High energy X-ray diffraction and IR spectroscopy of Pt/Al2O3 during CO oxidation in a novel catalytic reactor cell

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ABSTRACT
The operando methodology dictates not only that catalysts are analysed during reaction while activity and selectivity are monitored by analytical methods, but also that the cell in which the measurement is carried out performs as a catalytic reactor. A cell (Chiarello et al., Rev. Sci. Inst. 85 (2014) 074102) used to conduct spectroscopy and diffraction measurements under operando conditions was tested for CO oxidation on a 2 wt% Pt/Al2O3 catalyst and compared with measurements in a conventional quartz catalytic reactor to demonstrate its suitability to derive kinetic data. High energy X-ray diffraction data were collected during alternate CO and O2 pulses under differential conditions to demonstrate the extent of loss of order of the Pt particles upon exposure to the O2 pulse. The presence of a surface oxide species places the catalyst in a higher activity regime compared to the fully reduced one.

Introduction
The investigation of solid catalysts under reaction conditions, i.e. in situ [1], and while monitoring the catalytic event simultaneously, i.e. operando [2], using various spectroscopic and diffraction characterization methods is a central topic in heterogeneous catalysis and in material science in general. This approach allows obtaining deeper insights into the role that selected portions of the material under study may fulfil within a reaction mechanism and identifying their structure. A stricter definition of the operando methodology involves the analysis of the catalyst structure while following its catalytic performance in a reactor that is the closest possible to realistic conditions [3]. The sole identification of certain species is not sufficient to prove that they are involved in the catalytic reaction [4]. The rate of change associated with this species should be determined and compared with the global reaction rate, e.g. determined using online analytics. The growing awareness of the poor suitability of certain cell systems for adequate operando experimentation, for example based on fluid-dynamic simulations and especially temperature control issues, has stimulated the modification and development of operando cells that allow for the structural characterization under realistic conditions [5–7]. This is particularly true for experiments where infrared radiation is used to explore the nature of adsorbed species during reaction. The ideal combination of vibrational spectroscopy with X-ray based methods to study catalytic reactions in a single measurement [8] makes such issue critical; because of its low energy characteristics, the design and the specific technical requirements of cells for infrared spectroscopy...
are more delicate compared to high material penetration of X-rays.

We recently reported on a novel cell that was designed to perform simultaneously diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy and extended X-ray absorption fine structure spectroscopy (EXAFS) in a single measurement [9] following the paradigm of the operando methodology [10,11]. This type of combination in one single experiment makes it possible to associate the complementary information from a surface sensitive method (infrared spectroscopy) and from a bulk sensitive method (EXAFS) without the need to repeat the measurements in two separate occasions. Other cell designs have become available in the past years that follow this concept [12–14]. In our cell, the sample environment for diffuse reflectance investigation is adapted from the design of EXAFS cells rather than from commercially available units for infrared spectroscopy, but high quality infrared spectra can be obtained. We have soon realized that the cell can be used for experimentation with various spectroscopic and diffraction methods simply by substitution of the cell window. Alongside EXAFS and DRIFT, X-ray diffraction (XRD) [15], X-ray emission spectroscopy (XES) [16–18] and energy dispersive EXAFS [19] have been performed on various catalysts demonstrating the versatility of the cell.

Here, we demonstrate that this cell can be used as catalytic reactor by comparing the reaction rate for CO oxidation with that obtained in a lab scale catalytic reactor. Therefore, we can consider that when the cell is used under operando conditions, the rate of structural change obtained from spectroscopy and diffraction data is a direct measure of the kinetics of the catalytic system under study.

**Experimental**

The Pt/γ-Al₂O₃ catalyst (2 wt% from elemental analysis; 140 m²/g; ca. 4.2 nm mean particle size according to electron microscopy [20]) was kindly provided by Umicore and was received after calcination in air at 500 °C for 4 h.

