

Self-oscillating Behaviour in the Selective Catalytic Reduction of NO by Propene

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Periodical self-oscillating behaviour in the reaction rate was observed in the selective catalytic reduction of NO by propene on alumina in a tubular fixed-bed reactor.

The selective catalytic reduction of nitrogen oxides to N₂ under conditions of net oxidation, an important process for depolluting combustion gases, is possible using ammonia as the reducing agent. Recently, hydrocarbons have been found effective as reducing agents using zeolite, alumina and other metal oxide-based catalysts.¹⁻⁶ Considerable effort is being made to find the most efficient catalyst under ordinary conditions. During our screening test of alumina for the

selective reduction of NO by propene, we observed distinct, periodical self-oscillating behaviour in the reaction rate in a tubular fixed-bed reactor.

Commercially available γ -alumina pellets were crushed into a 60–150 mesh powder, 1 g of which was packed between silica-fibre filters in a tubular quartz reactor (16 mm i.d.). The catalyst bed was about 10 mm in height. The reactor was heated with an electric furnace controlled with a non-linear

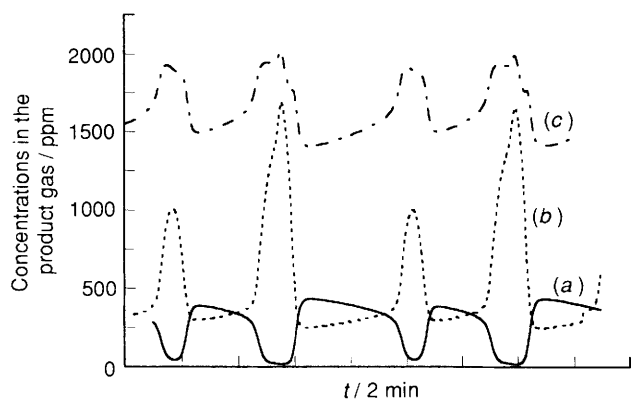


Fig. 1 Variation in (a) NO_x , (b) CO_2 and (c) CO concentrations in the product gas observed in the selective catalytic reduction of NO by propene with a tubular fixed-bed reactor. Catalyst, 1 g γ -alumina in 60–150 mesh. Reactant, 1300 ppm NO , 5% O_2 and 883 ppm propene diluted in He at atmospheric pressure. Flow rate, 160 ml min^{-1} , T , 502°C .

feedback system, whose monitoring thermocouple was attached to the furnace. With this arrangement, there was no possibility for the temperature controlling system to provoke artificial instability by interference with the reaction inside the reactor. The temperature variation of the furnace was below the resolution of the measurement (0.1°C). Another sheath thermocouple (1 mm in outer diameter) was inserted in the middle of the catalyst bed to monitor the catalyst temperature. A reactant mixture of NO , O_2 and propene diluted in He was prepared from standard gases. The concentrations of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$), CO_2 and CO in the product were analysed continuously; N_2 was analysed intermittently with gas chromatography.

Among ten kinds of alumina tested, only one species having the highest efficiency for NO conversion caused oscillatory behaviour, *i.e.*, periodical variation in the concentrations of NO_x , CO_2 and CO in the product gas, as an example shown in Fig. 1. The temperature inside the catalyst bed varied with the oscillation, being maximal when CO_2 formation was maximal, but its amplitude was rather slight, only $2\text{--}3^\circ\text{C}$ for the above case. Oscillation occurred under limited concentration and temperature conditions, the latter being between 490 and 530°C , where NO conversions were maximal. Of the products, NO_x pattern appeared most simple, being mostly a repetition of a singular peak or alternative double peaks.

Fig. 2 shows maximal and minimal conversions of NO during oscillation along with other data without oscillation, as a function of NO concentration in the reactant. At low NO concentrations up to 900 ppm, the reaction system was stable and the NO conversion rate, *i.e.*, the slope of the dotted line in Fig. 2 was close to unity. At NO concentrations from 900 to 1400 ppm, oscillation occurred. The lower limit of the NO concentration at oscillation corresponded to propene concentration in the reactant. At NO concentrations higher than 1500 ppm, the reaction system became again stable. Under all the oscillation conditions, the amplitude of NO conversion ranged from *ca.* 880 ppm to almost complete consumption. These results suggest that there are at least two paths in the NO reduction process, one very fast in which NO reacts with propene directly and another which exhibits oscillation phenomena.

