

Kinetics of the re-oxidation step in NH₃-SCR and Hg oxidation over a V/Mo/Ti catalyst

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Highlights

- Do NH₃-SCR and Hg-oxidation share the same V-redox cycle?
- We address the kinetics of V-reoxidation at laboratory and pilot scales.
- We find that $r_{red-Hg} \ll r_{red-SCR} \approx r_{ox}$ which justifies a different effect of O₂ on the reactions.
- The re-oxidation step is promoted by NO.

1. Introduction

Mercury emission from coal power plants is a primary environmental concern. It can be largely mitigated where an SCR unit is installed, since Hg oxidation (more properly an oxychlorination) occurs over the V-catalysts with formation of HgCl₂ which can be more easily removed in the downstream wet scrubber. The fundamental understanding on the mechanism and kinetics of the Hg → HgCl₂ reaction is at an early stage but it is of enormous importance in view of developing enhanced catalysts and processes with improved mercury oxidation performance. In a previous study we have addressed a systematic investigation on the kinetics of Hg oxidation over a V/Mo/Ti catalyst; by studying the single and combined effects of temperature and HCl content we could explain why the conversion curve typically passes through a maximum and presents a negative temperature dependence at high temperature. This is due to the strong limiting effect of HCl coverage which saturates the V-sites below 300°C, but rapidly decreases at higher temperatures. A rate expression was developed (first order dependent on Hg concentration and second order dependent on HCl coverage), based on a step-wise process Hg → HgCl → HgCl₂ coherently with recent theoretical findings [2].

In this work we address another key issue, that is the characterization of the redox kinetics of Hg oxidation. We proceed by first studying the redox kinetics of NH₃-SCR, assuming it as a probe reaction of the V-cycle. Kinetic modelling allows to explain why the two chemical processes exhibit entirely different O₂-dependences at the monolith scale.

2. Results and discussion

Pilot-scale data – Hg-oxidation and NH₃-SCR tests were carried out in a pilot-scale rig, where the catalyst was tested in the form of slabs cut from a V₂O₅/MoO₃/TiO₂ plate-type catalyst. The rig, the analytical equipment and the methodology for the evaluation of Hg conversion have been reported in [1]. Notably, the Hg and HCl content of the feed reproduces typical flue gas compositions, being in the range of 1-10 ppb and 10-100 ppm respectively. Figure 1 shows the results of Hg-oxidation experiments that were performed at varying O₂ concentration from 3.5% down to 100 ppm, at high space velocity (AV = 21 NI/h) and a temperature of 300°C. Tests were run under DeNOx-inactive conditions, that is in the absence of NO and NH₃, to better focus on the intrinsic kinetics and avoid the complexity of surface coverage effects. A certain loss of conversion was observed in between 3.5 and 2%, although well within the experimental uncertainty, but a constant value of about 40% conversion was kept even at extremely low O₂ content.

NH₃-SCR experiments were also performed over the same catalyst in between 0.2 and 3.5% O₂ at AV = 21 NI/h and various T levels. A weak but systematic promoting effect of O₂ on NO conversion was found, coherently with previous data from the literature.

The comparison among the two cases is striking, since Hg oxidation and NH₃-SCR are expected to share the same active sites and pass through the same V-reoxidation step.

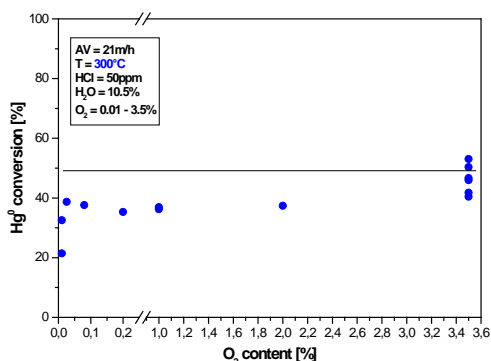


Figure 1 – Hg oxidation in slab-reactor. Measured and predicted effect of O₂ on Hg conversion.