Catalytic activity data for CO oxidation in the custom-made cell [9] (termed “operando cell” in the following) were obtained using 35 mg of the catalyst (100–150 μm sieve fraction) firmly fixed between two quartz wool plugs. The cell was closed using a graphite window (thickness, 0.5 mm) and a CaF₂ window (0.5 mm) enabling the measurement of operando diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy data or a second graphite window (thickness, 0.5 mm) for X-ray diffraction (XRD) measurements. The cell can be operated up to 450 °C; the sample temperature was monitored by a thermocouple inserted 0.5–1 mm within the inlet section of the sample bed (length, ca. 4 mm). Measurement of the sample temperature is critical in DRIFT spectroscopy, especially when kinetic information should be derived [21]. Careful determination of the sample temperature can be obtained in commercial cells using a pyrometer [21,22]. In the present cell, the position of the sample bed between the two heat cartridges [9] provides homogeneous sample temperature.

Prior to reaction, the sample was reduced in 5 vol% H₂/Ar at 300 °C for 30 min and cooled to 25 °C in Ar. Catalytic activity was tested by subjecting the catalyst to a continuous linear temperature ramp (5 °C/min; first set of experiments) or to incremental temperature steps with a temperature ramp of 10 °C/min (second set of experiments). In the latter case the catalyst was left 15 min at selected temperatures during the ramp to allow the system to reach steady-state. The feed to the cell consisted in both sets of experiments of 50 mL/min of 1 vol% CO and 1 vol% O₂ (bal. Ar). CO conversion was determined from online mass spectrometric (MS, Omnistar, Pfeiffer) data obtained by following m/z signals corresponding to CO (28), O₂ (32), Ar (40) and CO₂ (44).

Catalytic activity data for CO oxidation was obtained using 50 mg of the catalyst (100–150 μm sieve fraction) sandwiched between two quartz wool plugs in a tubular quartz reactor (D = 6 mm; termed “catalytic reactor” in the following) that we have used also for other purposes [23,24]. A thermocouple was inserted in the middle of the catalyst bed for the continuous monitoring of the temperature. Prior to activity test the catalyst was reduced in 5 vol% H₂/N₂ at 300 °C for 30 min. The activity tests were conducted in the temperature range of 25–300 °C using 100 mL/min of a gas feed consisting of 0.5 vol% O₂ / 0.5 vol% CO (bal. N₂; the gas hourly space velocity (GHSV) was 118,000 mL g⁻¹ h⁻¹ at STP). The exhaust of the catalytic reactor was monitored online by FTIR (Thermo Scientific Antaris). To estimate the activation energy, the catalytic reactor was operated under differential conditions so as to keep the conversion below 12%.

In situ high energy X-ray diffraction data (78.4 keV, λ = 0.0158 nm) were collected at beamline ID11 of the European Synchrotron Radiation Facility (ESRF, Grenoble) using a FReLoN camera positioned at 330 mm from the sample position and a beam size of 0.25 × 0.25 mm². For these experiments, the operando cell was used and the sample bed provided an X-ray transmission path length of 2 mm through the catalyst. Prior to the concentration modulation experiments at 150 °C, the sample was reduced in 5 vol% H₂/He at 300 °C for 30 min, cooled to room temperature, purged with He and heated in 1 vol% O₂/He to 150 °C at 10 °C/min. The modulation experiment started when the MS signals were stable at this temperature and under this gas feed. The gas manifold, consisting of mass flow controllers and two solenoid three ports switch valves (Parker), enabled the rapid switch of the feed composition to the cell. The exhaust of the cell was connected to the same
MS for online residual gas analysis of He, CO, O\textsubscript{2}, Ar and CO\textsubscript{2}. A full modulation period (T) is defined as the time required for concluding a 1 vol% CO/He vs. 1 vol% O\textsubscript{2}/He sequence. The two gases were admitted to the cell consecutively for an equal time at 50 mL/min flow rate at 150 °C. During a full modulation period, high energy XRD patterns (0.5 ms time resolution) were collected providing modulation periods of 40, 120 or 230 s. Under these conditions, the time required for gas molecules to reach the MS from the switch valves was 6 s. The experiment was started with the admittance of CO to the cell and the XRD acquisition. The synchronization of XRD acquisition and valve switching was realized using the Spec software. The full set of time-resolved high energy XRD data was processed into a set of phase-resolved spectra by the phase sensitive detection algorithm (PSD, hereafter demodulation) implemented in Matlab \cite{25−27}. Only data demodulated at the fundamental frequency (k = 1) are reported.

