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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.

Keywords: NO_x; Octane; Ag/alumina

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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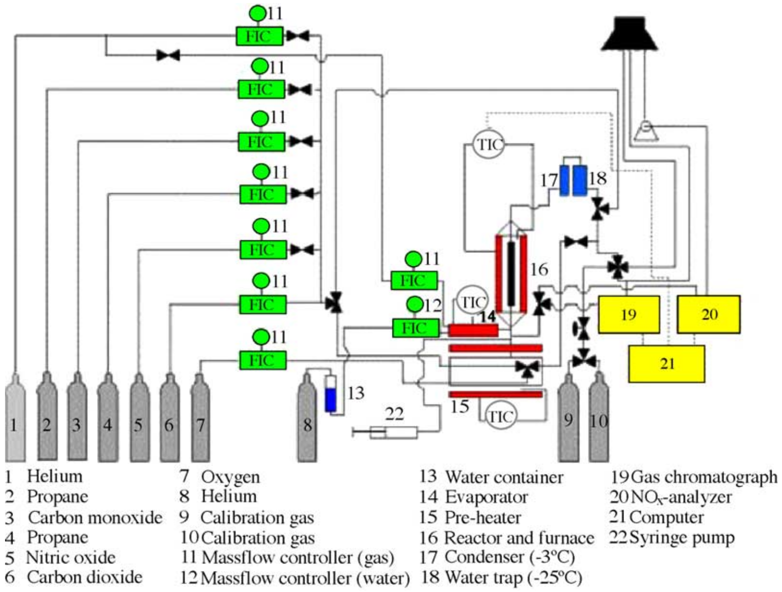

Fig. 1. The microreactor system used for activity testing of catalyst samples.

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:

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

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

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

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \tag{4}$$

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

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

$$\begin{gathered} r_1 = k_1 x_{NO}^{m_1} x_{OCT}^{n_1} x_{O_2}^{o_1}, \qquad r_2 = k_2 x_{OCT}^{n_2} x_{O_2}^{o_2}, \\ r_3 = k_3 x_{OCT}^{n_3} x_{O_2}^{o_3}, \qquad r_4 = k_4 x_{CO}, \\ r_5 = k_5 x_{NO}^{m_2} x_{OCT}^{n_4} x_{O_2}^{o_4} \end{gathered} \tag{6}$$

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

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

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 rate 10 °C/min) and cooling it back to 150 °C in the same mixture.

2.1. Diffusion

Special experiments were carried out to ensure that the kinetics is measured in the absence of external and internal diffusion limitations. The internal mass-transfer resistance over the Ag/alumina was tested using particle sizes of 1.0–1.41, 0.250–0.500 and 0.09–0.180 mm with equal mass of the bed. The external mass-transfer experiments were carried out using three different lengths of the Ag/alumina bed keeping the GHSV constant: 0.35, 0.7 and 1.05 cm. The results confirmed, that there are no internal and external mass-transfer limitations over the Ag/alumina catalyst.

3. Results and discussion

3.1. Results from the activity tests

The results from the activity tests over the alumina supported silver catalyst for reduction of NO_x under excess of oxygen with varying NO, octane and O_2 concentrations are presented in Figs. 2 and 3. From the results it can be concluded that the overall reduction rate over the catalyst is strongly dependent on the amount of hydrocarbon used. When the concentration of hydrocarbon, as HC_1, was increased from 1500 to 3000 ppm, keeping the $HC_1/NO = 6$ ratio constant, the maximum NO_x to N_2 activity was almost doubled (Fig. 2). A minimum of 2100 ppm of HC_1 (octane) was required to obtain a reasonably high NO_x conversion.

Further evidence that octane concentration strongly influences on the reaction rate was obtained, when the HC_1/NO ratio was varied between 1 and 6 by keeping the NO at constant level on 500 ppm and changing the amount of octane in the feed (Fig. 3). When the HC_1/NO ratio was kept at 1, no reduction of NO was obtained over the used temperature range. After that, the amount of hydrocarbon was increased stepwise and higher activity patterns were recorded corresponding to the amount of octane added. The results presented in Figs. 2 and 3 clearly prove that the reduction rate of NO is not limited only by the octane concentration but also by the ratio between NO and octane over the Ag/alumina catalyst.

