

Performance of a Non-Platinum Group Metal Perovskite Catalyst for Gasoline Emissions Control: Kinetics, Reaction Mechanism and Catalyst Sizing Study

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Highlights

- $\text{La}_{0.8}\text{FeO}_3$, with the perovskite structure, is an active catalyst for the reduction of NO with CO to N_2
- CO-NO reaction over the perovskite proceeds according to a Mars-van Krevelen mechanism
- Under optimal conditions, equivalent catalyst performance was achieved with double the volume of the $\text{La}_{0.8}\text{FeO}_3$ compared to a supported 0.01% wt. Rh catalyst

1. Introduction

An A-site deficient perovskite material, namely $\text{La}_{0.8}\text{FeO}_3$, has been tested as a catalyst for the reduction of nitrogen oxide with carbon monoxide. This non-platinum group metal (PGM) containing material, as well as other similar materials, has been previously suggested as a support for, or a complete alternative to, typical PGM containing three-way catalysts on gasoline vehicles [1-3]. A combination of catalyst testing, kinetic parameter estimation and atomistic modelling has been applied to gain a greater understanding of the non-PGM material as a gasoline three-way catalyst. The kinetic parameters were then used in a catalyst sizing study to compare PGM and non-PGM catalysts, and tentative mechanistic information has also been elucidated from the study.

2. Methods

$\text{La}_{0.8}\text{FeO}_3$ and 0.01 wt.% Rh on CeZr catalysts (250-355 μm ; catalyst:diluent = 0.2 g:0.2 g) were tested for CO-NO light-off in a 12 mm i.d. quartz reactor in a Hiden Catlab microreactor. The reactor temperature was ramped (100 – 500 °C at 10 °C min⁻¹), and the gas composition was made up of various gasoline relevant concentrations of CO and NO with a balance of N_2 (no other gases were used in the tests). Outlet gas compositions were measured at regular intervals by a Multigas 2030 Fourier Transform Infra-red analyser.

Kinetic parameter estimation and catalyst sizing was carried out using Athena Visual Studio[®] software [4]. In general, the non-linear least squares estimation method was used for initial discrimination of each of the kinetic models, and subsequently the Bayesian estimation method was used to fine tune the parameter estimation outputs. For the sizing study, a flow through monolith channel model was constructed in the Athena Visual Studio[®] software.

Atomic scale modeling was performed through spin polarised generalised gradient approximation density functional theory (GGA DFT) in the CASTEP software package. The model comprises a perovskite slab with an overall cell size of 7.90 × 11.17 × 28.70 Å. The particular surface used in this study is a non-polar, oxygen terminated [110] plane.

3. Results and discussion

The light-off performance of the two catalysts was measured under a range of CO and NO concentrations, and the results for the $\text{La}_{0.8}\text{FeO}_3$ are shown in Figure 1A. It can be seen that the light-off looks to consist of two distinct regions. Parameter estimation was then carried out using various models, with a power law model used as a baseline, and then Langmuir-Hinshelwood and Mars-van Krevelen (MvK) kinetic equations interrogated. The $\text{La}_{0.8}\text{FeO}_3$ catalyst was best described by the MvK equation, meaning a two-step process in which CO first reduces the perovskite surface to form active site vacancies ($k_{mvk,CO}$), and then NO is reduced at these vacancies ($k_{mvk,NO}$). The Rh catalyst was best described by a Langmuir-Hinshelwood expression.