Operando DRIFT spectra were collected during the linear temperature ramp experiment of CO oxidation using the operando cell placed within the mirror set of a commercial Praying Mantis unit (Harrick) installed in the sample compartment of a Bruker Vertex 70 V spectrometer equipped with a liquid nitrogen cooled MCT detector. Spectra were obtained by co-adding 25 interferograms at 2 cm\textsuperscript{-1} resolution and 10 kHz scanner velocity at intervals of 60 s. Prior to reaction, the sample was reduced as mentioned above and cooled to 35 °C at which point a background spectrum was recorded in Ar flow.

**Results and discussion**

**Evaluation of the spectroscopy cell**

The CO conversion profile of the 2 wt% Pt/Al\textsubscript{2}O\textsubscript{3} catalyst during a linear temperature ramp in the operando cell is shown in Figure 1(a) and (b). The reaction proceeded according to a characteristic scheme consisting of a low activity regime (below ca. 220 °C in the present case) and a high activity regime (above ca. 220 °C) \cite{28,29}. The low activity regime was characterized by CO conversion increasing exponentially up to ca. 40% with increasing temperature and by CO adsorption poisoning the active sites, inhibiting the adsorption of oxygen and thus reaction. The high coverage of CO under this regime was confirmed by the operando diffuse reflectance Fourier transform infrared (DRIFT) spectra recorded simultaneously to the CO oxidation experiment (Figure 2). After reduction at 300 °C, CO adsorbed at 35 °C on metallic Pt sites in the CO/O\textsubscript{2} feed provided a signal at 1838 cm\textsuperscript{-1} corresponding to bridged coordinated CO (CO\textsubscript{B}) and two signals at 2091 and 2071 cm\textsuperscript{-1}. These latter species have been assigned to a-top CO coordinated to (1 1 1) terraces and to co-ordinatively unsaturated Pt atoms (steps, edges and kinks of metal nanoparticles) on this material \cite{20}. No significant signals of carbonate species were observed. The CO speciation and the overall intensity of CO signals changed only slightly while increasing the temperature with the linear ramp. The slow red-shift of the signals is associated with the gradual loss of CO coverage with increasing temperature and the resulting decrease of extent of dipole-dipole coupling.

The sudden and sharp increase of CO conversion from 45% to above 90% during the linear ramp within 2 °C is termed ignition (Figure 1(a)). In this high activity regime, oxygen can dissociate on metallic Pt thus promoting CO oxidation, as shown by the sudden disappearance of adsorbed CO in the DRIFT data of Figure 2. The intensity of the spectrum recorded at 222 °C was significantly attenuated compared to the previous ones suggesting that reaction was activated between 217 and 222 °C. This spectrum was the last one displaying adsorbed CO; the next spectrum at 227 °C presented negligible signals of CO species supporting the extremely narrow regime of CO oxidation during ignition. The sudden removal of CO at ignition is common to Pt-based catalysts displaying metal nano-particles of a few nanometer in size \cite{30}.

A similar type of temperature ramp experiment was performed, but this time the heating ramp was hold at selected temperatures so that steady state measurements...
under kinetic control. The slope of the Arrhenius graph obtained from the two datasets (Figure 3) demonstrates that both measurements provided a value of $E_{\text{app}}$ (31 kJ/mol), which is on the same order of magnitude as that reported earlier [28,31]. Rigorous kinetic measurements reported ca. 80 kJ/mol [22,32] suggesting that our measurements may be still suffering from mass transfer limitations. The shift of the points obtained in the catalytic reactor to lower $y$-values is associated again with the uncertainty in the temperature measurement (different placement of thermocouples) that caused a shift of the two activity profiles measured in the continuous linear temperature ramp. Based on the convincing results of Figure 3 we conclude that the operando cell that we have designed for the measurement of the same type of chemistry using various physico-chemical characterization methods [9] can be considered a catalytic reactor. Therefore, the kinetic data of structural changes extracted from spectroscopic and diffraction datasets using this reactor can be directly related to the kinetics of the catalytic reaction under study.