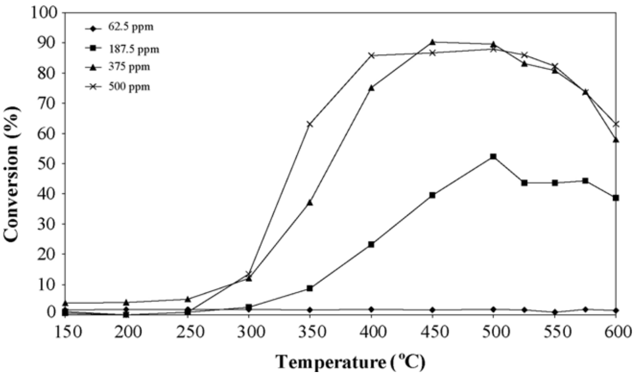

Fig. 3. Activity test over Ag/alumina, constant NO = 500 ppm and varying HC_1 (octane) concentration between 62.5 and 500 ppm, GHSV = 60,000 h^{-1}.

When the NO to N_2 conversion versus octane concentration was plotted separately at different temperatures, an interesting observation was made (Fig. 4). At low temperatures (300–350 °C) the concentration of hydrocarbon strongly affects the reduction rate over the catalyst in the concentration range 135–500 ppm. However, at higher temperatures (400–550 °C) the beneficial effect of the concentration increase is limited to 135–375 ppm. This indicates that at low temperatures the catalyst is not able to produce the necessary amount of the active hydrocarbon species on the catalyst surface to react with NO to form N_2. Whether these species are some ad-species or active gas phase radicals generated by the surface is not clear yet, but at low temperatures their concentration seems to be too low, therefore limiting the reaction rate. Thus by increasing the concentration of the hydrocarbon in the feed activity is increased over the whole test range. On the other hand, at high temperatures, introducing more than 350 ppm hydrocarbons into the gas mixture, activity cannot be increased indicating zero order in octane.

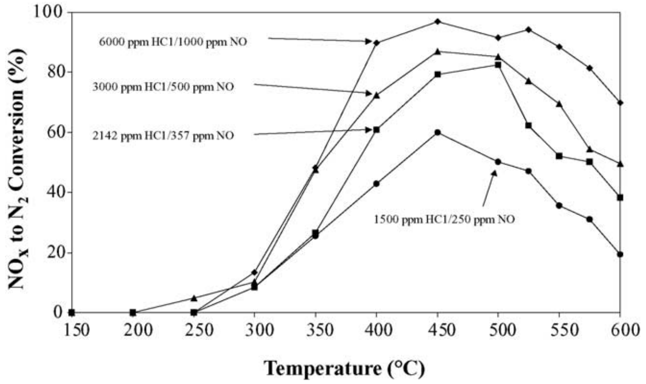

Fig. 2. Activity test over Ag/alumina with varying concentrations of octane and NO but keeping HC_1/NO ratio equal to 6 and GHSV = 60,000 h^{-1}.

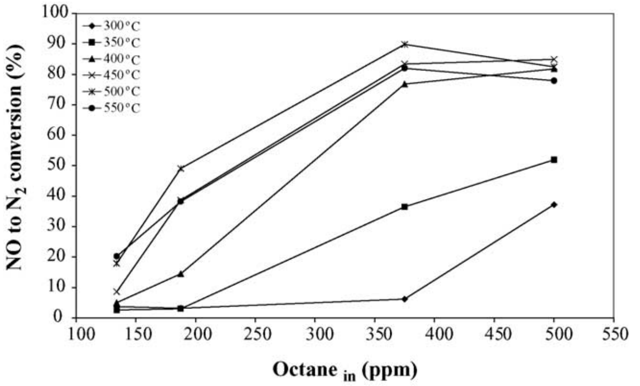

Fig. 4. Influence of HC_1-concentration on the NO to N_2 reduction at different temperatures, $HC_1/NO = 6$ and GHSV 60,000 h^{-1}.

