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Microreactors for environmental catalysis—Selective catalytic reduction of NO_X with hydrocarbons over a Ag/alumina catalyst

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Abstract

Microstructured-etched plates previously coated with Al_2O_3, were further impregnated with Ag. The plates were characterized by means of laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) and scanning electron microscopy (SEM). The silver loading on the alumina-coated plates was determined to be between 0.8 and 1.6% and the distribution along the microchannels was proved to be almost uniform. The microplates were tested in a microreaction chamber for selective catalytic reduction of NO using different hydrocarbons (HC-SCR). A clear relationship between the number of carbon atoms in the hydrocarbon chain and the NO reduction was found. The results are compared to those obtained in minireactors under similar reaction conditions. The outcome indicates that microreactors are a useful, fast and effective way for studying selective catalytic reduction of NO with hydrocarbons.

Keywords: Microreactor; NO_X reduction; Ag/Al_2O_3; HC-SCR; Impregnation

1. Introduction

Global climate warming has become an issue of tremendous importance nowadays. CO_2 is the main component that produces the greenhouse effect leading to the increase of the temperature in our planet. Referring to the Kyoto protocol, it is necessary to diminish carbon dioxide emissions from vehicles. Hence, new technologies have appeared during the last years, i.e., lean burn engines, which operate under a large excess of oxygen. These engines are able to reduce the fuel consumption, consequently the CO_2 formation. The main problem arises with the NO_X emissions. Due to the excess of oxygen present in the exhaust and to the hydrothermal conditions needed (high content of H_2O, i.e., up to 12 vol.%), the NO_X cannot be removed by conventional three-way catalysts. In this sense, the selective catalytic reduction using hydrocarbons (HC-SCR) is an attractive and effective way for depleting the NO_X emissions [1,2].

On the other hand, in the last two decades powerful processes have been developed for the fabrication of three-dimensional microdevices from a wide variety of materials based on electronic technologies. The advantages of microreactors have been previously demonstrated and have been found to be vast [3,4]. One of the main features of these devices is their high surface-to-volume ratio, which tends to be from 100 to 500 times higher compared to conventional laboratory vessels [5]. Moreover, the heat transfer in these devices has been determined to be very good. The high transfer ratio is very convenient in cases where highly exothermic or endothermic reactions occur. In the cases where a catalyst is present, an efficient heat transfer allows to exploit the full potential of the catalyst, avoiding hot spots as it was demonstrated in [6]. Higher reaction temperatures are permitted, leading to reduced reaction volumes and amounts of catalyst. This results in a reduction of the operation costs of the reactor, and in having smaller and lighter reaction devices. Delsman et al. [7] presented a comparison study between conventional fixed-bed and microreactor technology for a portable hydrogen production case. However, a more detailed economic analysis escapes from the scope of our predominantly exploratory paper.

In addition, because of the sizes of the microchannels, the amount of reagents employed for the catalytic testing tends to be much lower compared to the total quantity needed in conventional reactors, resulting in a significant improvement in safety while dealing with dangerous chemicals: using microreactors greatly reduces the hazardous potential associated with

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reactions that are highly exothermic or potentially explosive. This is a key issue in laboratory research and it is important to consider it when doing catalytic testing.

One of the challenges in microtechnology is to find suitable materials for manufacturing these devices. The aim is either to manufacture the plates with a catalytically active metal or to have a material that is able to be coated/impregnated with a catalyst. The latter option is scientifically far more interesting since it allows the coating/uncoating procedure to be repeated in the microchannels with an active mixture of interest (usually a combination of metal/support). Likewise, it gives more adaptability to the different chemical reaction systems. Furthermore, the wash-coating procedure is commonly used at industrial level, e.g., coating of monoliths. Hence, the coating and impregnation of the microplates is essentially an extension of this widely employed method.

In this study we have investigated the possibility of using microreactors in studying the NO_X conversion over Ag/Al_2O_3 catalyst by means of HC-SCR. The plates containing the microchannels previously coated with Al_2O_3 were successfully impregnated with Ag. Pulse experiments inside the microreactor were also carried out in order to determine the flow patterns inside the microchannels.