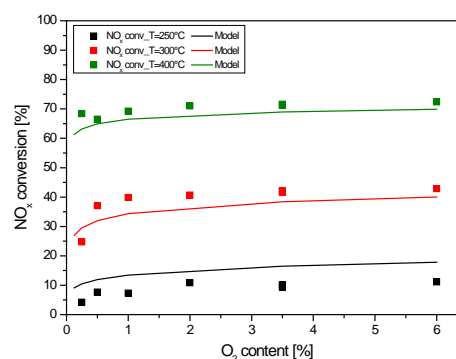


Figure 2 – NH₃-SCR in slab-reactor. Measured and predicted effect of O₂ on NO conversion.

Microreactor data. Dedicated experiments were performed on powers scratched from the plate-type catalyst to focus on the kinetics of the re-oxidation step. NH₃-SCR was taken as probe reaction and activity tests were performed in a micro-packed bed reactor at largely varying O₂ content. Figure 3 shows the results of tests at 300 ppm NO and NH₃, GHSV = 175000 Nl/kg_{cat}/h. Data were quantitatively analyzed by a pseudo-homogeneous PFR-model of the microreactor, assuming a redox rate equation, in line with the dynamic studies of Nova, Tronconi et al. [3]:

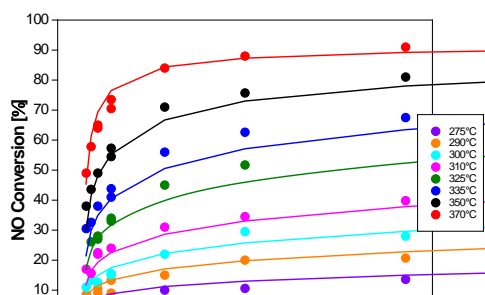


Figure 2 – NH₃-SCR in micro-reactor. Measured and calculated effect of O₂ on NO conversion.

As shown by the solid lines in Figure 3, the kinetic model nicely adapted to the data, and intrinsic parameters were estimated (herein not reported for brevity). Further tests at largely varying NO and NH₃ concentration showed that both reduction and re-oxidation steps of NH₃-SCR are promoted by NO concentration.

$$r_{DeNOx} = \left(\frac{1}{r_{red-SCR}} + \frac{1}{r_{ox}} \right)^{-1} = \left(\frac{1}{k_{DeNOx} C_{NO} \theta_{NH_3}} + \frac{1}{k_{ox} (P_{O_2})^{1/4}} \right)^{-1} \quad (1)$$

oxidation steps of NH₃-SCR are promoted by NO concentration.

Modelling of the pilot scale reactor – The intrinsic rate equation (1) was introduced in a previously developed model of the slab-reactor (which accounts for the flow distribution among channels and the impact of gas-solid and intraporous mass transfer limitations [1]) and applied to predict the effect of O₂ on NH₃-SCR at the monolith scale. Solid lines in Figure 2 show a good match with data and allow to appreciate that the important role of diffusion limitations weakens the extent of the O₂ effect, that was considerably more pronounced on powders. Concerning the oxidation of Hg, we also “built” the redox rate equation (2) where the rate of the oxidation step is the same as in the NH₃-SCR process (r_{ox}), and the reduction step has the same rate as proposed in our previous kinetic study [1]:

$$r_{Hg\ Oxidation} = \left(\frac{1}{r_{red-Hg}} + \frac{1}{r_{ox}} \right)^{-1} = \left(\frac{1}{k_{Hg} C_{Hg} \theta_{HCl}^2} + \frac{1}{K_{ox} (P_{O_2})^{1/4}} \right)^{-1} \quad (2)$$

By introducing rate equation (2) in the model of the plate-reactor, the straight line of Figure 1 was obtained, that is a complete insensitivity of the Hg-oxidation process on O₂ concentration was predicted.

The reason behind the different phenomenology observed is the relative rate between reduction and oxidation steps of the V-cycles. Being r_{red-Hg} << r_{ox}, then Hg oxidation is limited by the reduction kinetics and insensitive to O₂; instead, being r_{red-SCR} ≈ r_{ox} then NH₃-SCR is influenced by both steps and is O₂ sensitive.

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