The rate constants for the $\text{La}_{0.8}\text{FeO}_3$ perovskite reduction and NO reduction processes have been calculated, and these are also shown in Figure 1A. From this we can tentatively infer:

- $< 200^\circ\text{C}$: $k_{mvk,CO}$ faster than $k_{mvk,NO}$. Rate is controlled by slow $k_{mvk,NO}$ value
- $200 - 350^\circ\text{C}$: $k_{mvk,NO}$ faster than $k_{mvk,CO}$ but not by enough to stop the rate improving
- $> 350^\circ\text{C}$: $k_{mvk,NO}$ significantly faster than $k_{mvk,CO}$. No rate enhancement for MvK mechanism

Finally Figure 1B shows the results of the catalyst sizing simulations for the two catalysts to achieve 75% CO conversion. It can be seen that double the volume of the $\text{La}_{0.8}\text{FeO}_3$ is required for equivalent performance to the 0.01% Rh catalyst under these ideal reaction conditions (only CO and NO in the exhaust gas). However, catalyst testing and atomistic DFT modelling has shown that other components present in a real exhaust, i.e. H_2O , O_2 , will strongly compete with NO for the vacancies created in the perovskite, with the surface preferring O_2 .

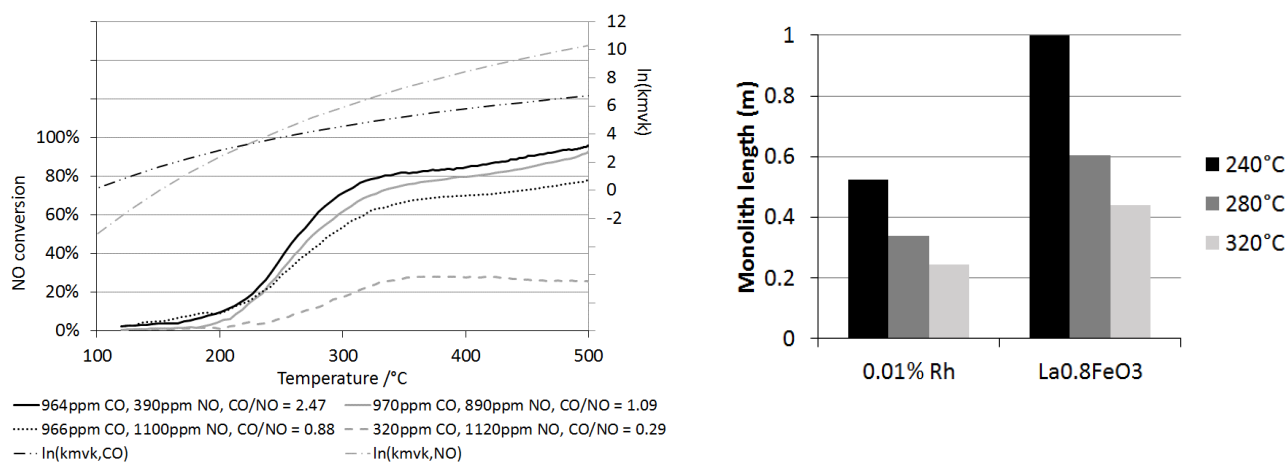


Figure 1. A) Measured NO conversion (CO conversion not shown) at different CO/NO ratios over the $\text{La}_{0.8}\text{FeO}_3$ catalyst, and calculated rate constants for the surface reduction and NO reduction steps in the MvK mechanism, B) Comparison of the simulated monolith length required to achieve 75% conversion of CO over $\text{La}_{0.8}\text{FeO}_3$ and the Rh catalyst.

4. Conclusions

The CO-NO reaction over the $\text{La}_{0.8}\text{FeO}_3$ is described by a MvK mechanism, with the measured light-off behavior described by the rate constants for the two reaction steps: surface reduction by CO and then reduction of NO at the surface vacancy. The Rh catalyst is best described by a Langmuir-Hinshelwood model. Kinetic parameters were derived and applied to a monolith reactor model for catalyst sizing comparisons: equivalent catalyst performance was achieved with double the volume of the $\text{La}_{0.8}\text{FeO}_3$ compared to the supported Rh. Atomistic modelling studies show that other species typically present in an exhaust gas will strongly compete for the active vacancy surface sites, and this has also been seen in catalyst testing. Therefore, under real conditions the catalyst is likely to be much larger than that predicted for the simple system.

References

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Keywords

“Gasoline emissions”, “base metal catalyst”, “kinetics”, “catalyst sizing”.