2. Experimental

The used microreactor was designed and built at the Institut für Mikrotechnik Mainz GmbH (IMM). It consists of a two-piece housing sealed with graphite gaskets. Fig. 1 presents a view of the bottom part of the housing where the mixing plates and the catalytic ones are positioned. Ten mixing plates stacked one above the other are placed alternating their position (so the two inlet mixture of gases can be mixed in the diffusion path between the mixing and the catalytic zones) followed by ten catalytic microplates. Fig. 2 shows the upper view of the reactor. As it can be seen, the reactor has integrated heating/cooling capabilities. Two inlets for the reactants and one outlet can be observed in the same figure.

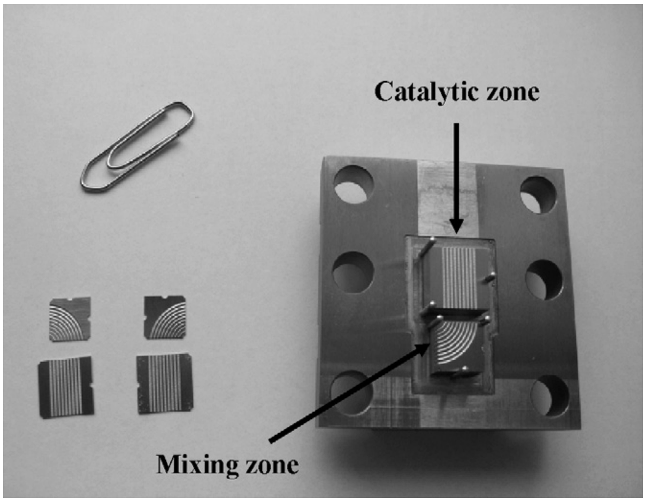

Fig. 1. Microreactor chamber (mixing and catalytic zones).

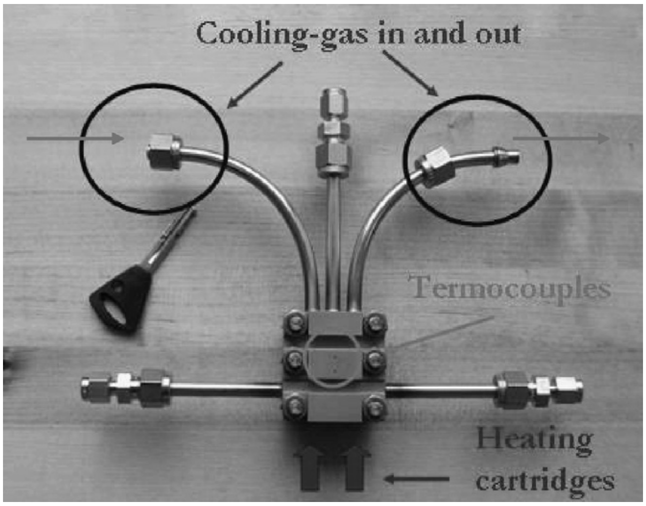

Fig. 2. Upper view of the microreactor.

It has been shown that Ag/alumina is a very active catalyst for continuous reduction of NO_X, where the metal loading in the catalyst is a key feature for the efficient conversion of NO_X [8,9].

For comparison purposes, a conventional tube reactor (internal diameter 10 mm) is referred to as minireactor, in order to distinguish it from the microreactor (diameter of the microchannels 0.44 mm). A scheme of the tubular minireactor with catalyst bed can be seen in Fig. 3. This reactor was previously applied extensively by our research group for HC-SCR of NO_X [1,2,8].

2.1. Impregnation of the plates with Ag

In order to use microstructures for catalytic testing, there is a need to introduce an active catalytic phase. Among the most common coating techniques one can find anodic oxidation, sol–gel method, chemical vapor deposition and washcoating [10]. The plates present in the catalytic zone (see Fig. 1) were previously coated with Al_2O_3 at IMM. The mass of alumina deposited on each plate was found to be 0.7 mg. Hence, the total mass of alumina in the reaction chamber was 7 mg. The specific surface area of the alumina was 70 m^2/g. The plates were further impregnated with silver at our laboratory by means of washcoating. The alumina-coated plates were introduced in a silver nitrate solution (0.022 M) at room temperature and were left during 24 h with mild stirring. After impregnation, the plates were dried during 3 h at 100 °C and further calcined for 3 h at 550 °C in air.