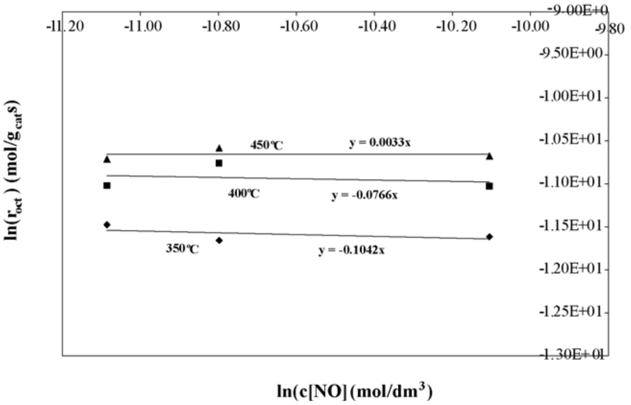

Fig. 5. Plot of $\ln(r_{oct})$ vs. ln[NO] at different temperatures. (r_{oct}) = rate of octane, [NO] = 1.53E−5, 2.04E−5 and 4.08E−5 mol/dm^3. GHSV = 60,000 h^{-1}.

To perform a kinetic study and use it as a tool to determine the mechanistic model for NO_x to N_2 reduction under lean conditions over the highly active Ag/alumina catalyst, information from such experiments as presented in Figs. 2 and 3 is crucial. However, before the final reaction mechanism can be derived, the behaviour of the different species involving the reaction should be known. Therefore it is very useful to study phenomenological kinetics by doing isothermal experiments systematically by varying partial pressures of reagents. Some of the results are presented in Figs. 4–6.

In Fig. 5 reaction orders for octane combustion as a function of NO concentration are presented at 350, 400 and 450 °C. As it can be seen from the figure, oxidation of octane is almost zero order in the concentration of NO (375, 500, 1000 ppm) in the gas mixture. Thus it can be concluded that the hydrocarbon combustion is not dependent on the NO concentration. However, results from the separate activity tests, which were made to study the impact of oxygen, originating from NO, on octane oxidation over the catalyst (described in Section 2) clearly show (Fig. 6) that in the presence of NO, octane oxidation to CO_2 is more efficient. It indicates that even if the concentration of NO is not substantial, it affects very strongly hydrocarbon combustion. As shown above at low temperatures hydrocarbon concentration (coverage) is limiting the overall reaction rate. Fig. 7 depicts the NO to N_2 conversion versus octane to CO_2 conversion, showing a very clear linear dependence. The mechanistic explanation for it is, that both reaction routes (e.g. octane combustion to CO_2 and NO reduction to N_2) have a common step.

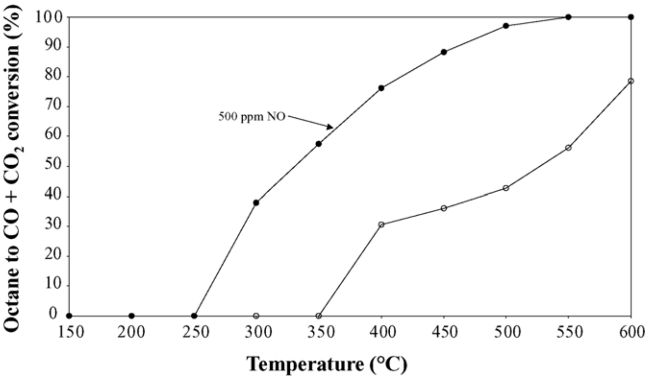

Fig. 6. Octane oxidation in the absence and presence (500 ppm) of NO. HC_1/NO = 6 and GHSV 60,000 h^{-1}.