**High energy X-ray diffraction**

The Pt/Al$_2$O$_3$ catalyst was subjected to alternate pulses of CO and O$_2$ in the operando cell while simultaneously collecting high energy X-ray diffraction data at 0.5 s time resolution. The experiments were conducted at 150 °C, thus within the low conversion regime preceding ignition (differential conditions). Figure 4(a) shows the set of time-resolved data obtained for a modulation period of 230 s. The 2θ scale corresponds to $\lambda = 0.0158$ nm. The XRD patterns exhibited primarily the reflections of the γ-Al$_2$O$_3$ phase [33]. Prior to the experiments, the catalyst was reduced at 300 °C, thus reflections of metallic Pt were visible at 3.95, 4.52, 6.44 and 7.59° and strongly overlap with those of γ-Al$_2$O$_3$. Faint changes are visible around these reflections but the structural...
patterns over the number of periods. This technically is to split the modulation periods and to average the modulation period. A first step of the PSD algorithm confirmed that there was in principle no need to skip any temporal dependence of the selected XRD signals considered that the system reached equilibrium from the third period, but the analysis of the MS data and the consideration that the intensity changes (positive and negative) are maximum, we observe that the reflections of metallic Pt possess a negative sign when the broad features exhibit positive sign. This supports the interpretation that the very broad features do not originate from false compensation of Al\(_2\)O\(_3\) signals but from a Pt-containing phase. The data of Figure 4 suggests that in the CO–O\(_2\) modulation experiment on reduced Pt/Al\(_2\)O\(_3\) the Pt nano-particles with a nominal diameter of 4.2 nm remained predominantly reduced during the experiment because the intensity changes around the reflections enhanced by PSD were very small compared to the overall intensity of the time-resolved 

\[ \text{Figure 4. (a) Time-resolved XRD data obtained during a CO–O}_2 \text{ modulation experiment with } T = 120 \text{ s and (b) corresponding phase-resolved data (}\phi^{\text{PSD}} = 0–170^\circ\text{); the in-phase pattern is shown in black.} \]

changes occurring during the measurement are better highlighted by the use of phase sensitive detection (PSD) [15]. In the present data evaluation, it was considered that the system reached equilibrium from the third period, but the analysis of the MS data and the temporal dependence of the selected XRD signals confirmed that there was in principle no need to skip any modulation period. A first step of the PSD algorithm is to split the modulation periods and to average the patterns over the number of periods. This technically improves the signal-to-noise ratio [34], which in the case of the presented high energy XRD was already excellent. Moreover, it allows plotting the kinetics of selected reflections over the modulation time with improved resolution compared to the same data extracted from the raw time-resolved data-set. The phase-resolved XRD data of the experiment with a modulation period of 230 s is shown in Figure 4(b). The data is simplified relative to the time-resolved data. It shows only that portion of the material that responded reversibly to the periodic stimulation induced by the alternate CO and O\(_2\) pulses. As a result, the PSD data of this experiment showed two types of signals. Sharp signals at \(2\theta\) 3.98, 4.59, 6.49, 7.61 and 7.94° were readily assigned to reflections of metallic Pt, i.e. (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes, respectively by comparison with reference diffraction data [35]. Very broad features were visible at ca. 3.5 and 5.8° 2\(\theta\) and between the Pt\(^0\) reflections. Inspection of the diffraction patterns of various Pt oxide references did not allow assigning any specific structure and composition to these broad features because of the absence of defined reflections. Based on the position of reflections of Pt oxides, we assign these broad features to oxidized Pt, which has reflections in the same 2\(\theta\) range. We also note that identical results were obtained in comparable experiments in independent synchrotron measurements on this Pt/Al\(_2\)O\(_3\) sample. If the in-phase XRD pattern is considered, the one where the intensity changes (positive and negative) are maximum, we observe that the reflections of metallic Pt possess a negative sign when the broad features exhibit positive sign. This supports the interpretation that the very broad features do not originate from false compensation of Al\(_2\)O\(_3\) signals but from a Pt-containing phase. The data of Figure 4 suggests that in the CO–O\(_2\) modulation experiment on reduced Pt/Al\(_2\)O\(_3\) the Pt nano-particles with a nominal diameter of 4.2 nm remained predominantly reduced during the experiment because the intensity changes around the reflections enhanced by PSD were very small compared to the overall intensity of the time-resolved patterns (Figure 4(a)). However, the intensity change in the PSD data (Figure 4(b)) suggests that the degree of crystallinity and hence the extent of order of the Pt nano-particles decreased in the modulation experiment. Simultaneously, the reflections that we attributed to oxidized Pt developed suggesting that the modulation experiment was able to probe partial re-oxidation of the Pt particles. The intensity and the width of the signals attributed to the oxidized Pt indicate that re-oxidation was not extensive and that a disordered oxide structure was obtained under these conditions [36]. Therefore, the data of Figure 4 indicate that high energy powder XRD was able to provide evidence on the occurrence of surface oxidation of Pt particles on a nano-particulate catalyst, while this is typically obtained on extended surfaces using surface sensitive methods, e.g. surface XRD, X-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM).

