Kinetic behaviour of HC-SCR over Ag/alumina catalyst using a model paraffinic second generation biodiesel compound

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ABSTRACT

The effect of longer paraffins on the mechanism of the HC-SCR reaction over a 1.91 wt.% Ag/alumina catalyst was investigated by kinetic studies. Hexadecane (C$_{16}$H$_{34}$) was chosen as a model compound as it is also a representative molecule for a second generation biodiesel consisting of only long-chain paraffins. The kinetic behaviour of the catalytic reduction of NO$_x$ was examined at steady-state conditions in the temperature range 250–550 °C (50 °C ramping) and by using the following gas concentrations: P_{NO} = 100, 250, 500, 750 or 1000 ppm, $P_{hexadecane}$ = 31, 94, 188, 281 or 375 ppm and P_{O_2} = 1.5, 3, 4.5, 6 or 9 vol.%. Results showed that in the temperature range 250–425 °C high hexadecane concentration had an inhibiting effect on the NO reduction. At temperatures above 350 °C the apparent reaction orders for hexadecane with respect to hexadecane increased to close or above 1. Reaction orders towards NO were close to 0.55 indicating that NO adsorption on the catalyst surface is stronger than hexadecane adsorption. Based on the experimental data it is proposed that small clusters alone cannot be the active sites for HC-SCR over Ag/Al$_2$O$_3$ but the important requirement for high activity over the catalyst is the local concentrations of hydrocarbon and NO on the interface of silver and the support.

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1. Introduction

The development of catalytic materials to reduce nitrogen oxides (NO$_x$) under excess oxygen has been intensive during the past decades and several catalytic techniques, such as selective catalytic reduction with ammonia or hydrocarbons (NH$_3$-SCR, HC-SCR) and NO$_x$-storage have shown promising results [1–5]. However, none of these techniques can yet provide a fully satisfactory package to meet the new strict emission standards for NO$_x$ reduction from diesel vehicles. Especially reduction activity at low temperatures (below 250 °C) and in fast transient conditions, resistance against catalyst deactivation and cost effectiveness need to be improved.

Among the different NO$_x$ reduction techniques developed for automotive applications selective catalytic reduction with hydrocarbons (HC-SCR) offers a very simple solution compared to other techniques. Since the early work of Iwamoto [1] and Held [2] on the hydrocarbon selective catalytic reduction, several catalytic formulations have been suggested [6–27]. Among the tested materials, silver supported on alumina (Ag/Al$_2$O$_3$) has been reported as one of the most promising candidate. Moreover, it has been proven in laboratory, engine bench and full-scale vehicle

tests with model compounds and special (MK1) diesel fuels to be a very active catalyst [8,9,12,17]. However, the high activity is mainly connected to the use of model compounds or extra pure commercial diesel and elevated temperatures (>300 °C). Especially the requirements of high temperature represent a severe drawback for the system to be used in combination with modern diesel engines having exhaust gas temperature of 200 °C or less for most of the time during the NEDC test [9].

An additional challenge for HC-SCR system is the gradual increase in the use of bio-based fuels, since especially over the silver system the reduction activity is strongly connected to the nature of the reducing agent [11–15,21,22]. Fuels derived from triglycerides can be used as substitutes for fossil based diesel fuels directly and thus fatty acid methyl and ethyl esters derived via transesterification of triglycerides have attracted most attention [23]. In addition, the catalyst activity in HC-SCR is related to the sulphur and aromatic content of the fuel, poisoning or blocking the active sites. Thus, biofuels may here offer a solution to improved low temperature HC-SCR activity, as they do not contain sulphur or aromatics.

In this paper a kinetic study of C$_{16}$H$_{34}$-SCR of NO$_x$ over Ag/Al$_2$O$_3$ catalyst under lean conditions is presented. Emphasis has been put on experiments with simulated diesel exhaust mixtures, where the concentrations of the reactants (NO, C$_{16}$H$_{34}$ and O$_2$) are varied at steady-state conditions. Based on the experimental results the kinetic behaviour for NO reduction and hydrocarbon oxidation at

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different temperature and concentration regions as well as apparent reaction orders are reported in this paper. In addition, the kinetic behaviour of $C_{16}H_{34}$-SCR is compared to our previous work with C_8H_{18}-SCR [26] and an explanation for the different behaviour between the two compounds is proposed. Hexadecane is also an interesting substance as it can be considered as a representative model compound for the fully formulated second generation biodiesel produced by the Finnish oil company Neste Oil. In this process, called NextBTL, high quality biodiesel consisting of only higher paraffins, mainly in the C_{15}–C_{18} range, are produced. Traditionally commercial diesel fuel is not preferred in mechanistic studies due to its complex composition including impurities which might lead to incorrect interpretation of the results, especially concerning the reaction mechanism. However, biodiesel produced with the NextBTL process is already in test use in the local traffic in the capital city region of Finland and moreover it is used, after hydrotreating and isomerisation of bio-based oils as such, not only as a blend. Thus the results from the laboratory studies with hexadecane are of high relevance and can be used for catalyst development per se. Moreover, the known composition of the used fuel (NextBTL biodiesel) could offer possibilities for precise and optimized hydrocarbon feeding system in the exhaust aftertreatment system of a vehicle.

In addition, the relevance of kinetic models in the case of HC-SCR is discussed. For catalytic processes, where the knowledge of reaction mechanism and active catalytic sites is limited, the development of a kinetic model can be challenging. This is rather because of the very complex reaction mechanism of HC-SCR where the activity depends on the nature, spatial arrangement and functional groups of the reducing agent, but not a consequence of insufficient experimental work. Therefore, creating a proper kinetic model is a very difficult task for HC-SCR over Ag/Al_2O_3 but at the same time a global model able to predict the catalytic performance under the operational conditions is of great importance.

