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Kinetics of NO_x reduction over Ag/alumina by higher hydrocarbon in excess of oxygen

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Abstract

Continuous NO_x reduction by octane under lean conditions over a highly active Ag/alumina catalyst was studied. Experimental data, observed at steady-state conditions, was used to produce a phenomenological kinetic model to determine the rate orders in NO, hydrocarbons and O_2. The results showed that the reaction order in NO was equal to zero in the temperature range of 300–550 °C. However, at the same time reaction orders in octane exceeded unity, and were dependent on the NO concentration. Mechanistic model was developed, which takes into account kinetic regularities.
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1. Introduction

During the last 10 years improved fuel economy in vehicles has become a dominating factor when developing engines, due to the concern of the growing CO_2 greenhouse emissions. Car manufacturers have been forced to come up with new type of engines, which can meet the ambitious pollution targets (e.g. EURO5, ULEV, EZEV). A perfect example of such advanced technology is demonstrated by the common-rail turbo diesel engine, which operates under highly lean-burn conditions, resulting in decreased fuel consumption. These oxygen rich conditions, however, make the conventional three-way catalysts unsuitable for the reduction of NO_x emissions. Therefore developing novel type of catalysts, which are able to reduce NO_x to N_2 under highly oxidising conditions, has attracted a lot of interest throughout the world. In this paper we have investigated the application of a silver–alumina catalyst for selective catalytic reduction of NO_x using hydrocarbons (HC-SCR). Eränen et al. [1,2] have demonstrated the efficiency of Ag/alumina both in laboratory and engine bench tests using octane and diesel fuel as reducing agent. Since HC-SCR is based on the use of unburned hydrocarbons together with added hydrocarbons it is of highest

interest to study the reaction kinetics in order to understand reaction mechanism and optimise the process conditions in the engine and the catalytic converter. Kinetic data is essential for understanding how different species on the catalyst surface and in the gas phase are involved in the reaction pathway. Although it is known that kinetics is a very efficient tool to elucidate rate constants, concentrations of adsorbed species and reaction mechanisms, there are surprisingly few papers in the literature describing kinetic studies for HC-SCR of NO_x with higher hydrocarbons [3,4] when reactant concentrations are changed at different temperatures in an isothermal mode. The present study is devoted to experiments with simulated diesel exhaust mixtures, where the concentration of the reactants were varied and the results were mathematically treated to determine orders in NO, HC and O_2.

2. Experimental

A 2 wt.% Ag/alumina catalyst was prepared by impregnation of a commercial alumina support (LaRoche Industries Inc.), which is a mixture of χ, ρ, η and pseudo-γ phases, with a 0.022 M silver nitrate solution of high purity. After impregnation, the catalyst was filtered and dried for 24 h at room temperature. Thereafter the catalyst was dried for 3 h at 100 °C and calcination was carried out for 3 h at 550 °C in

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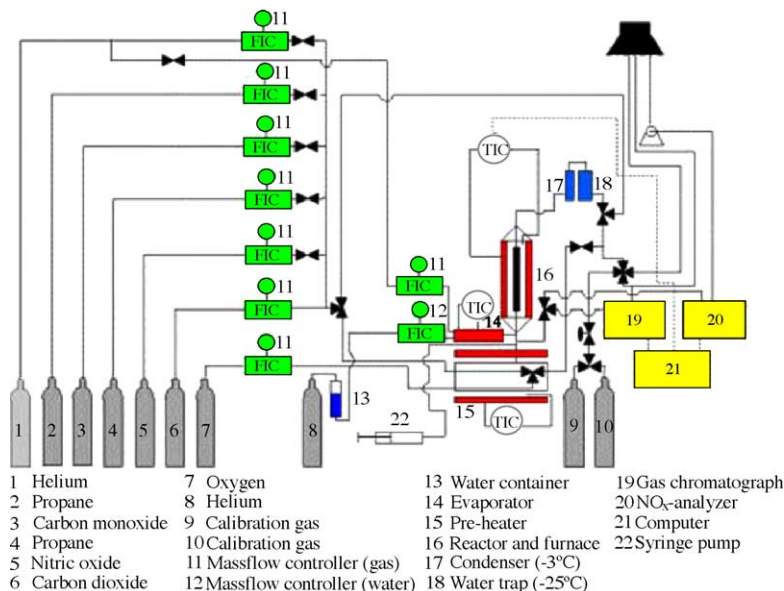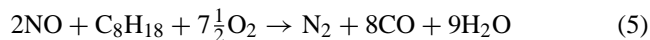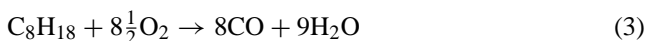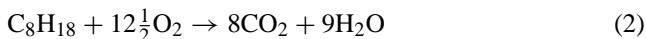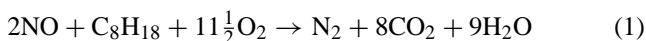 *E-mail address:* dmurzin@abo.fi (D.Yu. Murzin).