That re-oxidation was not extensive was confirmed by the observation that the measurement shown in Figure 4 was the one with the longest modulation period. Experiments with modulation periods of 40 and 120 s exhibited very similar intensity changes around the same reflections. This is shown in Figure 5(a). Figure 5(b) shows instead the temporal dependence of reduction and oxidation obtained from plotting the intensity of the Pt (1 1 1) reflection at 3.98° clearly identified in the PSD data. Figure 5(c) confirms the reversibility of the structural changes along the modulation periods. The behaviour of all reflections of Pt\(^0\) was identical (not shown), the behaviour of all broad signals assigned to Pt oxide-like reflections was their mirror image.
from the partially oxidized state to the reduced state of the catalyst that we can consider a comparable situation to the hysteresis in CO oxidation (see above). The dominant contribution of the $\text{O}_2 \rightarrow \text{CO}$ switch to the evolution of $\text{CO}_2$ is in agreement with previous similar experiments combining DRIFT and EXAFS data from two different reactors on the same catalyst [38]. It is also in line with the observation of various oxide structures on Pt single crystal surfaces [40–43], also under high activity regime in experiments of similar nature to those shown here [41], and Pt-based catalysts [18,36,37]. Hence, the oxide layer that was formed on the Pt nano-particles was a more reactive species than the fully reduced CO-covered Pt nano-particles.

**Conclusions**

In this work, we have compared CO oxidation performed on 2 wt% Pt/Al$_2$O$_3$ with a cell recently designed for combined spectroscopic and diffraction studies of heterogeneous catalysts under reaction conditions with CO oxidation in a lab scale catalytic reactor. The apparent activation energy of CO oxidation determined in both reactors was identical, indicating that the spectroscopic cell can be considered a catalytic reactor and thus that it can be used to derive relevant kinetic information from operando spectroscopy and diffraction measurements.
The same Pt/Al₂O₃ catalyst was then subjected to modulation experiments using this reactor cell to demonstrate the level of information that can be obtained by high energy X-ray diffraction on such a nano-particle catalyst. It was demonstrated through analysis of the phase-resolved datasets that XRD is able to capture the partial oxidation of Pt in the O₂ pulse upon alternate CO and O₂ pulsing in terms of loss of structural order of the bulk reduced Pt-nanoparticles. The change from partially oxidized Pt to fully reduced Pt coincided with the largest extent of CO₂ evolution from CO oxidation in agreement with similar observations from well-known studies on single crystal surfaces and suggesting that the most active phase is partially oxidized Pt.

Acknowledgments

The authors kindly acknowledge the financial support from the Swiss National Science Foundation (SNF) and the Competence Center for Materials Science and Technology (CCMX). Beamtime allocation at beamline ID 11 of the ESRF and the support by Dr. M. Di Michiel are highly appreciated.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the financial support from The Swiss National Science Foundation (SNF) and The Competence Center for Materials Science and Technology (CCMX).