To measure carbon and nitrogen balance in an oscillation cycle, another fixed catalyst bed was prepared, in which a Pt/alumina layer was placed downstream of the alumina layer. Total carbon emission was measured from CO_2 concentration in the product, since all carbon-containing species were to be converted to CO_2 by Pt. Total nitrogen emission was estimated from NO_x and N_2 emissions, since under the

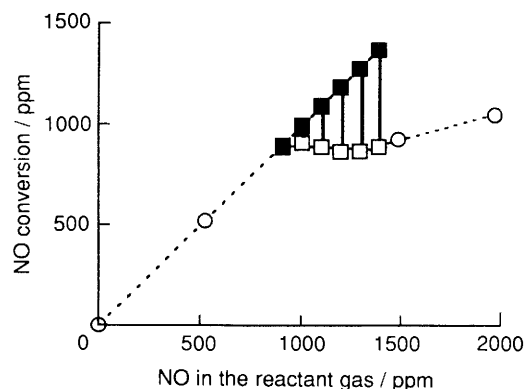


Fig. 2 Maximal and minimal conversions of NO at oscillations along with other data under non-oscillating conditions, as a function of NO concentration in the reactant. The reaction conditions are the same as in Fig. 1 except that NO concentration was varied. ■ and □ are maximal and minimal points at oscillation, respectively. ○ are points for non-oscillation.

conditions used, reacted NO yielded only N_2 . Under an oscillating condition having NO_x emission ranging from *ca.* 20 to 300 ppm, the total nitrogen emission was almost constant, indicating that there was no accumulation and removal for nitrogen. By contrast, the CO_2 concentration varied drastically from 2490 to 3110 ppm in an oscillating cycle. It is obvious that certain carbonaceous deposits accumulate on and are removed from the alumina. The deposits were confirmed mostly not to be nitrogen-containing substances.

Carbonaceous deposits were present also under conditions without oscillation. In Fig. 2, the deposits varied from negligible to appreciable amounts by changing NO concentration from lower to higher than the oscillating region, and when NO was cut off after the deposits had accumulated, a substantial amount of CO_2 was temporarily emitted. NO thus promotes deposits accumulation by suppressing their oxidation.

The mechanism of the selective reduction has not been well understood. We previously reported that carbonaceous deposits accumulate on alumina surface during the reaction and reduce NO while being oxidized.⁷ The present study has confirmed that the carbonaceous deposits are involved in the reaction and the oscillating behaviour is due to their temporal accumulation and removal whose rate is controlled by NO . The reaction inhibiting effect of NO can be attributed to its nature as a radical and simultaneously an efficient radical scavenger.⁸ NO may terminate radical reactions considered to be involved in the deposit oxidation. Although further experiments and mathematical consideration will be necessary for the quantitative explanation for the occurrence and pattern observed, the mechanism of oscillation may be outlined as follows: Fast reaction takes place between NO and propene, resulting in NO conversion and the deposit accumulation. Under moderately abundant NO conditions, excess NO further reacts with the deposits, first slowly in radical deficient circumstances. As the deposits increase, NO consumption increases and radical reactions begin to occur, causing acceleration of deposit oxidation and simultaneous NO reduction to negligible with the synergetic effect of rise in temperature, and eventually the deposits are mostly removed.

Oscillation phenomena in heterogeneous catalytic reactions have long been problems in chemical kinetics^{9,10} and also have become subjects relating to non-equilibrium thermodynamics.¹¹ Considerable oscillating behaviour has been reported in broad systems. However, as far as a tubular fixed-bed reactor is concerned,^{12,13} heat has been exclusively the cause for rate acceleration. The rather slight variation in the temperature of the catalyst indicates that in the present reaction system

chemical factors, *i.e.*, the accumulation of carbonaceous deposits and reaction inhibition by NO, are the main cause for oscillation.

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