
- Somorjai GA, McCrea KR, Zhu J (2005) *Top Catal* 18:157–166
- Védrine JC (2014) *Appl Catal A Gen* 474:40–50
- Hunger M, Weitkamp J (2001) *Angew Chem Int Ed* 40:2954–2971
- Zhang WP, Xu ST, Han XW, Bao XH (2012) *Chem Soc Rev* 41:192–210
- Zhang SR, Nguyen L, Zhu Y, Zhan SH, Tsung CK, Tao F (2013) *Acc Chem Res* 46:1731–1739
- Dixit L, Gerrard DL, Bowley HJ (1986) *Appl Spectrosc Rev* 22:189–249
- Brückner A (2003) *Catal Rev Sci Eng* 45:97–150
- Fan FT, Xu Q, Xia HA, Sun KJ, Feng ZC, Li C (2009) *Chin J Catal* 30:717–739
- Fan FT, Feng ZC, Li C (2010) *Acc Chem Res* 43:378–387
- Grunwaldt JD, Schroer CG (2010) *Chem Soc Rev* 39:4741–4753
- Smit ED, Swart I, Creemer JF, Hoveling GH, Gilles MK, Tyliszczak T, Kooyman PJ, Zandbergen HW, Morin C, Weckhuysen BM, Groot MF (2008) *Nature* 456:222–226
- Panella B, Vargas A, Ferri D, Baiker A (2009) *Chem Mater* 21:4316–4322
- Andanson JM, Baiker A (2010) *Chem Soc Rev* 39:4571–4584
- Yu ZW, Zheng AM, Wang Q, Chen L, Xu J, Amoureux JP, Deng F (2010) *Angew Chem Int Ed* 49:8657–8661
- Blasco T (2010) *Chem Soc Rev* 39:4685–4702
- Knözinger H, Mestl G (1999) *Top Catal* 8:45–55
- Wachs IE, Roberts CA (2010) *Chem Soc Rev* 39:5002–5017
- Li C, Stair PC (1996) *Stud Surf Sci Catal* 101:881–890
- Stair PC, Li C (1997) *J Vac Sci Technol A* 15:1679–1684
- Stair PC (2007) *Adv Catal* 51:75–98
- Kim HS, Kosuda KM, Duyne RVP, Stair PC (2010) *Chem Soc Rev* 39:4820–4844
- Li C (2003) *J Catal* 216:203–212
- Chase DB (1986) *J Am Chem Soc* 108:7485–7488
- Porterfield DR, Campion A (1988) *J Am Chem Soc* 110:408–410
- Asher SA, Johnson CR (1984) *Science* 225:311–313
- Asher SA (1993) *Anal Chem* 65:59–66
- Long DA (2002) *The Raman effect: a unified treatment of the theory of Raman scattering by molecules*. John Wiley & Sons Ltd., Chichester
- Hartmann M, Kevan L (1999) *Chem Rev* 99:635–663
- Taramasso M, Perego G, Notari B (1983) *US Patent* 4410501
- Notari B (1996) *Adv Catal* 41:253–334
- Sayari A (1996) *Chem Mater* 8:1840–1852
- Pérez-Ramírez J, Kapteijn F, Mul G, Xu XD, Moulijn JA (2002) *Catal Today* 76:55–74
- Ricchiardi G, Damin A, Bordiga S, Lamberti C, Spanò G, Rivetti F, Zecchina A (2001) *J Am Chem Soc* 123:11409–11419
- Fan WB, Duan RG, Yokoi T, Wu P, Kubota Y, Tatsumi T (2008) *J Am Chem Soc* 130:10150–10164
- Li C, Xiong G, Xin Q, Liu JK, Ying PL, Feng ZC, Li J, Yang WB, Wang YZ, Wang GR, Liu XY, Lin M, Wang XQ, Min EZ (1999) *Angew Chem Int Ed* 38:2220–2222
- Li C, Xiong G, Liu JK, Ying PL, Xin Q, Feng ZC (2001) *J Phys Chem B* 105:2993–2997