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References

[1]. Topsoe H. Developments in operando studies and in situ characterization of heterogeneous catalysts. J Catal. 2003;216:155–164.
[2]. Weckhuysen BM. Snapshots of a working catalyst: possibilities and limitations of in situ spectroscopy in the field of heterogeneous catalysis. Chem Comm. 2002;97–110.
[3]. Banares MA. Operando methodology: combination of in situ spectroscopy and simultaneous activity measurements under catalytic reaction conditions. Catal Today. 2003;100:71–77.
[4]. Bravo-Suárez JJ, Bando KK, Lu J, Haruta M, Fujitani T, Oyama T. Transient technique for identification of true reaction intermediates: Hydroperoxide species in propylene epoxidation on gold/titanosilicate catalysts by X-ray absorption fine structure spectroscopy. J Phys Chem C. 2008;112:1115–1123.
[5]. Grunwaldt JD, Caravati M, Hannemann S, Baiker A. X-ray absorption spectroscopy under reaction conditions: suitability of different reaction cells for combined catalyst characterization and time-resolved studies. PCCP. 2004;6:3037–3047.
[6]. Meunier FC. The design and testing of kinetically-appropriate operando spectroscopic cells for investigating heterogeneous catalytic reactions. Chem Soc Rev. 2010;39:4602–4614.
[7]. Tsakoumis NE, York APE, Chen D, Ronning M. Catalyst characterization techniques and reaction cells operating at realistic conditions; towards acquisition of kinetically relevant information. Catal Sci Technol. 2015;5:4859–4883.
[8]. Newton MA, van Beek W. Combining synchrotron-based X-ray techniques with vibrational spectroscopies for the in situ study of heterogeneous catalysts: a view from a bridge. Chem Soc Rev. 2010;39:4718–4730.
[9]. Chiarello GL, Nachtegaal M, Marchionni V, Quaroni L, Ferri D. Adding diffuse reflectance infrared Fourier transform spectroscopy capability to extended X-ray-absorption fine structure in a new cell to study solid catalysts in combination with a modulation approach. Rev Sci Instrum. 2014;85:074102.
[10]. Bentrup U. The design and testing of kinetically-appropriate operando spectroscopic cells for investigating heterogeneous catalytic reactions. Chem Soc Rev. 2010;39:4718–4730.
[11]. Brückner A. Killing three birds with one stone—simultaneous operando EPR/UV-vis/Raman spectroscopy for monitoring catalytic reactions. Chem Comm. 2005;1761–1763.
[12]. Brieger C, Melke J, vanderBosch N, Reinholz U, Riesemeyer H, Buzanich AG, Kayarkate MK, Derr I, Schökel A, Roth C. A combined in situ XAS–DRIFTS study unraveling adsorbate induced changes on the Pt nanoparticle structure. J Catal. 2016;339:57–67.
[13]. Marinkovic NS, Wang Qi, Frenkel AI. In situ diffuse reflectance IR spectroscopy and X-ray absorption spectroscopy for fast catalytic processes. J Synchrotron Radiat. 2011;18:447–455.
[14]. Newton MA. Applying dynamic and synchronous DRIFTS/EXAFS to the structural reactive behaviour of dilute (≤1 wt%) supported Rh/Al2O3 catalysts using quick and energy dispersive EXAFS. Top Catal. 2009;52:1410–1424.
[15]. Ferri D, Newton MA, Di Michiel M, Chiarello GL, Yoon S, Lu Y, Andrieux J. Revealing the dynamic structure of complex solid catalysts using modulated excitation X-ray diffraction. Angew Chemie Int Ed. 2014;53:8890–8894.
[16]. Kopelent R, van Bokhoven JA, Szlachetko J, Edebeli J, Paun C, Nachtegaal M, Safonova OV. Catalytically active and spectator Ce3+ in ceria-supported metal catalysts. Angew Chemie Int Ed. 2015;54:8728–8731.
[17]. Marchionni V, Szlachetko J, Nachtegaal M, Kambolis A, Kröcher O, Ferri D. An operando emission spectroscopy study of Pt/Al2O3 and Pt/CeO2/Al2O3. PCCP. 2016;18:29268–29277.
[18]. Szlachetko J, Ferri D, Marchionni V, Kambolis A, Safonova OV, Milne CJ, Kröcher O, Nachtegaal M, Sa J. Subsecond and in situ chemical speciation of Pt/Al₂O₃ during oxidation-reduction cycles monitored by high-energy resolution off-resonant X-ray spectroscopy. J Am Chem Soc. 2013;135:19701–19704.
[19]. Marchionni V, Nachtegaal M, Petrov A, Kröcher O, Ferri D. Operando XAS study of the influence of CO and NO on methane oxidation by Pd/Al2O3. J Phys Conf Series. 2016;712:012051.
[20]. Matam SK, Kondratenko EV, Aguirre MH, Hug P, Rentsch D, Winkler A, Weidenkaff A, Ferri D. The impact of aging environment on the evolution of Al2O3 supported Pt nanoparticles and their NO oxidation activity. Appl Catal B Environmental. 2013;129:214–224.

[21]. Li H, Rivallan M, Thibault-Starzyk F, Travert A, Meunier FC. Effective bulk and surface temperatures of the catalyst bed of FT-IR cells used for in situ and operando studies. PCCP. 2013;15:7321–7327.

