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Is reactor light-off data sufficiently discriminating between kinetic parameters to be used for developing kinetic models of automotive exhaust aftertreatment catalysts? The effect of hysteresis induced by strong self inhibition

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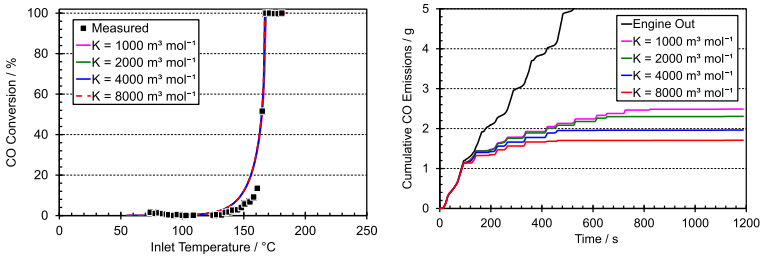
HIGHLIGHTS

- Different kinetic parameters give comparable predictions of reactor light-off data.
- But these kinetic parameters give different predictions over a vehicle test cycle.
- Effect due to these parameters giving different predictions during light-out.
- Multiple steady-states due to strong self-inhibition and external mass transport.
- Crucial to consider when developing kinetics to predict performance on a vehicle.

GRAPHICAL ABSTRACT

Different kinetic parameters give the same prediction of reactor light-off data (left), but different predictions over a vehicle test cycle (right).



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ABSTRACT

Mathematical models of automotive exhaust aftertreatment catalysts are often based on reaction kinetics developed using laboratory reactor light-off data. This paper investigates an effect observed while developing CO oxidation kinetics for a Diesel Oxidation Catalyst: it was found that while several different sets of kinetic parameters would give an equivalent prediction of the reactor data, they gave different predictions over a vehicle drive cycle. This represents a major problem when developing an aftertreatment catalyst model. This effect may be observed with any reaction which is strongly inhibited by one of the reactants and which can become external transport limited.

The main cause of this effect is that the reaction exhibits hysteresis; kinetic parameters which predict the same behaviour when the temperature is increasing, give different predictions when the temperature is decreasing. The size of the hysteresis increases with the magnitude of the self-inhibition constant in the rate equation and with reactant concentration.

A second cause for this effect is that if lower concentrations are encountered in the drive cycle than were used for kinetic development; kinetic parameters which give equivalent predictions at higher concentration may give different predictions at lower concentration.

Abbreviations: DOC, Diesel Oxidation Catalyst; EGR, Exhaust Gas Recirculation; NEDC, New European Drive Cycle; ODE, Ordinary Differential Equation; PGM, Platinum Group Metal.

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To avoid this problem, reactor data during both temperature ramp up and ramp down should be used for developing kinetics. However, it should be noted that it has been found that (i) not all experiments exhibit hysteresis and (ii) that discretisation of the catalyst into an exceptionally large number of elements is required for accurate prediction during ramp down.

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1. Introduction

The use of catalytic exhaust gas aftertreatment systems has considerably reduced pollution from automotive sources since their introduction in the late 1970s [1–4]. The considerable progress made in developing improved aftertreatment catalysts and technologies has been complimented by the development of mathematical models of these catalysts [5,6]. These models are used for designing aftertreatment systems and for improving understanding of the way these systems function.

The kinetics (rate equations and kinetic parameters) for these models are generally developed using data measured with a laboratory reactor with the catalyst either in the form of a core cut from a catalyst monolith or as a packed bed of ground up monolith. Reactor data has the advantage over data measured on an engine or vehicle of greater control of reactant composition, the ability to look at individual reactions separately and greater reproducibility. Packed bed reactors are often used as their better heat and mass transfer compared to monoliths minimises the influence of heat and mass transfer on the measured conversions so the measured kinetics are as close to intrinsic kinetics as possible [7–10].

This paper investigates an effect observed by the authors while developing CO oxidation kinetics for a Diesel Oxidation Catalyst (DOC). It was found that several different sets of kinetic parameters for CO oxidation gave comparable predictions of light-off curves measured on a packed bed reactor, but when these kinetics were used to simulate DOC performance over the New European Drive Cycle (NEDC) they gave different predictions. This effect has important consequences for the development of kinetics since it means that kinetics developed from reactor data may not predict the correct performance over a vehicle test cycle; there appears to be no obvious way to know which of the many sets of kinetic parameters that give a good prediction of the reactor data will work for a vehicle test cycle. Koutoufaris and Koltsakis [11] have also recently reported this effect. While this paper discusses CO oxidation, it is believed that this effect could occur for any reaction with a strong self-inhibition.