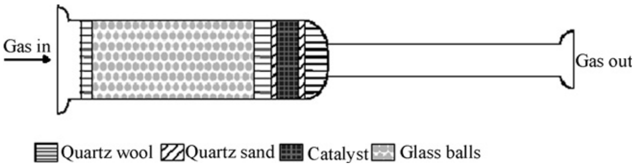

Fig. 3. Schematic view of the minireactor.

2.2. Experimental setup

2.2.1. Microreactor

The catalyst-coated plates were tested in the microreactor connected to a temperature controller and thermocouples for monitoring the temperature in the catalytic area. The experiments in the microreactors were carried out under atmospheric pressure at 150–500 °C. The catalyst-coated plates were always pretreated with a 6% O_2/Ar mixture at 150 °C for 30 min. The reaction mixture contained 0.5 vol.% NO, 6 vol.% O_2 and the corresponding hydrocarbon amount (the ratio between HC_1 and NO was kept to 5 in all the experiments, thus in the case of C_2H_4 the used amount was 1.25 vol.%, while in the cases of C_3H_8 and C_8H_{18} it was set to 0.83 and 0.3125 vol.%, respectively). Ar was used for balance. The total flow rate was set to 50 ml/min. All the gases were of high purity (AGA) and were introduced into the reactor by means of mass flow controllers (Brooks 5850). Oxygen was fed alone in one of the inlets to avoid the oxidation of NO before the catalytic zone. The reaction mixture was analyzed after the reactor through a capillary going to a quadrupole mass spectrometer (MS, Balzers Omnistar GSD 300 O) and the mass numbers of interest were monitored.

2.2.2. Flow experiments – microreactor

Pulses of argon were injected using nitrogen as a carrier gas. A schematic view of the system for the flow experiments is presented in Fig. 4. The gas feed of pure nitrogen was introduced in the two inlets (1) and (2). Ar was further introduced with a syringe in (4). The mass spectrometer was connected to the outlet of the reactor (3) in order to measure experimentally the residence time distribution (RTD) of Ar inside the microchannels. It was possible to connect the MS just after the injection of the pulse. In order to determine if the equipment line was accounting for some of the calculated dispersion, MS was also connected by-passing the reactor just after the injection point (dashed line in Figs. 4 and 5, point 5).

Since the inlet and outlet of the microreactor are in “mini” scale (points 1–3 in Figs. 4 and 5, Ø = 0.71 mm), a thinner tube (Ø = 0.5 mm) was introduced from the injector directly into the microreactor chamber. Fig. 5 represents this scheme.

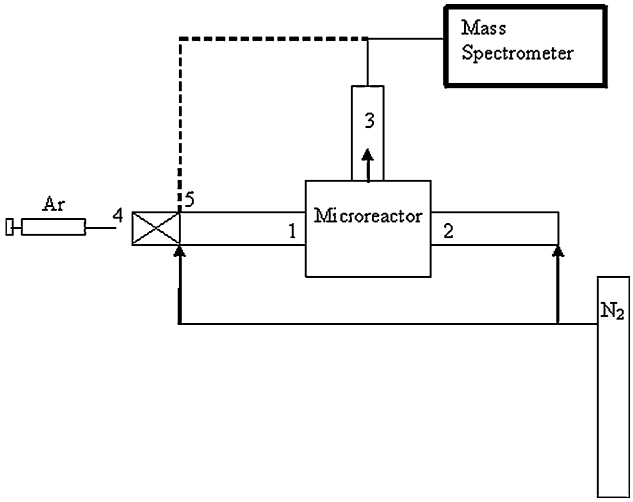

Fig. 4. Scheme of the used system for flow experiments. Large-diameter tube.