- Sun KJ, Fan FT, Xia HA, Feng ZC, Li WX, Li C (2008) *J Phys Chem C* 112:16036–16041
- Yu Y, Xiong G, Li C, Xiao FS (2000) *J Catal* 194:487–490
- Yu JQ, Feng ZC, Xu L, Li MJ, Xin Q, Liu ZM, Li C (2001) *Chem Mater* 13:994–998
- Li Y, Feng ZC, Lian YX, Sun KQ, Zhang L, Jia GQ, Yang QH, Li C (2005) *Microporous Mesoporous Mater* 84:41–49
- Yang QH, Wang SL, Lu JQ, Xiong G, Feng ZC, Xin Q, Li C (2000) *Appl Catal A Gen* 194–195:507–514
- Cundy CS, Cox PA (2005) *Microporous Mesoporous Mater* 82:1–78
- Kirschhock CEA, Kremer SPB, Grobet PJ, Jacobs PA, Martens JA (2002) *J Phys Chem B* 106:4897–4900
- Kirschhock CEA, Kremer SPB, Vermant J, Tendeloo GV, Jacobs PA, Martens JA (2005) *Chem Eur J* 11:4306–4313
- Burkett SL, Davis ME (1994) *J Phys Chem* 98:4647–4653
- Thompson RW (1992) *Zeolites* 12:837–840
- Gonthier S, Gora L, Güray I, Thompson RW (1993) *Zeolites* 13:414–418
- Valtchev VP, Bozhilov KN (2005) *J Am Chem Soc* 127:16171–16177
- Nikolakis V, Vlachos DG, Tsapatsis M (1998) *Microporous Mesoporous Mater* 21:337–346
- Weckhuysen BM, Baetens D, Schoonheydt RA (2000) *Angew Chem Int Ed* 39:3419–3422
- Dutta PK, Shieh DC, Puri M (1987) *J Phys Chem* 91:2332–2336
- Dutta PK, Puri M (1987) *J Phys Chem* 91:4329–4333
- Grandjean D, Beale AM, Petukhov AV, Weckhuysen BM (2005) *J Am Chem Soc* 127:14454–14465

57. O'Brien MG, Beale AM, Catlow CRA, Weckhuysen BM (2006) *J Am Chem Soc* 128:11744–11745
58. Fan FT, Feng ZC, Li GN, Sun KJ, Ying PL, Li C (2008) *Chem Eur J* 14:5125–5129
59. Fan FT, Feng ZC, Sun KJ, Guo ML, Guo Q, Song Y, Li WX, Li C (2009) *Angew Chem Int Ed* 48:8743–8747
60. Fan FT, Feng ZC, Li C (2010) *Chem Soc Rev* 39:4794–4801
61. Fan FT, Li C (2013) *Sci Sin Chim* 43:1818–1830
62. Fan FT, Sun KJ, Feng ZC, Xia HA, Han B, Lian YX, Ying PL, Li C (2009) *Chem Eur J* 15:3268–3276
63. Lewis DW, Catlow CRA, Sankar G, Carr SW (1995) *J Phys Chem* 99:2377–2383
64. Fejes P, Nagy JB, Halász J, Oszkó A (1998) *Appl Catal A Gen* 175:89–104
65. Twu J, Dutta PK, Kresge CT (1991) *Zeolites* 11:672–679
66. Xiong G, Yu Y, Feng ZC, Xin Q, Xiao FS, Li C (2001) *Microporous Mesoporous Mater* 42:317–323
67. Mcmillan P (1984) *Am Mineral* 69:622–644
68. Zhang FZ, Guo XW, Wang XS, Li G, Zhou JC, Yu JQ, Li C (2001) *Catal Lett* 72:235–239
69. Damin A, Bordiga S, Zecchina A, Lamberti C (2002) *J Chem Phys* 117:226–237
70. Zhuang JQ, Yang G, Ma D, Lan XJ, Liu XM, Han XW, Bao XH, Mueller U (2004) *Angew Chem Int Ed* 43:6377–6381
71. Wells DH, Delgass WN, Thomson KT (2004) *J Am Chem Soc* 126:2956–2962
