

A kinetic Study of NO Oxidation on Pt/Al₂O₃ at Conditions Relevant to Industrial Nitric Acid Production

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Highlights

- Pt/Al₂O₃ is capable of oxidizing NO at conditions relevant to the Ostwald process.
- A power rate law of the form $r=k[\text{NO}]^{0.46}[\text{O}_2]^{0.48}$ is established.
- Approximately 25% of Pt is oxidized to PtO₂ during reaction.

1. Introduction

Nitric acid is an important industrial chemical, especially in the production of fertilizers. Commercial production of nitric acid takes place via the Ostwald process in which ammonia is oxidized with atmospheric oxygen to produce nitric oxide. Typical concentrations at the exit of the ammonia combustor are NO (10%) and H₂O (15%). Nitric oxide is oxidized in a homogeneous gas phase reaction to nitrogen dioxide, which is subsequently dissolved in water to yield nitric acid. [1]

Gas phase oxidation of nitric oxide is a 3rd order reaction with a negative dependence on temperature. [2] It is a slow reaction and use of a catalyst for NO oxidation can potentially speed up the process, enable significant heat recovery and reduce CAPEX.

Catalytic oxidation of NO has been thoroughly investigated with respect to diesel exhaust treatment at NO concentrations in the range 100-1500 ppm and 0.1-30% O₂. Supported platinum catalysts have been reported to be the most active catalyst with typical conversions as high as 85-90% at 250-300°C. [3-4]

However, there are hardly any reports of using a catalyst for oxidizing NO to NO₂ at industrial conditions. [6] In this work we investigate the performance and kinetics of a Pt/Al₂O₃ catalyst at conditions relevant to an industrial nitric acid plant.

2. Methods

A 1 wt% Pt/Al₂O₃ catalyst was synthesized using incipient wetness impregnation. The catalyst was characterized by CO chemisorption, TPR, N₂ physisorption and XRF. In addition, the catalyst was studied by in-situ XAS and XRD at the European Synchrotron Radiation Facility (ESRF).

Catalyst activity was investigated at reactant concentrations (10% NO, 6% O₂) partially simulating nitric acid plant conditions. An experimental setup for catalytic activity measurement was built with focus on minimization of homogeneous gas phase reactions by mixing reaction gasses at reactor inlet, and by reducing dead volume in the experimental setup and diluting reactor effluent with inert gas. The reaction has been carried out at atmospheric pressure to minimize gas phase contributions. Blank tests were performed to monitor this contribution. Catalyst performance at higher pressures are also studied.

The catalyst was activated by reduction in 7.5% H₂/Ar mixture at 450°C for 2 hrs. The effect of temperature on the catalytic activity was investigated by ramping the temperature from 100 to 450°C at a rate of 5°C/min.

The products were analyzed by on-line FTIR analyzer. The reactor was predominantly operated in differential mode (low conversion) to extract meaningful kinetics.

3. Results and discussion

Figure 1a shows the conversion of NO as function of temperature. A blank run shows the contribution of gas phase reactions which decreases with increasing temperatures. No significant contribution of gas phase reactions was observed at diesel exhaust oxidation conditions (400ppm NO, 6% O₂).

For the Pt/Al₂O₃ catalyst, the conversion is higher than for the blank run also at lower temperatures. This can be attributed to better mixing of reactant gases in the high surface area catalyst bed compared to the empty bed. The conversion declines up to 250°C with the same trend as for the gas phase reactions. The catalytic activity starts to increase at 250°C and maximum conversion is achieved at 400°C. The reaction becomes thermodynamically limited above 400°C.

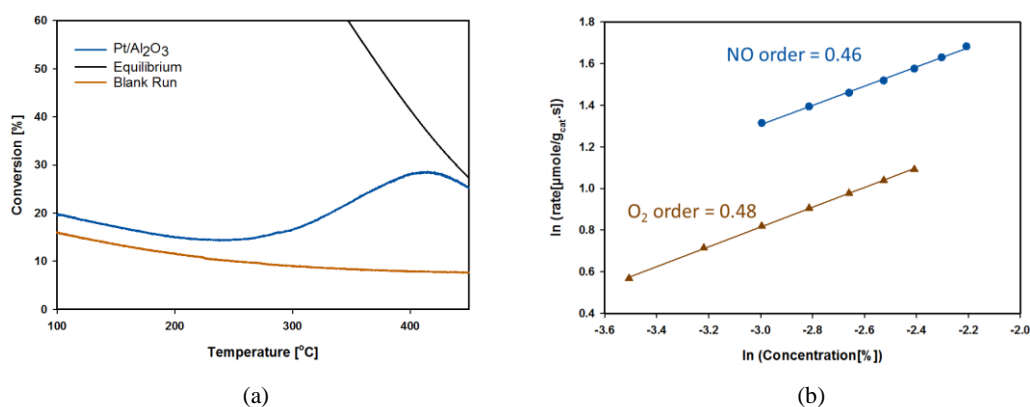


Figure 1. (a) Conversion of NO to NO₂ as a function of temperature for a feed comprising of 10% NO, 6% O₂ and balance Argon with GHSV of 6500h⁻¹. (b) NO oxidation rate of reaction dependence on NO and O₂ concentrations at 300 °C: Feed for NO order: 5-11% NO, 6% O₂; feed for O₂ order: 3-9 % O₂, 10% NO in balance Argon.

As shown in Figure 1b, the reaction order of the oxidation of nitric oxide is 0.46 and 0.48 with respect to NO and O₂ respectively giving a power rate law $r=k[\text{NO}]^{0.46}[\text{O}_2]^{0.48}$, whereas an order of 1 is reported for both NO and O₂ at diesel exhaust oxidation conditions. [4]

XAS spectra collected during in-situ NO oxidation over Pt/Al₂O₃ show that platinum is present as 25% PtO₂ and 75% as Pt at steady state.

4. Conclusions

The effect of temperature and reactant concentration on the activity of a Pt/Al₂O₃ catalyst were investigated at conditions relevant to the Ostwald process. Pt/Al₂O₃ possess significant catalytic activity capable of oxidizing nitric oxide at high concentrations (10%). NO Oxidation is of the order 0.46 & 0.48 with respect to NO and O₂ respectively. Approximately 25% of Pt is oxidized to PtO₂ during steady state reaction at 300°C.

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Keywords-

Ostwald Process ; Nitric acid ; NO oxidation ; reaction orders