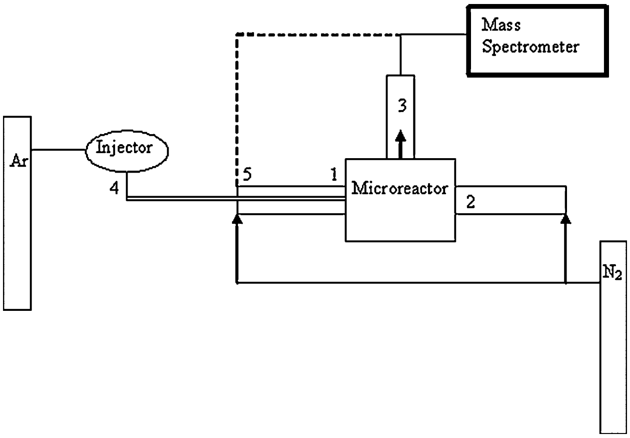

Fig. 5. Scheme of the used system for flow experiments. Small-diameter tube.

2.2.3. Minireactor

Ag/alumina catalyst was used for catalytic testing in the minireactor of a particle size of 250–500 μm. The reactor was placed in an oven equipped with a temperature controller. The experiments were carried out under atmospheric pressure at 150–500 °C. The total flow rate was set to 700 ml/min and the amount of catalyst placed in the bed was 0.1 g (in order to keep constant the ratio flow rate/mass of catalyst in both the mini- and microreactor systems). The reaction gases were analyzed with the mass spectrometer as well. All the other reaction conditions were kept the same as in the microreactor cases but the carrier gas was helium instead of argon. Additionally, a portion of the gas was measured by a chemiluminescence NO_X analyzer (API model 200AH). Fig. 6 shows the schematic of both the micro- and the minireactor systems with all their capabilities.

3. Results and discussion

3.1. Catalyst characterization

The metal uptake by the alumina in the plates was determined by LA-ICP-MS (New Wave Research UP-213 Laser Ablation system with PerkinElmer SCIEX ICP Mass Spectrometer Elam 6100 DRC Plus) measuring the silver content with respect to Al_2O_3. The results of these measurements are presented in Table 1 for two different silver nitrate concentrations.

Fig. 7 shows the LA-ICP-MS spectra of the plates after impregnation with the $AgNO_3$ solution. In the upper-right of the figure, the silver counts are presented alone.

Table 1
Silver concentration (with respect to alumina) in the plates measured by LA-ICP-MS at different silver nitrate concentrations

