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COMMUNICATION

Shaping up *operando* spectroscopy:
Raman characterization of a working honeycomb monolith

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A new monolithic reactor for *operando* Raman spectroscopy studies of honeycomb-shaped catalysts has been developed to obtain complete information on these systems considering the effect of conformation on structure-activity relationships; this is illustrated with Raman-GC monitoring of alumina-supported vanadium phosphorous oxide phases during propane ammoxidation with monolithic and powdered beds.

KEYWORDS. Raman, *operando* reactor, monolith, honeycomb, VPO, ammoxidation, propane.

The emergence and increasing demand for green chemical processes entails the need for their rational optimization and a stringent control of all process variables at both laboratory and industrial scale. The *operando* methodology has become a valuable approach to understand heterogeneous catalysts and catalysis, the cornerstone of the future sustainable society, because it combines the spectroscopic characterization of the solid during reaction (*in situ*) with simultaneous assessment of the actual catalytic performance. The idea was introduced several decades ago,[1-3] and the research for the development and the application of increasingly representative and informative reactor-cells has exponentially grown since the term *operando* was coined in 2002.[4-6] However up to now this approach has essentially looked at catalysts in powder form, even though structured shaped solids are increasingly applied in many catalytic fields. The fabrication of catalytic bodies provides them with distinctive thermal, mechanical and fluid-dynamic properties that depend on their geometry and on the active phase/support/binder/additives interplay;[7, 8] this justifies an effort for their characterization during operation in the final form.[9-12] The *operando* approach provides catalyst developers with a tool to understand the behavior of the active solid in an industrial plant through carefully designed laboratory tests performed with representative time-space relations. Finally, the implementation of this methodology at industrial level can detect operating problems or predict deactivation phenomena before the quality of the product is affected,[11, 13] thus optimizing the product quality control and reducing the waste of material. We have been developing new reaction cells to expand the *operando* approach to monitoring catalytic monoliths at work. First, we have developed a transmission FTIR *operando* cell for honeycombs[12], and in this communication we present a monolithic reactor monitored by Raman microscopy. To our knowledge these are the first attempts which deal with vibrational spectroscopy *operando* studies of monoliths.

Partial oxidation processes, in which contact time and fluid dynamics influence selectivity and must be well controlled, can be used as example to show the benefits of this approach that could be a new process analytical technology (PAT).[14] The oxidation state and structure of the catalytic bodies at work can be examined by Raman and correlated with their activity and selectivity. This rationalization will pave the way to easier scale up of monolithic reactors from laboratory scale to industrial or pilot plant size. This work reports the first successful Raman-GC *operando* study of a honeycomb monolith using a home-made alumina-supported vanadium-phosphorous oxide (VPO) catalyst. Stabilized vanadia-based powdered heterogeneous catalysts were selected as a proof of concept of the *operando* monolithic reactor because they have been thoroughly studied with Raman spectroscopy during the last decade.[15-18] Raman spectroscopy is ideally suited to study these catalysts because the distribution of V(V) and V(IV) species population strongly depends on the history of the catalytic sample.[19] A sketch of the new Raman-GC *operando* cell designed to study monolithic catalysts is included in Figure 1. It basically consists of a 4.5-cm-long squared quartz cuvette of 1 cm with glass blown cylindrical ends (made by Hellma according to our design) connected with ¾" stainless steel fittings and Teflon cones to a gas inlet system and the GC. The cuvette fits in an oven with a small

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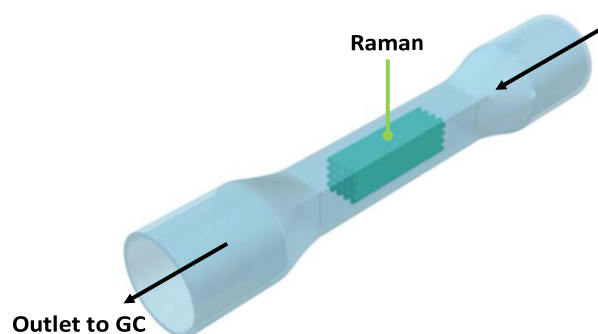
Figure 1. Schematic drawing of the Raman *operando* reaction cell for monoliths.

opening for the laser beam to reach the sample across the optical quality cuvette wall in a similar design to the *operando* Raman setups previously reported for powdered catalysts.[4] The monolith is carefully cut into the exact size of the inside dimensions of the cuvette in a way that the optical quartz walls serve as the outer walls of the monolith. The monolith was fitted tightly to minimize the contribution from wall-bypassing gas, which would increase the difference between powder and monolith data. The upper monolith wall can be totally or just partially removed, keeping part of the wall after polishing it to a thickness <100 μm (see graphical abstract), so that spectroscopic monitoring of the inside channel is possible by focusing either on the bottom channel wall or the upper wall.