Fig. 1. The microreactor system used for activity testing of catalyst samples.

air. Finally the silver content of the prepared catalyst was determined with XRF measurements (XRF: X-MET 880, Outokumpu electronics). The crushed and sieved Ag/alumina (0.4 g, 250–500 μm) catalyst was tested in a fixed bed quartz microreactor inserted in an oven equipped with a temperature controller. A temperature range of 150–600 °C with sampling at steady-state conditions with GHSV = 60,000 h^{-1} and total flow rate of 550 ml/min was used for the catalytic activity runs. The reaction orders of NO, octane and O_2 were determined by varying the concentration of the components in the gas mixture used in activity test: 250–1000 ppm NO, 134–750 ppm octane, 1–12 vol.% O_2, and He as a balance and treating the obtained results mathematically. The concentration of H_2O was kept constant at 12 vol.% in each run. All the gases were of high purity (AGA) and were introduced into the reactor by means of mass flow controllers (Brooks 5850). The addition of octane took place via a syringe pump (CMA 102/Microdialysis). Oxygen was fed separately into the reactor to avoid oxidation of NO before the catalyst bed. The effluent gas was analysed by a GC (HP 6890 series) equipped with a GS Q column, a GS Molesieve column (J&W Scientific), and FI as well as TC detectors. High purity calibration gases (AGA) were used for calibration of the NO_x analyser and the gas chromatograph. The experimental set-up for the catalytic activity runs is illustrated in Fig. 1. The flows were controlled by means of mass flow controllers (Brooks).

The reaction was assumed to follow the simplified reaction scheme:

$$2NO + C_8H_{18} + 11\tfrac{1}{2}O_2 \rightarrow N_2 + 8CO_2 + 9H_2O \quad (1)$$

$$C_8H_{18} + 12\tfrac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O \quad (2)$$

$$C_8H_{18} + 8\tfrac{1}{2}O_2 \rightarrow 8CO + 9H_2O \quad (3)$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \quad (4)$$

$$2NO + C_8H_{18} + 7\tfrac{1}{2}O_2 \rightarrow N_2 + 8CO + 9H_2O \quad (5)$$

A phenomenological power-law kinetic model of exponential order was set up for the reactions:

$$r_1 = k_1 x_{NO}^{m_1} x_{OCT}^{n_1} x_{O_2}^{o_1}, \qquad r_2 = k_2 x_{OCT}^{n_2} x_{O_2}^{o_2},$$

$$r_3 = k_3 x_{OCT}^{n_3} x_{O_2}^{o_3}, \qquad r_4 = k_4 x_{CO},$$

$$r_5 = k_5 x_{NO}^{m_2} x_{OCT}^{n_4} x_{O_2}^{o_4} \quad (6)$$

The rate constants and reaction orders were estimated with simplex and Levenberg–Marquardt methods implemented in the software ModEst 6.0 [5]. The concept of a plug flow reactor was applied

$$\frac{dx_i}{dz} = \frac{m_{cat}}{\dot{n}} r(x_i) \quad (7)$$

where z is length coordinate in reactor, m_{cat} the catalyst mass and x the molar fraction. The mass balances were solved with the backward difference method during the parameter estimation procedure.

To study the impact of oxygen, originating from NO, on octane oxidation over the catalyst, separate activity runs were done in the absence and presence of NO. In addition, the effect of a pre-nitrated Ag/alumina surface was investigated. The gas mixture used in these runs was either 375 ppm octane, 6 vol.% O_2, 12 vol.% H_2O and He balance or 375 ppm octane, 500 ppm NO, 6 vol.% O_2, 12 vol.% H_2O and He balance. The first two runs were carried out over the Ag/alumina catalyst described previously in the absence and presence of NO. Thereafter the catalyst was pre-nitrated by treating it for 2 h in 1000 ppm NO (excess of oxygen) at 350 °C (heating