$AgNO_3$ concentration (M)	4.00×10^{-3}	2.20×10^{-2}
[Ag] (wt.%)	0.8–1	1–1.6

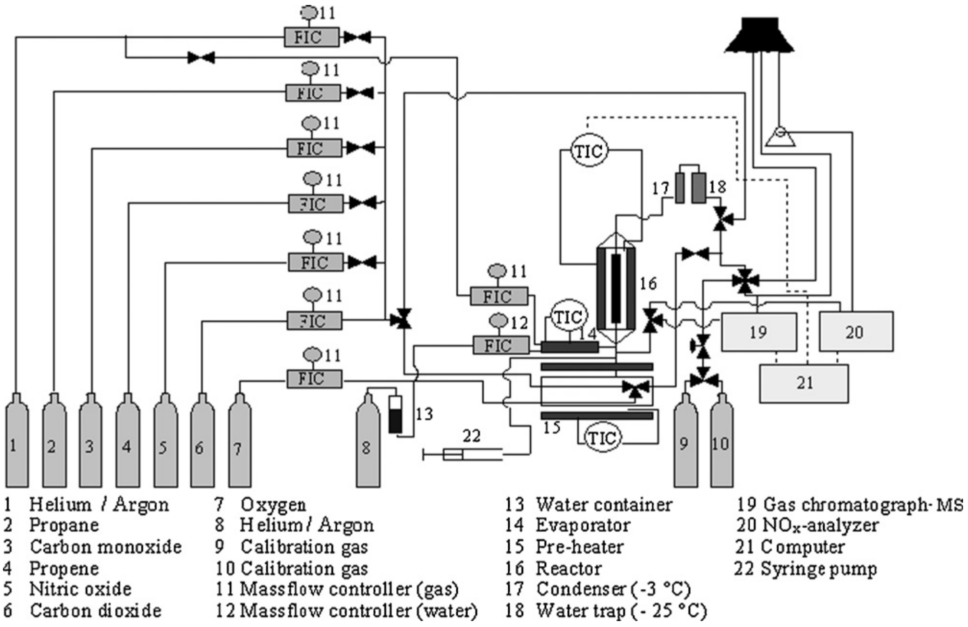

Fig. 6. Scheme of the used system.

The silver content was also investigated by SEM-EDXA (Cambridge Leica 360) yielding the same results as presented in Table 1 in the investigated areas. A SEM picture of the uncoated plates is shown in Fig. 8. Furthermore, Fig. 9 shows a comparison between uncoated (A), washcoated with alumina (B) and impregnated with Ag (C) plates.

In the minireactor system, the catalyst was prepared according to [8] from a 0.022 M Ag-nitrate solution with impregnation time of 24 h. The silver content obtained by this method was found to be close to 2 wt.%. A complete characterization of the catalyst can be found in [8]. Regarding the preparation of the catalyst, in the case of the minireactor, the effort should be put not only in the preparation of the catalysis as a powder, but also in impregnation of washcoated monolith. This is of utmost importance since exhaust gas catalysts require minimum pressure drop, which can be achieved using structural packings. In the case of the microreactor, the catalyst preparation consists of washcoating and impregnation of the plates. In principle, both procedures are not straightforward and require time and effort. According to the experience of our group in catalysis preparation, both routes are equally challenging.

3.2. Flow experiments

Fig. 10 shows the results of the calculated Peclet (*Pe*) number for the different systems (Figs. 4 and 5). The relationships given by Levenspiel [11] were used to calculate the dimensionless group characterizing the spreading rate for the microreactor. The data of the pulse response acquired by the MS was used for these purposes.

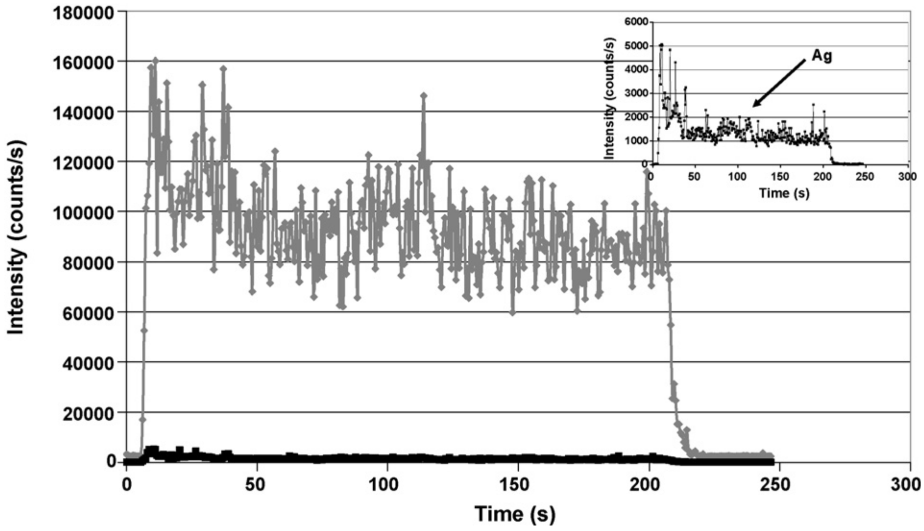

Fig. 7. LA-ICP-MS scan of Ag and Al in microchannels after impregnation with Ag. (♦—) Al counts, (■) Ag counts.