To validate the new *operando* monolithic reactor a pure γ-alumina honeycomb support piece (m=0.897 g, L=2.73 cm) was manufactured by extrusion of bohemite (Plural SB, Sasol) and subsequent calcination at 600 °C. The monolith has 4x4 squared channels, with a channel size of 1.6 mm and a wall thickness of 0.6 mm (pitch = 2.2 mm) which gives a density of 20.7 cells cm^{-2} (134 cells per square inch) and a geometric area of 1322 m^2 m^{-3}. A VPO precursor solution was prepared by dissolving 12 g of oxalic acid (Panreac Química S.A.) and 6 g of ammonium metavanadate (99%, Sigma Aldrich) in 8 ml of distilled water under stirring at 70 °C and adding 3.92 mol of phosphoric acid (85% H_3PO_4, Panreac Química S.A.). The monolith was impregnated with 2 monolayers of V+P by immersion during 30 s into the VPO phase precursor solution, removing the excess liquid by air blowing. Then the sample was allowed to settle overnight at room temperature in a humid atmosphere, and subsequently dried at 150 °C for 8 h. The calcination and activation of the monolith was performed *in-situ* and thereafter the *operando* propane ammoxidation experiments were run at 500 °C, varying the flow rate (F) at constant reaction volume and catalyst mass (W), *i.e.* modifying the space velocity and linear gas velocity of the system. For comparison, an equivalent powdered catalyst was prepared by incipient wetness impregnation and tested in the previously described *operando* powdered reactor.[4] Figure 2 displays C_3H_8 and O_2 conversion efficiencies obtained in the powdered and monolithic *operando* set-ups as a function of W/F (contact time multiplied by bulk density). Both systems behave similarly, with conversion values slightly lower for propane

than for oxygen, being the latter almost completely consumed at high contact times. For the monolithic sample, however, O_2 and C_3H_8 conversions are consistently somewhat higher and lower, respectively, than for the powder. A local temperature increase at the inlet of the monolithic channels, which is apparent to naked eye by the glowing red observed upstream the monolithic cell during reaction, may explain the more significant difference between the conversions of both reactants in the shaped catalyst. The lower effective thermal conductivity of the cellular catalyst than of the powdered material,[20] due to the larger heat-transfer surface and lower void volume of the latter and to the laminar flow within the parallel channels of the former, might explain the red glowing in the monolith, not observed for the powder. The local heating produced due to the exothermicity of the reaction is a well-known effect in monolithic catalysts[21] that affects the local and overall catalyst performance. Propane ammoxidation reaction would be less selective, at the hotter end of the monolith channels, forming more CO_X and therefore consuming more oxygen. Thus the reaction conditions would be comparatively oxygen leaner downstream, delivering a more selective but less active catalyst, which would result in an overall slightly less efficient catalytic system. Taking into account that in the monolithic reactor the void volume comprises 58% of the reaction volume (the part of the cross-sectional area corresponding to the open channels), it turns out that the monolith actually provides an interesting low-pressure-drop alternative, especially if the hot spot effect is minimized, *e.g.* by use of metallic monolithic structures with high thermal conductivity.[8, 22]

Figure 3 shows the *operando* Raman spectra (excitation wavelength 514 nm) and the products distribution (depicted as mass space-time yield) as a function of W/F. The product distributions are similar in both reactor configurations.
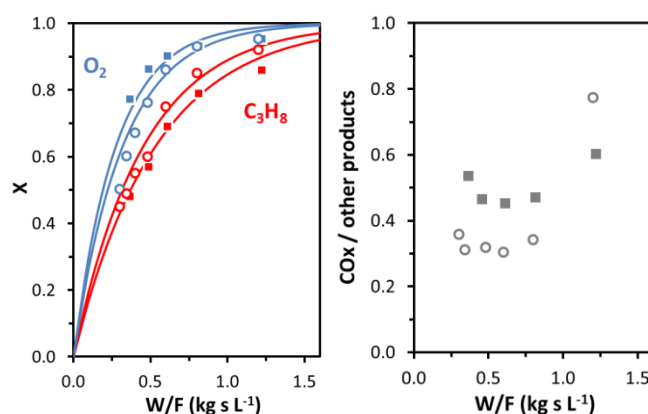

Figure 2. Molar conversion of propane and oxygen (left) and mineralization/non-mineralization products ratio (right) during ammoxidation reaction at 500 °C on **powder** (O) and **monolith** (■) *operando* Raman-GC reactors with the same VPO/alumina catalyst.

