Rapid-scan operando infrared spectroscopy

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Abstract: A novel methodology, referred to as *rapid-scan operando*, has been demonstrated to be a highly powerful tool for the study of reaction mechanisms in heterogeneous catalysis, because it combines *rapid-scan* for IR monitoring in the milliseconds time frame and *operando* methodology. As a proof of concept, the NO_x-CO and NO_x-H₂ reactions have been studied as model catalyzed reactions with practical interest for the removal of NO_x in Diesel exhausts. *Rapid-scan operando* experiments have confirmed the state-of-the-art knowledge concerning the reaction mechanisms, and more importantly, have allowed us to elucidate, for the first time, the different role of surface hydroxyls groups depending on the reductant used (CO or H₂). Moreover, this new tool has been used to distinguish the behavior of carbonates and nitrites under reaction conditions, which cannot be monitored by conventional IR approaches due to overlap of their absorbance bands.

Infrared spectroscopy (IR) is a powerful tool to investigate reaction mechanisms, being of special relevance for the study of reactions accelerated by solid catalysts. This technique is able to provide valuable information about the species formed and depleted on the catalyst surface.

In early spectroscopic studies performed at the end of the 19th century, obtaining a spectrum was a tedious job requiring 3-4 hours or more, since each point in the spectrum had to be measured separately.^[1] After World War II advances in electronics made it possible to obtain a spectrum in 1-2 hours,^[1] and this time was dramatically reduced to a few seconds in the 1970^s with the utilization of the fast Fourier transform algorithm^[2] and appropriate microcomputing.

Important advances were made in the study of reaction mechanisms by IR spectroscopy in the 1980^s with the development of *in situ* cells, where the sample to be analyzed is treated in a controlled thermal and chemical environment and the IR analysis is performed without contact with the ambient atmosphere. Further progress was achieved at the beginning of the 21st century with the design of *operando* systems, which combine spectroscopic monitoring with reaction rates measurements, by special attention given to the design of the reaction cells to ensure that the reaction takes place under kinetic control. In this article, it is demonstrated that these modern set-ups can be further improved and a new concept is introduced, which is referred to as *rapid-scan operando*. This new *rapid-scan operando* methodology is of special relevance for the study of heterogeneous catalysis. Other advances have been recently made in the available infrared techniques to improve the study of heterogeneously catalyzed reactions. For instance, Urakawa et al.^[3] combined DRIFTS analysis with Raman spectroscopy to obtain information about the catalyst surface and bulk.

The *Rapid-scan* methodology presented in this article consists of IR monitoring within fraction of seconds time frame, which can be achieved using high resolution modern spectrometers because few scans, or even only one, provide suitable signal to noise ratio and sufficient definition in the spectra. In the examples shown here, *rapid-scan operando* experiments were performed by recording one scan every 140 milliseconds. The reactions

selected as proof-of-concept are the reduction of NO_x with CO and H₂, which have practical interest for the removal of NO_x in Diesel exhausts.^[4] *Operando* DRIFTS-MS has demonstrated to be a powerful tool to study these reactions,^[5] and here is shown that further insights can be achieved when the spectrometer is operated in *rapid-scan* mode.

Two model NO_x Storage and Reduction (NSR) catalysts have been used, which are referred to as CuO/CeO₂ and CuO/Ce_{0.8}Zr_{0.2}O₂. These catalysts continuously chemisorb NO_x and are periodically regenerated by feeding pulses of a reductant following the NSR technology developed by Toyota.^[6] Figure 1 shows two DRIFT spectra recorded under reaction conditions with the CuO/Ce_{0.8}Zr_{0.2}O₂ catalyst in a conventional manner, that is, each spectrum was obtained by averaging scans over a period of 75 seconds. The temperature of the samples was 400°C.^[7] The nature of the species identified in both spectra are similar, regardless the nature of the reductant used (CO or H₂). The bands at 1550 and 1240 cm⁻¹, are consistent with the presence of nitrates on the catalyst,^[8] and the band at 3615 cm⁻¹ can be attributed to hydroxyl groups. The shoulders at 1438 cm⁻¹ could be assigned either to nitrites or to carbonates^[9] and the narrow peak at 2350 cm⁻¹, which is only observed during CO pulses, is due to the presence of gas phase CO₂ as a CO oxidation product.