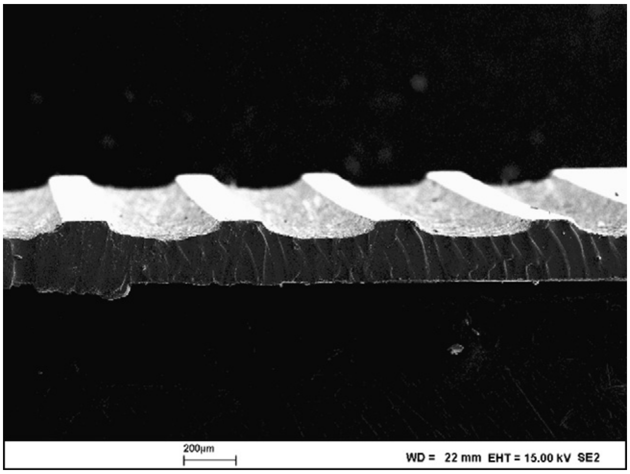

Fig. 8. Scanning electron microscope of an uncoated plate (50X).

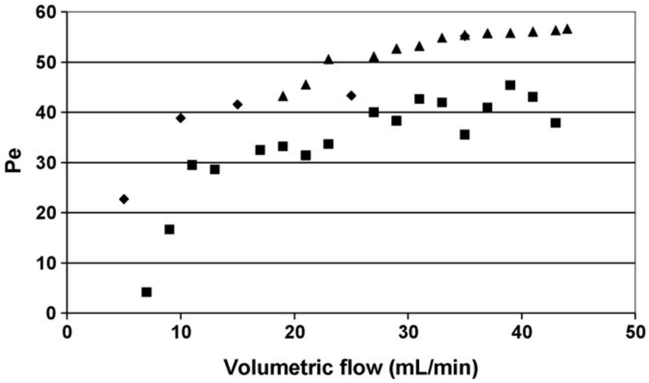

Fig. 10. *Pe* number inside the microchannels vs. volumetric flow. (■) Large diameter, Fig. 4; (◆) small diameter, Fig. 5; (▲) mass spectrometer alone.

The results indicate that in the case of the experiments with a small diameter tube, the Pe number became higher, approaching to ideal plug-flow. In general, the values were close for both cases with exception of very low volumetric flows (<10 mL/min). This indicated that the dispersion level inside the reactor was reduced by this method and the behavior was closer to an ideal plug-flow reactor. The pulses that were injected directly into the mass spectrometer (no microreactor in between – see Figs. 4 and 5, dashed lines) showed values of the *Pe* around 50. It was confirmed that the dispersion inside the microchannels is negligible (see Fig. 10).

3.3. Catalytic testing

Both mini- and microreactor were tested for catalytic activity under similar conditions. The ratio between the flow rate and the catalyst mass was kept alike for the two cases. Although the content of silver in the catalyst was not identical for the micro- and minireactor, they were still very close to 2%, which made the comparison possible. The content of silver in the microreactor was slightly lower than the one present in the catalyst used for the minireactor (see Table 1). The silver content of catalyst used for activity testing in the minireactor was close to the optimum for reducing NO [8]. In this sense, the minireactor had a small advantage compared with the microdevice. However, the outcome indicated that this difference was not affecting to great extent the reducing capabilities of the microplates impregnated with the active catalyst phase.

Three different hydrocarbons were tested in HC-SCR: ethylene, propane and octane. As expected, the NO reduction showed to be sensitive to the temperature and to the number of atoms of carbon present in the added hydrocarbon. The results over the alumina supported silver catalysts in the microreactor and minireactor in excess of oxygen are shown in Figs. 11–13 for the different hydrocarbons. As mentioned above, in all cases the HC_1/NO ratio was kept constant at 5. It has been previously found [12] that this ratio should be between 4 and 6 in order to