Acrylonitrile formation goes through a maximum, with slightly higher space-time yields for the powdered form at lower W/F values, although the monolith has a better performance at the highest space time due to a much reduced mineralization efficiency. In both configurations CO and propene yields increase at higher space time. ODH to propene is slightly favored for the powdered form of the catalyst, meanwhile in the monolithic cell oxidation to CO is favored and trace amounts of acetic acid are generated. These activity/selectivity variations may be caused by differences in heat and mass transfer phenomena, which depend on the catalyst geometry (the aforementioned local heating of the monolith serves as example). The effect of the active phase speciation should be considered as well, because the molecular structure of the V-P-O system is extremely dependent on the environment, readily changing upon fluctuations.[16, 23, 24] In fact, the Raman spectra of the powdered and the monolithic beds are similar but present differences that can be appreciated both during calcination or activation and operation. The Raman bands observed are the typical of alumina supported VPO catalysts, with vibrations between 1100-1150 cm^{-1} due to the terminal P=O, terminal V=O vibrations at 1010-1040 cm^{-1}, and modes at 870-950 cm^{-1} characteristic of polymeric species of P-O-M, V-O-M or Al-O-M (where M = V or P).[15, 25] The Raman bands of VPO phases are more evident in the spectra of the powdered packed beds,[17] while the bands of molecularly dispersed vanadia dominate those of the monolithic catalyst. The higher pressure drop across the packed bed might also contribute to the formation of different VPO species in both configurations, together with the unavoidable differences in the textural properties and the impregnation procedure of the powdered and extruded supports. It must be remarked that the experiments were performed in integral reactors and thus the spot of measurement is of paramount importance. In this first *operando* approach for monoliths the Raman spectra are taken at a given spot in the middle of the channel path, so they correspond to the state of the catalyst at this position (after the initial temperature increase), and the gas stream composition is measured at the reactor outlet. The formation of VPO phases is more apparent in the fixed-bed catalyst and much less apparent in the honeycomb one, but both systems produce acrylonitrile, since the presence of VPO phases is not critical for this reaction.[17] Fluctuations in the reaction environment promote the exchange between more oxidized and reduced V-P-O phases.[17] These fluctuations may be present along the monolith channel and affect the structure and performance. In future developments of the *operando* monolithic reactor, besides profiling the whole channel length by Raman spectroscopy, we envision implementing a combined temperature/gas analysis sniffer to simultaneously obtain activity/selectivity profiles along monolith channels at work.[26, 27] The combination of spectroscopy and gas phase analyses during the operation of monolithic reactors will provide further insight into the mass and heat transfer phenomena and structure/selectivity relationships.
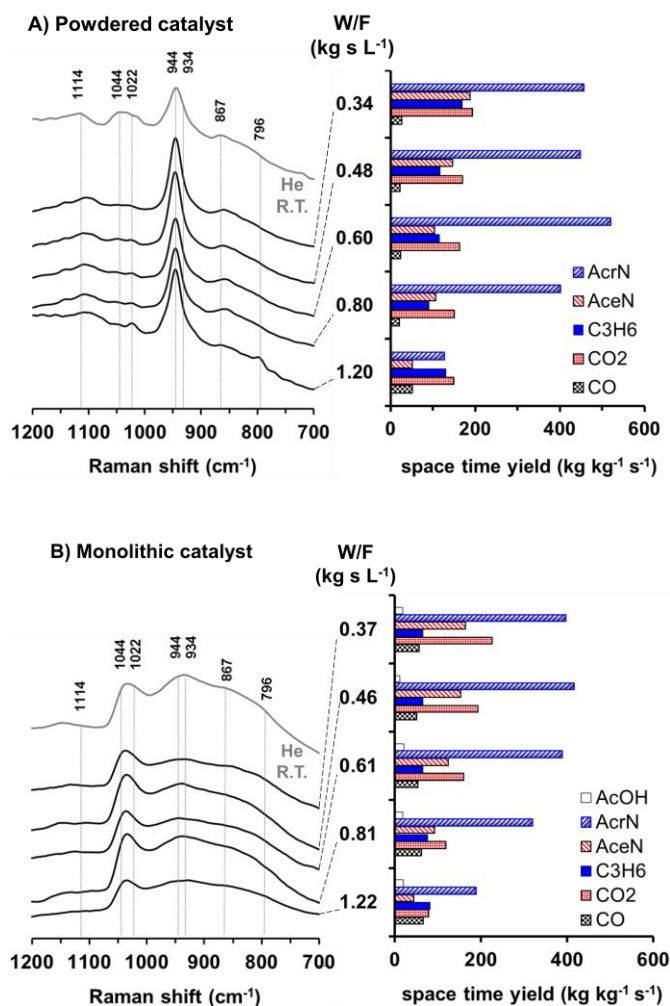