Figure 1. DRIFT spectra of CuO/Ce_{0.8}Zr_{0.2}O₂ recorded at 400°C in a 50 ml/min flow of 850 ppm NO_x + 5% O₂ + N₂ (balance) and 100 μL pulses of H₂ or CO every 30 seconds. A background spectrum recorded at 400°C in He flow has been subtracted.

The conclusions regarding the possible reaction mechanism as deduced from these spectra on Figure 1 are consistent with the generally accepted NSR reactions pathway.^[10] NO_x is chemisorbed on the catalyst mainly in the form of nitrates, which implies that nitrogen on NO (which is the main nitrogen oxide in the feed) is oxidized from 2+ to 5+. The NO_x removal curves (included in Figure 2) confirm the net removal of NO_x from the gas stream, and therefore, confirm that CO and H₂ reduce part of

the chemisorbed NO_x species closing the NO_x storage-reduction cycle.

However, there are several questions that cannot be answered on the basis of the spectra in Figure 1, such as the role of the hydroxyl groups or provide a less ambiguous assignment of the band at 1438 cm⁻¹. A deeper analysis of the reaction mechanism can be provided by *rapid-scan* monitoring.

Figure 2 shows the absorbance at selected wavenumbers as a function of time and the NO_x removed in the *operando* experiments performed with the catalysts CuO/Ce_{0.8}Zr_{0.2}O₂ (Figure 2a) and CuO/CeO₂ (Figure 2b). The general behavior of both catalysts is qualitatively similar. Initially, both catalysts remove NO_x from the gas stream and the nitrates signal (band at 1550 cm⁻¹) increases with time. The CuO/CeO₂ catalyst (Figure 2b) only form nitrates while CuO/Ce_{0.8}Zr_{0.2}O₂ additionally shows changes in the band at 1438 cm⁻¹ (Figure 2a) due to nitrites and/or carbonates. CO is unable to completely regenerate the catalyst during each pulse, and the NO_x removal capacity of the catalysts decreases with time upon CO pulses. On the other hand, H₂ is much more effective than CO, as previously reported,^[11] and NO_x removal increases progressively during H₂ pulses and the population of nitrates stored on the catalysts decreases concordantly. The better regeneration achieved by H₂ has been attributed to its higher reactivity.^[12]

The cyclic behavior of the NSR process is clear in most profiles in Figure 2, and this is an advantage of the *rapid-scan* methodology with regard to conventional *operando* experiments, because changes occurring in the milliseconds time frame can be studied. This is useful, for instance, to investigate the role of hydroxyl groups (3605-3615 cm⁻¹) which exhibit a quite particular behavior. Conventional spectra (Figure 1) show that the hydroxyls band is quite similar during CO and H₂ pulses. However, *rapid-scan* monitoring shows notable differences in the absorbance of hydroxyls over a shorter time frame. The absorbance of hydroxyls remains constant during pulses of CO, suggesting that hydroxyls are not participating in the reaction, but act as spectators, and this feature is similar for both catalysts. Hydroxyls were formed during the first minute under the NO_x + O₂ + N₂ mixture, and it is postulated that the chemisorption of NO_x leads to the decomposition of bicarbonates (and carbonates) initially present on the catalyst, emitting CO₂ and leaving hydroxyls on the surface. However, as mentioned, these hydroxyls do not participate further in the NSR reaction performed with CO as reductant. However, the absorbance of hydroxyls follows the shape of pulses during H₂ injections, and this means that hydroxyls in this case are created and depleted. This means that the role of hydroxyls is quite different during CO and H₂ pulses.

Figure 2. Absorbance at selected wavenumbers monitored by *rapid-scan* DRIFTS and NO_x removed in experiments performed with (a) CuO/Ce_{0.8}Zr_{0.2}O₂ and (b) CuO/CeO₂ in a 50 ml/min flow of 850 ppm NO + 5% O₂ + N₂ (balance) and 100 μ L pulses of CO or H₂ every 30 seconds.

To obtain further insight into the processes occurring in the short time frame, the pulses must be analyzed in more detail. Figure 3 shows, as example, the absorbance at selected wavenumbers monitored by *rapid-scan* and the NO_x removed in the experiment performed with CuO/Ce_{0.8}Zr_{0.2}O₂ for one pulse of CO (Figure 3a) and one pulse of H₂ (Figure 3b). The reductant pulses were fed every 30 s, and the dashed vertical lines indicate when a reductant micro-pulse was admitted. The removal of NO_x follows the same pattern as the band due to nitrates at 1550 cm⁻¹. As expected, the greater the extent of NO_x removal (ie longer lean period) the greater the absorbance due to nitrates. The nitrate band intensity decreases after the pulse of reductant because these species are removed from the catalyst. As mentioned, H₂ regeneration is more efficient than CO regeneration, as deduced from the greater rate at which band intensity at 1550 cm⁻¹ is reduced after the reductant pulse, and from the higher NO_x removal levels achieved with H₂ pulses compared to CO.