72. Spanò E, Tabacchi G, Gamba A, Fois E (2006) *J Phys Chem B* 110:21651–21661
73. Bordiga S, Bonino F, Damin A, Lamberti C (2007) *Phys Chem Chem Phys* 9:4854–4878
74. Guo Q, Sun KJ, Feng ZC, Li GN, Guo ML, Fan FT, Li C (2012) *Chem Eur J* 18:13854–13860
75. Bordiga S, Damin A, Bonino F, Ricchiardi G, Lamberti C, Zecchina A (2002) *Angew Chem Int Ed* 41:4734–4737
76. Guo Q, Feng ZC, Li GN, Fan FT, Li C (2013) *J Phys Chem C* 117:2844–2848
77. Pérez-Ramírez J, Gallardo-Llomas A (2005) *J Phys Chem B* 109:20529–20538
78. Sun Q, Gao ZX, Chen HY, Sachtler WMH (2001) *J Catal* 201:89–99
79. Zhu Q, Teeffelen RMV, van Santen RA, Hensen EJM (2004) *J Catal* 221:575–583
80. Panov GI, Uriarte AK, Rodkin MA, Sobolev VI (1998) *Catal Today* 41:365–385
81. Heyden A, Peters B, Bell AT, Keil FJ (2005) *J Phys Chem B* 109:1857–1873
82. Zecchina A, Rivallan M, Berlier G, Lamberti C, Ricchiardi G (2007) *Phys Chem Chem Phys* 9:3483–3499
83. El-Malki EM, van Santen RA, Sachtler WMH (2000) *J Catal* 196:212–223
84. Sun KQ, Xia HA, Feng ZC, van Santen R, Hensen E, Li C (2008) *J Catal* 254:383–396
85. Hensen EJM, Zhu Q, van Santen RA (2005) *J Catal* 233:136–146
86. Sun KQ, Xia HA, Hensen E, van Santen RA, Li C (2006) *J Catal* 238:186–195
87. Heyden A, Hansen N, Bell AT, Keil FJ (2006) *J Phys Chem B* 110:17096–17114
88. Hansen N, Heyden A, Bell AT, Keil FJ (2007) *J Phys Chem C* 111:2092–2101
89. Kondratenko EV, Perez-Ramirez J (2007) *Catal Today* 121:197–203
90. Dubkov KA, Ovanesyan NS, Shteinman AA, Starokon EV, Panov GI (2002) *J Catal* 207:341–352
91. Berrier E, Ovsitser O, Kondratenko EV, Schwidder M, Grünert W, Brückner A (2007) *J Catal* 249:67–78
92. Xia HA, Sun KQ, Sun KJ, Feng ZC, Li WX, Li C (2008) *J Phys Chem C* 112:9001–9005
93. Brunold TC, Tamura N, Kitajima N, Moro-oka Y, Solomon EI (1998) *J Am Chem Soc* 120:5674–5690
94. Yang G, Zhou LJ, Liu XC, Han XW, Bao XH (2007) *Catal Commun* 8:1981–1984
95. Carrano CJ, Carrano MW, Sharma K, Backes G, Sanders-Loehr J (1990) *Inorg Chem* 29:1865–1870
96. Jensen MP, Lange SJ, Mehn MP, Que EL, Que L (2003) *J Am Chem Soc* 125:2113–2128
97. Xia HA, Sun KQ, Fan FT, Sun KJ, Su WG, Feng ZC, Ying PL, Li C (2008) *J Catal* 259:269–275
98. Xia HA, Fleischman SD, Li C, Scott SL (2011) *J Phys Chem Lett* 2:190–195
99. Wang JY, Xia HA, Ju XH, Feng ZC, Fan FT, Li C (2013) *J Catal* 300:251–259
100. Xia HA, Sun KQ, Liu ZM, Feng ZC, Ying PL, Li C (2010) *J Catal* 270:103–109
101. Xia HA, Sun KQ, Feng ZC, Li C (2011) *J Phys Chem C* 115:542–548
102. Wang JY, Li GN, Ju XH, Xia HA, Fan FT, Wang JH, Feng ZC, Li C (2013) *J Catal* 301:77–82