Figure 3. *Operando* Raman-GC analysis of A) powdered and B) monolithic VPO/alumina catalyst. Raman spectra during propane ammoxidation and corresponding product yields as a function of contact time. The spectra obtained at room temperature under He flow after reaction is included for comparison. AcrN=Acrylonitrile, AceN=Acetonitrile, AcOH=Acetic acid.

Conclusions

This study demonstrates the feasibility of expanding the *operando* methodology to integral reactors, such as monolithic ones, by combining Raman spectroscopy and gas phase analysis in an adapted reaction cell. As a proof of concept we have monitored a VPO-alumina honeycomb catalyst with 1 mm wall thickness in action, revealing that this system is almost as highly active for propane ammoxidation as the powdered counterpart. The catalyst shape affects heat transfer phenomena, as illustrated by the local heating produced at the reactor inlet. This effect, observed in exothermic reactions, could be reduced by the use of monolithic structures with higher thermal conductivity, and longer pieces would minimize its significance in the global process.

The work evidences the need of more *operando* studies of catalysts in their final monolithic form, which can operate as near as possible to truly industrial conditions. Careful tuning of the Raman laser power and a well-designed cell can make it possible to mimic industrial conditions in lab scale in the monolithic channels, which could shed light on the molecular basis of deactivation routes and other relevant atomic-level features useful for chemical engineers for the macroscopic catalytic design. Further developments envisage the monitoring of Raman spectra, temperature and composition profiles along the whole monolithic channel path over time during reaction to get a detailed knowledge of conformed catalytic systems.

Funding Sources

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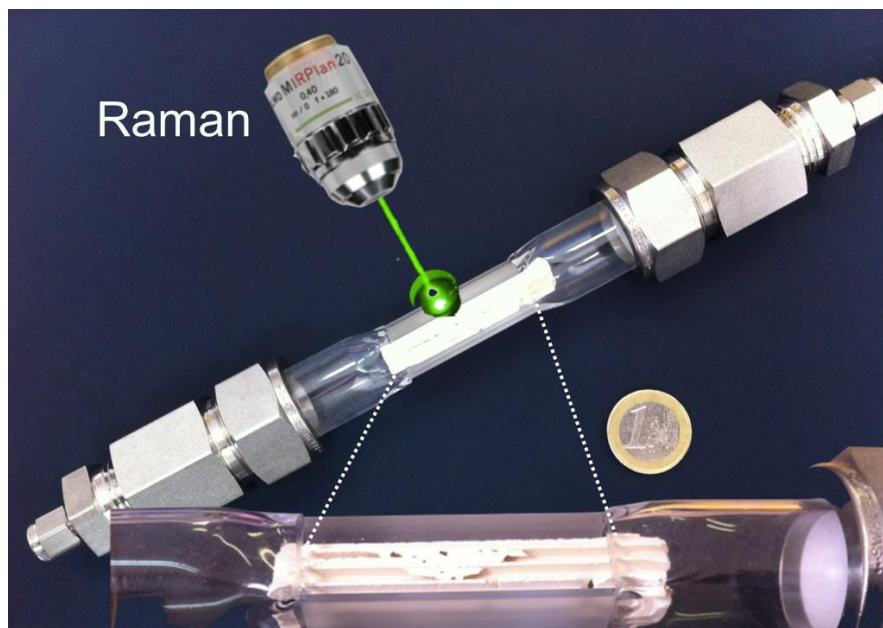
Operando reactor cell for honeycombs to study the conformation effect on structure-activity relationships by surface Raman spectroscopy and gas-phase analysis