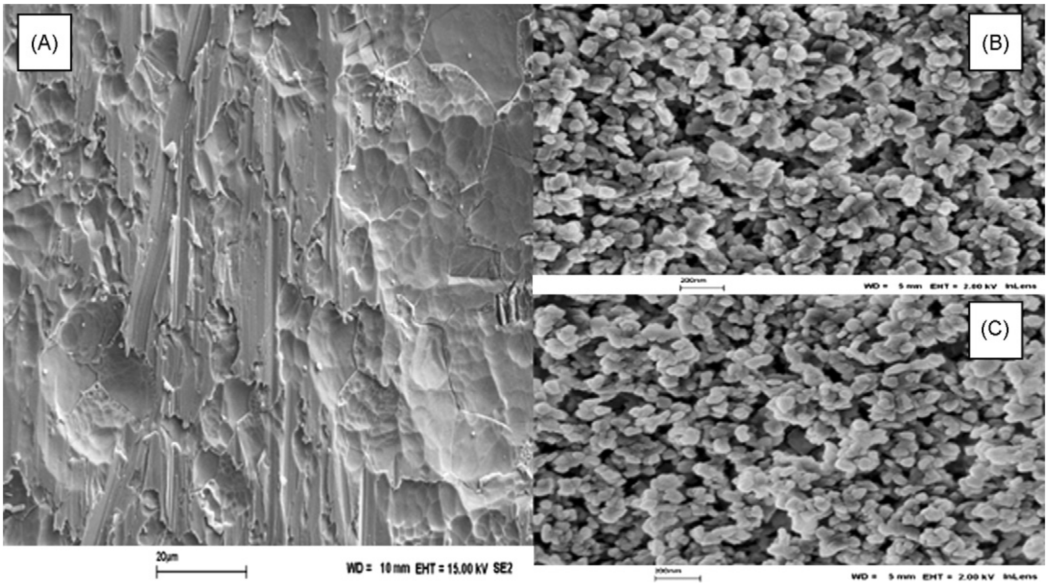

Fig. 9. Scanning electron microscope of an uncoated plate (1 kX (A)), plate covered with alumina only (50 kX (B)) and plate coated with Ag/alumina (50 kX (C)).

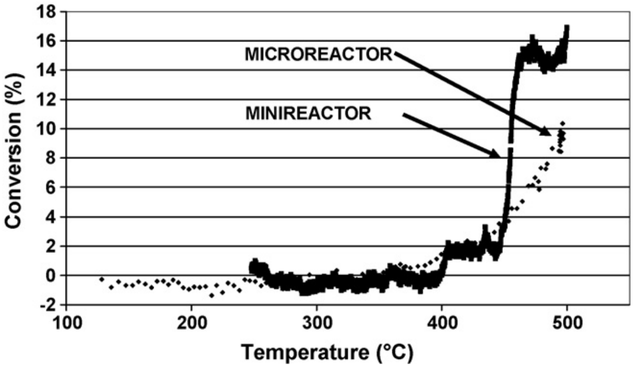

Fig. 11. Ethylene-SCR of NO. 6 vol.% O_2, 0.5 vol.% NO, 1.25 vol.% C_2H_4.

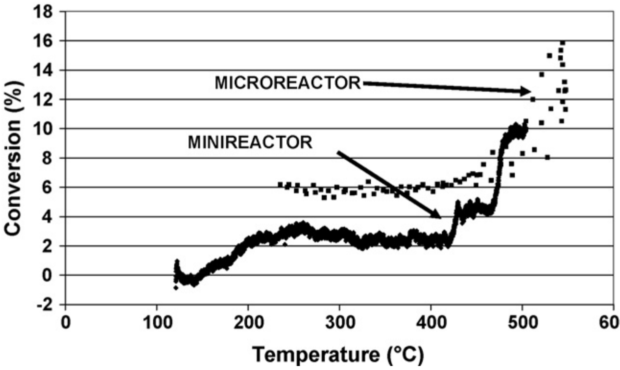

Fig. 12. Propane-SCR of NO. 6 vol.% O_2, 0.5 vol.% NO, 0.83 vol.% C_3H_8.