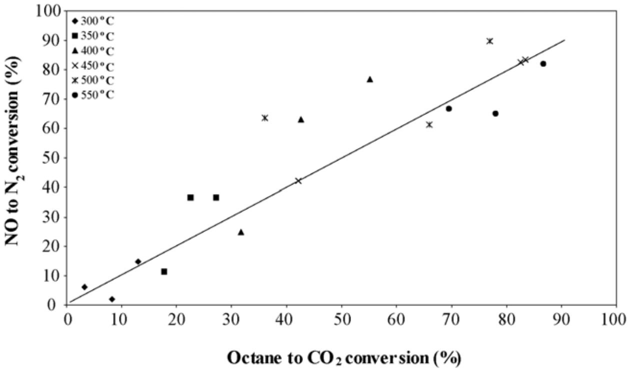

Fig. 7. Octane to CO_2 vs. NO to N_2 conversion (keeping octane = 375 ppm, O_2 = 6 vol.% and NO = 375–1000 ppm).

3.2. Kinetics

The rate constants and reaction orders of NO, O_2 and octane, received from the mathematical parameter estimation at different (350 and 400 °C) temperatures are presented in Table 1. In this temperature range the activity over the catalyst increases from moderate (ca. 50%) to highly active (ca. 90%). Reaction order close to zero in NO was calculated between 300 and 500 °C and at the final temperature of 550 °C it increased to 0.14, indicating that the reaction rate is almost independent of the concentration of NO. The strong dependence of the NO_x conversion on the hydrocarbon concentration is clearly seen, as the order varies from 1.7 at low temperatures to 0.8 at the highest temperature. In oxygen,

Table 1
Reaction orders of NO, octane and O_2 at different temperatures

Rate constant and reaction orders	350 °C	400 °C
k_1	476.20	512.92
NO	0.09	0.01
Octane	1.67	1.42
O_2	0.83	1.18
k_2	155.99	489.53
Octane	1.31	1.76
O_2	1.41	0.93
k_3	33.70	12.08
Octane	1.23	1.29
O_2	1.76	1.10
k_4	0.3167	0.3126
CO	1.10	1.10
k_5	328.01	1840.30
NO	0.97	1.03
Octane	2.58	0.79
O_2	1.11	1.58

on the other hand, the reaction order is close to 1 over the whole temperature range. Values for reaction (4) should be taken with care, as the rate is low, parameter estimation can be inaccurate.

Experimental data suggests that octane reactivity dominates the rate of NO reduction. The mechanistic explanation for observed kinetics could be that in the rate-determining step octane reacts with the aid of predominantly oxygen over the Ag/alumina catalyst to form an oxygenated hydrocarbon (via H-abstraction). Although the influence of NO is not manifested kinetically, meaning that the coverage of adsorbed NO or nitrates (nitrites) is small, the presence of NO is vital to create active intermediates for the reactions to proceed, as octane does not transform totally in the absence of NO in the gas feed. An alternative explanation, which could account for zero order in NO is that the surface is almost completely covered by NO*x* containing species.

4. Reaction mechanism

Shimizu et al. [6] have proposed a reaction mechanism for the HC-SCR of NO_x over Ag/alumina catalyst using *n*-hexane. According to Shimizu et al. the first step would involve partial oxidation of the hydrocarbon with O_2 on the catalyst surface, forming pre-oxidised hydrocarbon (possibly acetate). Parallel to the hydrocarbon oxidation, NO would react with O_2 forming ad-nitrate species. In the second step the adsorbed acetate species, which act as surface reductants, would then react further with adsorbed nitrates, finally forming N_2. The strong uniformity in the surface acetate consumption rate and in the NO reduction rate reported by Shimizu et al. [6] supported their conclusions. Eränen et al. [2] have shown that the NO_x to N_2 activity over the Ag/alumina catalyst in *n*-octane SCR was strongly affected by replacing *n*-octane by octanol and octanal (e.g. pre-oxidised hydrocarbon). In further FT-IR experiments it was shown [2] that the nitrate coverage on the surface was not affected by introducing *n*-octane in the feed unless oxygen was present. This observation is supported by Shimizu et al. [6], as they reported that acetate (e.g. pre-oxidised hydrocarbon) does not react with NO or O_2 but reacts preferentially with $NO + O_2$ (e.g. nitrates). Although, no formation of *iso*-cyanate and cyanide species, proposed as intermediates [6–13], were detected by Eränen et al. [2] in the absence of NO, it is reasonable to assume that *n*-hexane SCR is mechanistically similar to *n*-octane SCR.