[22]. Kale MJ, Christopher P. Utilizing quantitative in situ FTIR spectroscopy to identify well-coordinated Pt atoms as the active site for CO oxidation on Al2O3-supported Pt catalysts. ACS Catal. 2016;6:5599.

[23]. Pilger F, Testino A, Lucchini MA, Kambolis A, Tarik M, El Kazzi M, Arroyo Y, Rossell MD, Ludwig C. One-pot poloy synthesis of Pt/CeO2 and Au/CeO2 nanopowders as catalysts for CO oxidation. J Nanosci Nanotechnol. 2015;15:3530–3539.

[24]. Kambolis A, Ferri D, Lu Y, Yannopoulos SN, Okrol M, Ferri D, Newton MA, Nachtegaal M. Modulation of Ni/g-Al2O3 with boron for enhanced carbon resistance during CO methanation. Chem Cat Chem. 2015;7:3261–3265.

[25]. Phase sensitive detection (PSD): where T is the length of one period, ω is the modulation frequency, k is the demodulation index (k = 1), qω,PSD is the demodulation phase angle for kω demodulation frequency and I and Iκ are the responses in the time- and phase-domains, respectively.

[26]. Baurecht D, Fringeli UP. Quantitative modulated excitation Fourier transform infrared spectroscopy. Rev Sci Instrum. 2001;72:3782–3792.

[27]. Caliandro R, Chernyshov D, Emerich H, Milanesio M, Palin L, Urakawa A, van Beek W, Viterbo D. Patterson peak at 2.66, 4.23 and 7.30° could not be assigned of the various platinum oxides and chemisorbed carbides and nitrides, Phys Rev Series 3 B-Cond Matter. 1993;48:11685–11691.

[28]. Newton MA, Chapman KW, Thompsett D, Chupas PJ. Chasing changing nanoparticles with time-resolved pair distribution function methods. J Am Catal. 2012;134:5036–5039.

[29]. Newton MA, Nachtegaal M. Modulation excitation X-ray absorption spectroscopy to probe surface species on heterogeneous catalysts. Top Catal. 2011;54:1070–1078.

[30]. Singh J, Alayon EMC, Tromp M, Sañonova OV, Glatzel P, Nachtegaal M, Fremh J, van Bokhoven JA. Generating highly active partially oxidized platinum during oxidation of carbon monoxide over Pt/Al2O3: in situ, time-resolved, and high-energy-resolution X-ray absorption spectroscopy. Angew Chemie Int Ed. 2008;47:9260–9264.

[31]. Newton MA, Chapman KW, Thompsett D, Chupas PJ. Chasing changing nanoparticles with time-resolved pair distribution function methods. J Am Catal. 2012;134:5036–5039.

[32]. Ackermann MD, Pedersen TM, Hendriksen BLM, Robach O, Bobaru SC, Popa I, Quiros C, Kim H, Hammer B, Ferrer S, Hansen J, Frenken JWM. Structure and reactivity of surface oxides on Pt (1 1 0) during catalytic CO oxidation. Phys Rev Lett. 2002;89:046101.

[33]. Hendriksen BLM, Frenken JWM. CO oxidation on Pt (1 1 0): scanning tunneling microscopy inside a high-pressure flow reactor. Phys Rev Lett. 2002;89:046101.

[34]. Ackermann MD, Pedersen TM, Hendriksen BLM, Robach O, Bobaru SC, Popa I, Quiros C, Kim H, Hammer B, Ferrer S, Frenken JWM. Structure and reactivity of surface oxides on Pt (1 1 0) during catalytic CO oxidation. Phys Rev Lett. 2005;95:255505.

[35]. Butcher DR, Grass ME, Zeng Z, Aksay F, Bluhm H, Li WX, Mun BS, Somorjai GA, Liu Z. In situ oxidation study of Pt (1 1 0) and its interaction with CO. J Am Chem Soc. 2011;133:20319–20325.

[36]. Miller D, Sanchez Casalongue HS, Bluhm H, Ogawara H, Nilsson A, Kaya S. Different reactivity of the various platinum oxides and chemisorbed oxygen in co oxidation on Pt (1 1 1). J Am Chem Soc. 2014;136:6340–6347.