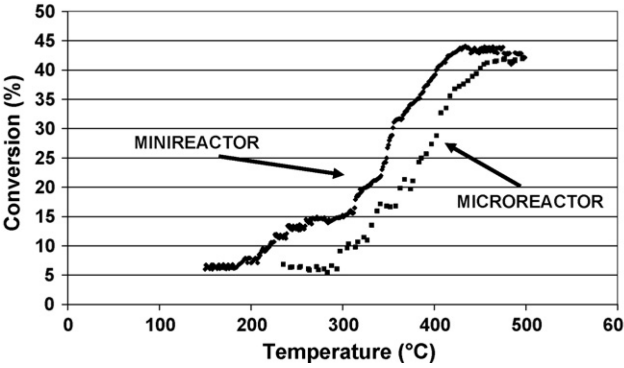

Fig. 13. Octane-SCR of NO. 6 vol.% O_2, 0.5 vol.% NO, 0.3125 vol.% C_8H_{18}.

achieve maximum conversion with the HC-SCR method. The results showed that the reduction rate was dependant on the amount of carbon atoms present in the molecule, i.e., octane exhibited the highest NO_X reduction, followed by propane and ethylene, which showed the lowest activity for both reactor systems. In general, the behavior of the microreactor and minireactor was similar. However, for the case of the NO reduction with propane, the microreactor outperformed the minireactor system (Fig. 12).

The NO reduction was strongly affected by the reaction temperature. At lower temperatures, almost no conversion of NO was achieved, while in the temperature range of 400–500 °C, the highest conversions for NO were obtained. When octane was present, though, the temperature window for the highest NO reduction was shifted to lower values. Yet, there is a need for low temperature activity for these types of catalysts. This problem has been considered in the literature for Cu-Mn oxides catalyst [13] and for Ag/Al_2O_3 also [14].

The influence of the concentration of hydrocarbons as well as the HC_1/NO ratio has been previously investigated by our group in a minireactor and engine bench tests [11,12]. In this work, optimal conditions of the reaction were assumed to be the same in microdevices in studying these types of systems. The obtained results of this effort are very much in line with those obtained in fixed-bed minireactors indicating the wide potential of microstructures for research in environmental catalysis and their eventual industrial implementation. Due to challenges in the catalyst preparation very often laboratory data are not fully consistent with the experiments performed using structural packing. It is not, therefore, surprising that catalytic data in the microreactor are not identical to the minireactor, since there are several variables (e.g., metal particles size, thickness of the layer, mass and heat transfer conditions) which are obviously not exactly the same. Moreover, due to the small sizes in the channels and high surface-to-volume ratio, the occurrence of homogeneous gas-phase reactions is considerably reduced, leaving the heterogeneous wall reactions as the only ones present in the system, contributing to a better understanding of the kinetic phenomena inside the microdevice. Such homogeneous–heterogeneous reactions were shown to be of importance in selective catalytic reduction of NO_X by hydrocarbons over Ag/Al_2O_3 [2]. The suppression of surface-mediated homogeneous reactions in microchannels is presented and studied by Chattopadhay and Veser [15]. Furthermore, microreactors present better heat exchange possibilities than conventional flow reactors. Hence, hot spots, which result in unwanted side, consecutive and decomposition reactions, can be suppressed in microreactors. Moreover, microreactors also intensify mixing and mass transfer of the system. In this sense, the results obtained in a microdevice are even more reliable compared with those obtained in the minireactor. Use of microreactors also offers straightforward scale-up or ‘‘number-up’’ (several devices in parallel), since the flow and catalytic conditions would be the same in the ‘‘pilot plant’’ and in the ‘‘real plant’’, avoiding the problems of scaling-up from laboratory conditions to industrial ones.

4. Conclusions

Microchannels washcoated with alumina were successfully impregnated with silver reaching concentrations up to 1.6 wt.%. The silver distribution along the microchannels was found to be uniform. Continuous NO reduction by hydrocarbons in excess oxygen was investigated over the impregnated microchannels in the temperature range 150–500 °C. The impregnated metal/support catalyst showed a good activity, compared to that in minireactors in the reduction of NO with hydrocarbons under lean conditions similar to those in fixed-bed minireactors. The NO reduction increased with the chain length of the hydrocarbon.

The outcome indicates that microreactors are a fast and effective way for studying catalytic gas-phase reactions of industrial importance. Compared to the minireactors, the microdevices present several advantages, i.e., faster results, fewer chemicals used and security improved.

Acknowledgements

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