The object of this paper is to demonstrate this effect using the simplest possible system. Thus, this paper only considers CO oxidation; all the other reactions occurring over a DOC will be ignored. Similarly, the reactor model used for simulating drive cycles was also kept as simple as possible, *i.e.* the monolith reactor was assumed to behave adiabatically, flow across the catalyst front face was assumed to be uniform and diffusion in the washcoat was neglected. While these assumptions may affect the magnitude of the effect, they will not affect the occurrence of the effect itself.

The rest of the paper is structured as follows: After describing the collection of the experimental data and the reactor model in the experimental section (Section 2), the kinetics used for modelling CO oxidation will be discussed (Section 3.1). The effect itself will be demonstrated in Section 3.2. The next section (Section 3.3) looks at understanding the origin of this effect, *viz.* (i) that different sets of kinetic parameters which give comparable predictions to reactor data may give different predictions when the CO concentration is much less than that used in the reactor tests and (ii) that CO oxidation exhibits hysteresis such that different sets of kinetic parameters that give comparable predictions when the temperature is increasing can give very different predictions when the temperature is decreasing. Finally, Section 3.4 highlights two further complications, which the model developer needs to be aware of when trying to overcome the problems caused by this effect.

2. Experimental

2.1. Reactor testing

Laboratory reactor testing was carried out on a commercial DOC with a Platinum Group Metal (PGM) loading of 120 g ft^{-3} and a Pt:Pd ratio by weight of 2:1, which had been hydrothermally aged for 10 h at 780 °C. This catalyst was tested in the form of a packed bed of catalyst obtained by grinding and sieving cores taken from a monolith sample to give tiny catalyst pellets of well-defined size (250–355 μm). The original catalyst was on a 118.4 (diameter) × 91.4 mm, 400/4.3 (620,000 cells/m^2, 0.11 mm wall thickness), cordierite substrate.

The catalyst sample (0.8 g) was placed in a stainless steel reactor (diameter 8 mm). The flows of reactant gases and diluent (N_2) were controlled by mass flow controllers. The total gas flow was 2.0 L min^{-1}. All tests were run with 4.5% CO_2 and 4.5% H_2O in the gas feed, since these gases are always present in vehicle exhaust. The flow of liquid H_2O into the reactor was controlled by a peristaltic pump. The reactor was heated in an oven. There was a flow of gas through a jacket around the outside of the reactor (within the oven) to remove heat and hence bring the reactor closer to isothermal operation. Experiments were run with a temperature ramp of 5 °C min^{-1}. The catalyst gas inlet temperature was measured by a thermocouple placed approx. 15 mm in front of the catalyst bed. Gas from the reactor outlet was led to analysers by heated lines. Separate analyser units were used to measure the concentration of CO (infra-red), CO_2 (infra-red) and O_2 (electrochemical cell).

Since this reactor data is to be used for developing kinetics which will be applied to a different reactor configuration (*i.e.* a monolith), it is important to be sure that the data is free from the influence of transport phenomena so that intrinsic kinetics can be developed [12,13]. Table 1 lists tests applied to ensure freedom from transport effects and Appendix A discusses the avoidance of falsification of kinetics further.

2.2. Vehicle testing

Engine out emissions from a diesel and a gasoline engine over the NEDC were measured on a chassis dynamometer using standard procedures. Diesel engine emissions were measured on a 1.5 L, EU4 passenger car with a common rail fuel system and EGR, which had been used in a previous study [14]. Gasoline engine emissions were measured on a 1.6 L, EU3 passenger car. In each case, a number of repeat tests were done to ensure the data was representative. The temperature of the exhaust gas before the catalyst was measured using a 1.5 mm diameter thermocouple placed 25 mm in front of the catalyst with the tip in line with the centre of the catalyst.

2.3. Simulation

Computer simulations of reactor and vehicle tests were carried out using a one-dimensional model, which has been described in

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