Figure 3. Detail of one pulse monitored by *rapid-scan operando* DRIFTS-MS in experiments performed with CuO/Ce_{0.8}Zr_{0.2}O₂ in a 50 ml/min flow of 850 ppm NO + 5% O₂ + N₂ (balance) and 100 μ L pulses of (a) CO or (b) H₂ every 30 seconds.

The pattern of the hydroxyls absorbance during pulses of H₂ (Figure 3b) is the same as those of nitrates and NOx removal. The H₂ pulse cleans the catalyst surface, reducing nitrites and nitrites and also releasing hydroxyls as H₂O. Once the surface is clean, NOx chemisorption begins again and also H₂O molecules are chemisorbed restoring the population of hydroxyls. This observation cannot be deduced without *rapid-scan* monitoring. For instance, it is known that hydroxyls are suitable chemisorption sites for NOx,^[13] but this is not occurring on the experiments in Figure 3b. If this were the case and NOx were chemisorbed on hydroxyls, the shape of the nitrites and nitrates profiles would be opposed to those of the hydroxyls, that is, the formation of nitrites and nitrates should lead to the depletion of hydroxyls, and this is not occurring. Therefore, it is possible to rule out that NOx chemisorption on hydroxyls plays an important role, and this conclusion can be only achieved using *rapid-scan*.

Figure 3 profiles are also useful in identifying the species responsible for the band at 1438 cm⁻¹, which could be assigned to either nitrites and/or to carbonates. Carbonate bands cannot grow during H₂ pulses (Figure 3b) due to the absence of carbon source, and in this case the 1438 cm⁻¹ band must be assigned to nitrites. On the other hand, carbonates may be formed after CO oxidation, hence contributing to the absorbance at 1438 cm⁻¹ together with nitrites (Figure 3a). This would explain why the absorbance at 1438 cm⁻¹ changes with time to a greater extent in Figure 3a (CO pulses) than in Figure 3b (H₂ pulses). The competition between carbonates and nitrogen oxides for the chemisorption sites of the catalyst would be an additional argument to explain the less effective regeneration achieved by CO compared to H₂.

In summary, it has been demonstrated that the new concept introduced in this paper, referred to as *rapid-scan operando*, is a highly powerful tool in the study of reaction mechanisms of heterogeneous catalysis, because it combines *rapid-scan* for IR monitoring in the milliseconds time frame and *operando* methodology. As a proof of concept, the NOx-CO and NOx-H₂ reactions have been studied as model catalyzed reactions with practical interest for the removal of NOx in Diesel exhausts. *Rapid-scan operando* experiments have provided further insight into the reaction mechanisms, and more importantly, have

allowed us to elucidate, for the first time, the different role of hydroxyls depending on the reductant used (CO or H₂). Moreover, this procedure tool has been used to distinguish the behavior of carbonates and nitrites under reaction conditions, which cannot be achieved by conventional IR approaches as they fail to distinguish the two due to overlapping. Overall, this work provides a remarkable contribution towards the implementation of *rapid-scan operando* methodology as a powerful tool to gain further insights in the mechanism of many other heterogeneous catalysis reactions.

Experimental Section

Rapid-scan operando DRIFTS experiments were performed using a Shimadzu (IR Tracer-100) Spectrometer with a Harrick reaction cell coupled to an EcoSys-P mass spectrometer. The model CuO/CeO₂ and CuO/Ce_{0.8}Zr_{0.2}O₂ catalysts were prepared by wet impregnation of copper nitrate on CeO₂ and Ce_{0.8}Zr_{0.2}O₂ to obtain 5 wt.% Cu loading after calcination at 500°C. For CeO₂ and Ce_{0.8}Zr_{0.2}O₂ preparation, the nitrate precursors were dissolved in the minimum volume of water and the solution was introduced into a furnace previously heated at 200°C, and after 1 h, the temperature was raised to 500°C. Detailed catalysts characterization is included in the supplementary material.

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COMMUNICATION

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