103. Jung KT, Bell AT (2000) *J Mol Catal A* 163:27–42
104. Zhang J, Xu Q, Feng ZC, Li MJ, Li C (2008) *Angew Chem Int Ed* 47:1766–1769
105. Sakata Y, Nakagawa T, Nagamatsu Y, Matsuda Y, Yasunaga R, Nakao E, Imamura H (2014) *J Catal* 310:45–50
106. Li C, Li MJ (2002) *J Raman Spectrosc* 33:301–308
107. Li MJ, Feng ZC, Ying PL, Xin Q, Li C (2003) *Phys Chem Chem Phys* 5:5326–5332
108. Zhang J, Li MJ, Feng ZC, Chen J, Li C (2006) *J Phys Chem B* 110:927–935
109. Zhang J, Xu Q, Li MJ, Feng ZC, Li C (2009) *J Phys Chem C* 113:1698–1704
110. Xu Q, Zhang J, Feng ZC, Ma Y, Wang X, Li C (2010) *Chem Asian J* 5:2158–2161
111. Wang X, Xu Q, Fan FT, Wang XL, Li MR, Feng ZC, Li C (2013) *Chem Asian J* 8:2189–2195
112. Wang X, Xu Q, Li MR, Shen S, Wang XL, Wang YC, Feng ZC, Shi JY, Han HX, Li C (2012) *Angew Chem Int Ed* 51:13089–13092
113. Shen S, Wang XL, Chen T, Feng ZC, Li C (2014) *J Phys Chem C* 118:12661–12668
114. Playford HY, Hannon AC, Barney ER, Walton RI (2013) *Chem Eur J* 19:2803–2813
115. Yanagida T, Sakata Y, Imamura H (2004) *Chem Lett* 33:726–727
116. Wang X, Shen S, Jin SQ, Yang JX, Li MR, Wang XL, Han HX, Li C (2013) *Phys Chem Chem Phys* 15:19380–19386
117. Kim HS, Stair PC (2009) *J Phys Chem A* 113:4346–4355
118. Jin SQ, Guo ML, Fan FT, Yang JX, Zhang Y, Huang BK, Feng ZC, Li C (2013) *J Raman Spectrosc* 44:266–269
119. Jin SQ, Fan FT, Guo ML, Zhang Y, Feng ZC, Li C (2014) *Rev Sci Instrum* 85:046105-(1-3)
120. Grunwaldt JD, Wagner JB, Dunin-Borkowski RE (2013) *ChemCatChem* 5:62–80
121. Weckhuysen BM (2009) *Angew Chem Int Ed* 48:4910–4943
122. Stavitski E, Weckhuysen BM (2010) *Chem Soc Rev* 39:4615–4625
123. Guo ML, Feng ZC, Li GN, Hofmann JP, Pidko EA, Magusin PCMM, Guo Q, Weckhuysen BM, Hensen EJM, Fan FT, Li C (2012) *Chem Eur J* 18:12078–12084
124. Guo ML, Feng ZC, Hofmann JP, Weckhuysen BM, Fan FT, Li C (2013) *Chem Eur J* 19:14200–14204
125. Park KD, Kim YH, Park JH, Park JS, Lee HS, Yim SY, Lee YH, Jeong MS (2012) *J Raman Spectrosc* 43:1931–1934

126. Nijhuis TA, Tinnemans SJ, Visser T, Weckhuysen BM (2003) *Phys Chem Chem Phys* 5:4361–4365
127. Brandhorst M, Cristol S, Capron M, Dujardin C, Vezin H, Lebourdon G, Payen E (2006) *Catal Today* 113:34–39
128. Guerrero-Pérez MO, Bañares MA (2006) *Catal Today* 113:48–57
129. Zhao CL, Wachs IE (2008) *J Phys Chem C* 112:11363–11372
130. Patlolla A, Carino EV, Ehrlich SN, Stavitski E, Frenkel AI (2012) *ACS Catal* 2:2216–2223
131. Xu J, Deng YQ, Luo Y, Mao W, Yang XJ, Han YF (2013) *J Catal* 300:225–235