2. Experimental

The catalyst used in this study was a 1.91 wt.% Ag/alumina catalyst prepared by impregnation of a commercial alumina support (LaRoche Industries Inc.) with a 0.022 M silver nitrate solution followed by drying and calcination, resulting in a B.E.T. surface area of approximately 190 m^2/g of the final catalyst [20]. The crushed and sieved Ag/alumina (0.2 g, 250–500 μm) catalyst was tested in a fixed bed quartz reactor inserted in an oven equipped with a temperature controller. Special experiments according to [26] were carried out to ensure that the kinetics is measured in the absence of external and internal diffusion limitations. A temperature range of 250–550 °C with 50 °C ramping and sampling at steady-state conditions with GHSV = 60,000 or 120,000 h^{-1} (residence time 0.034 or 0.017 s) and total flow rate of 550 ml/min were applied for the catalytic activity tests.

To determine the effect of NO, $C_{16}H_{34}$ and O_2 concentrations on the NO to N_2 and $C_{16}H_{34}$ to CO + CO_2 conversions, the experiments were carried out by varying the concentration of one reactant at a time in the feed gas mixture while the concentrations of others were kept constant. The following concentrations were used: 100, 250, 500, 750 and 1000 ppm NO, 31, 94, 187, 281 and 375 ppm hexadecane, 1.5, 3, 4.5, 6 and 9 vol.% O_2 and He as a balance. The used hydrocarbon concentrations correspond to HC_1/NO ratios equal to 1, 3, 6, 9 and 12. The concentration of H_2O was kept constant at 12 vol.% in all tests using a syringe pump (IVAC P6000 Medical Systems) combined to a controlled evaporator mixer (Bronkhorst HI-TEC). 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 hexadecane 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 (both NO to N_2 and hexadecane to CO + CO_2) was analyzed 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 acidity of the catalyst was measured by infrared spectro-scopy (ATI Mattson FTIR) by using pyridine ($\geq$99.5%, a.r.) as a probe molecule for qualitative and quantitative determination of both Brønsted and Lewis acid sites. The catalyst was pressed into a thin self-supported wafer. Pyridine was first adsorbed for 30 min at 100 °C and then desorbed by evacuation at different temperatures (250, 350 and 450 °C) with subsequent measurements to obtain a distribution of acid site strengths. All spectra were recorded at 100 °C with a spectral resolution of 2 cm^{-1}. Spectral bands at 1545 and 1450 cm^{-1}, respectively, were used to identify Brønsted and Lewis acid sites. The amounts of acid sites were calculated from the intensities of corresponding spectral bands by using molar extinction coefficients reported by Emeis [28].

3. Results and discussion

3.1. Results from activity tests

The NO to N_2 conversion in $C_{16}H_{34}$-SCR over a 1.91 wt.% Ag/alumina catalyst as a function of temperature is shown in Fig. 1 using GHSV = 60,000 h^{-1}. Previously [26] it has been demonstrated that NO reduction over a similar catalyst was optimized at HC_1/NO ratio equal to 6 when octane was used as the reducing agent. Therefore, the same ratio was chosen for the first screening of the catalytic activity with hexadecane. Moreover, for C_8H_{18}-SCR it has been shown that a clear beneficial effect on the NO reduction is achieved by increasing the hydrocarbon concentration until a saturation point was reached [26]. As the activities in C_8H_{18}- and $C_{16}H_{34}$-SCR are compared (Fig. 1) it can be seen that the reduction activity in the temperature range 150–350 °C is considerably higher with hexadecane as a reducing agent. However, above 350 °C the situation is quite the opposite; in octane-SCR the conversion of NO to N_2 continues to increase until reaching the maximum, approximately 95%, at 450 °C. Thereafter, the reduction activity slightly decreases along with the increasing temperature, which is due to competing total oxidation of octane leading to the lack of sufficient amount of reducing agent for SCR reaction.

As the high temperature (350–600 °C) NO conversion in $C_{16}H_{34}$-SCR only reaches roughly half of that in C_8H_{18}-SCR the result clearly deviates of those earlier reported for HC-SCR over Ag/
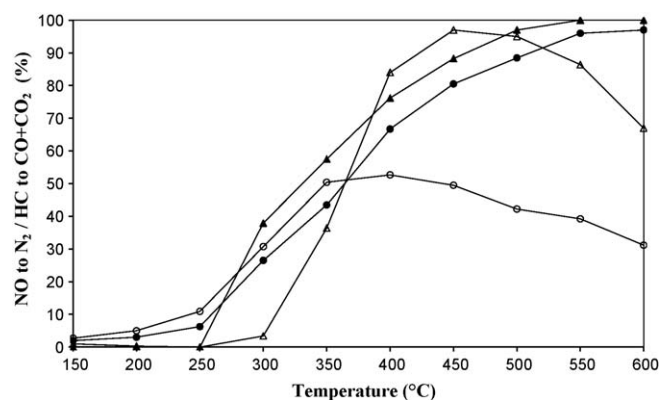

Fig. 1. NO to N_2 ($\triangle$, $\bigcirc$) and hydrocarbon to CO + CO_2 ($\blacktriangle$, $\bullet$) conversion over a 1.91 Ag/Al_2O_3 catalyst with 375 ppm n-C_8H_{18} ($\triangle$, $\blacktriangle$) or 188 ppm n-$C_{16}H_{34}$ ($\bigcirc$, $\bullet$), HC_1/NO = 6 in both cases. Gas flow: 500 ppm NO, 375 ppm n-C_8H_{18} or 188 ppm n-$C_{16}H_{34}$, 6 vol.% O_2, 12 vol.% H_2O and He balance. GHSV = 60,000 h^{-1}.