In HC-SCR by *n*-octane it is realistic to assume, that in the first step hydrocarbon pre-oxidises to oxygenates (e.g. aldehydes, alcohols) [2]. Meunier et al. [12] have shown that SCR over Ag/alumina is not significantly active for NO(g) to NO_2(g). Therefore it is likely that ad-nitrates, proposed as a key intermediates in the literature [6–8], are formed from the thermodynamically more reactive NO_2(g) than from NO(g) on the catalyst surface. Because Eränen et al. [2] could not detect any ad-*iso*-cyanate or ad-cyanide species unless NO was presence in the gas flow, it is presumable, that in the second step the adsorbed oxidised hydrocarbons react with either NO(g) through the Rideal–Eley mechanism to form ad-nitro-organic species or through a reaction between the oxidised hydrocarbons and adsorbed NO. The latter reaction seems to be more realistic, as activation energy for adsorbed species is significantly lower than for un-adsorbed species. Also other organic-nitrogen species, such as nitro groups ($R{-}NO_2$(g) or ads), which are reduced by adsorbed hydrocarbon further to amine, amide, *iso*-cyanate or nitrile-species (e.g. $R{-}NH_2/H_3$, R–CONH, R–NCO, R–CN) have been proposed in the literature [12,13]. These species can be considered as key intermediates in HC-SCR as, according to classical organic chemistry, they can easily be reduced to N_2. As shown in Fig. 7, NO reduction to N_2 goes hand in hand CO_2 formation. From the obtained activity test results it is known, that the parallel CO formation begins at the same temperature as the N_2 concentration becomes detectable.

The possible participation of homogeneous reactions must also be considered [2], especially at higher temperatures and bearing in mind that NO and NO_2 can be considered as radicals.

Based on the kinetic data obtained in the present study and the literature data, a tentative reaction mechanism could be proposed:

$$O_2 + * \rightarrow O_2^*$$

$$O_2^* + * \rightarrow 2O^*$$

$$C_8H_{18} + O^* + O^* \rightarrow C_8H_{17}^* + OH^*$$

$$C_8H_{17}^* + NO \rightarrow \text{(fast?)}\, C_8H_{17}NO^* \rightarrow \cdots \rightarrow N_2 + CO_2 + H_2O$$

$$C_8H_{17}^* \rightarrow C_8H_{17}^{\bullet}\ \text{(desorption of radicals to gas-phase)}$$

$$C_8H_{17}^* + O_2 \rightarrow \cdots \rightarrow CO_2 + H_2O$$

This mechanism assumes dissociative chemisorption of alkane involving the breaking of a C–H bond by abstraction of hydrocarbon atom by adsorbed oxygen, similar to suggestions of Burch et al. [3]. These surface species are either oxidised to CO_2 on the catalyst surface, escape to the gas-phase or react with nitrogen containing species finally leading to N_2. This simplified reaction mechanism qualitatively explains kinetic regularities reported above. However, elucidation of reaction mechanism requires rigorous numerical data fitting based on various mechanistic models, which is currently in progress.

5. Conclusions

Kinetics of continuous NO reduction by octane in excess oxygen was investigated over a 2 wt.% Ag/alumina catalyst in the temperature range of 300–550 °C. The reaction order in NO was equal to zero, indicating that the rate of NO reduction in the excess of oxygen was independent on NO partial pressure. At the same time reaction orders in octane clearly exceed unity. Reaction order in oxygen close to 1 was recorded over the measured temperature range. The mechanism of SCR by *n*-octane on Ag/alumina is proposed. At low temperatures strongly adsorbed nitrates seems to inhibit the reduction reaction.

Acknowledgements

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