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Engineering HC-SCR: Improved low temperature performance through a cascade concept

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A catalytic after treatment system for lean HC-SCR was constructed of two different catalyst beds, e.g. of a Ag/alumina and Cu-ZSM-5 catalyst (cascade concept). The improved activity especially at low temperature range was found to be due to the synergetic effect of the two catalysts, which combines the transformation of the feed gas over Ag/alumina to such compounds that are highly reactive towards N_2 over Cu-ZSM-5. The effluent coming from the Ag/alumina bed was analysed by GC–MS along with the NO to N_2 conversion over the whole system by GC. The results obtained from the GC–MS measurements revealed that hydrocarbon used as a reducing agent is oxidised and that besides oxygenates also various N-containing hydrocarbons are formed over the Ag/Al_2O_3.

KEY WORDS: engineering HC-SCR; Ag/alumina and Cu-ZSM-5 catalyst; catalyst cascade concept.

1. Introduction

Selective catalytic reduction of NO_x by hydrocarbons (HC-SCR) over Cu-ZSM-5 and Ag/alumina catalysts is well known and widely reported in literature [1–4]. Klingstedt *et al.* have shown [5] in full scale vehicle tests that Ag/alumina is a very active catalyst for the continuous removal of NO_x under real lean conditions. The drawback, however, is the non-existing low temperature activity (<350 °C) and the poor tolerance against aromatic compounds. Several authors [6–8] have shown that hydrogen in combination with hydrocarbons improves significantly the HC-SCR activity over Ag/alumina at low temperatures. In laboratory tests the activity is remained high even in presence of aromatic compounds when hydrogen is applied. On the other hand, such approach results in increased fuel penalty, as hydrogen should be produced onboard by fuel reforming. At the same time, Cu-zeolite has been reported to be active in HC-SCR at significantly lower temperatures than Ag/alumina [9]. The drawback with zeolites is the dealumination of the structure in steam and at elevated temperatures. In this study a cascade reactor consisting of a Ag/alumina bed, with empty space between, followed by Cu-ZSM-5 was tested for its activity to convert NO to N_2 during simulated lean burn (diesel) conditions. The reason for introducing empty space between beds was that HC-SCR over Ag/alumina involves heterogeneous–homogeneous reactions [6,10]. Results from the cascade reactor experiments were compared with corresponding single bed results keeping the GHSV constant.

2. Experimental

A 1.91 wt.% Ag/alumina catalyst was prepared by impregnation of a commercial (LaRoche) alumina support (specific surface area 289 m^2/g) according to [11]. The mean particle size of the silver particles is 5.08 nm determined by HRTEM and assuming spherical particles. A Cu-ZSM-5 catalyst was prepared by repeated ion-exchange of a commercial Na-ZSM-5 (Degussa, $Si/Al=22.6$) zeolite (specific surface area 398 m^2/g) with aqueous solution of copper acetate. After washing the catalyst was dried for 24 h at room temperature and thereafter for 1 h at 60 °C. The Cu content in the prepared catalyst was 0.45 $mmol/g_{cat}$ (analysed by DCP), which equals to $Cu/Al=0.53$.

The two catalysts were tested in a quartz tube reactor in the temperature range 150–500 °C with total $GHSV=60{,}000\ h^{-1}$, sampling at steady state conditions. The Ag/alumina (0.2 g, 250–500 μm) was placed prior to the copper containing zeolite (0.2 g, 250–500 μm) leaving 44 mm (= 3.5 ml) free space between the beds. The gas mixture used in the activity tests consisted of 500 ppm NO, 6 vol.% O_2, 10 vol.% CO_2, 350 ppm CO, 12 vol.% H_2O and He balance. Reducing agent used was either 375 ppm pure n-octane or 430 ppm pure toluene, equal to $C_1/NO=6$ in both cases. The effluent after (between the two beds) the Ag/alumina bed was analysed by means of a GC (HP 6890) and a GC–MS (Agilent GC-MS, 6890N/5973 combined with data library (Wiley7n) to reveal information of the species present in the gas phase between the beds. The effluent after the second bed (Cu-ZSM-5) was analysed by the GC to determine the total NO to N_2 and hydrocarbon to $CO+CO_2$ conversions over the whole

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system. Condensers were used to trap out water from the gas prior to GC analyses.

3. Results and discussion

3.1. Activity tests

In figure 1 the activities over the prepared Ag/alumina and Cu-ZSM-5 catalysts as single beds versus the cascade concept are presented. As can be seen, the Ag/alumina alone is superior catalyst in the high temperature range, e.g. >400 °C. However, there is no activity below 300 °C over the silver catalyst. Moreover, if aromatic compound (toluene) is applied (figure 2) the activity is shifted to even higher temperatures starting at approximately 450 °C. The peak maximum in case of toluene is only ca. 33% NO to N_2 above 500 °C compared to almost 100% with octane. In the same figure (figure 1), the activity pattern recorded over the prepared Cu-ZSM-5, tested alone as a single bed, is also presented. As it can be seen, the reduction of NO starts already between 200 and 250 °C and reaches ca. 30% at 250 °C. Compared to the Ag/alumina the activity window is shifted towards lower temperature region by approximately 100 °C. Moreover, a conversion of ca. 80% is reached at 300 °C over the Cu-ZSM-5. It is clear that the two catalysts work at totally different temperature regions having both their own advantages. Thus, by combining these two catalysts one could think that a good overall reduction activity could be achieved between 250–500 °C. At temperatures higher than 500 °C the Cu-ZSM-5 catalyst deactivates in presence of steam, whereas the Ag/alumina catalyst is stable up to 700 °C.

The NO to N_2 reduction activity over the cascade reactor, where Ag/alumina bed is placed prior to the Cu-ZSM-5 bed, is however detectable already at 200 °C (figure 1). This is peculiar because neither of the catalysts alone show any activity at this temperature. Furthermore the peak activity (ca. 70%) is reached at 250 °C, which means a shift of 50 °C towards lower temperature if compared to the Cu-ZSM-5 alone. As the reaction ignition is shifted to seemingly lower temperature when the cascade concept is applied, it cannot be explained by the fact that the activities of the two catalysts are simply combined. The result is a synergetic effect caused by the transformation of the feed gas over the Ag/alumina. Several authors have been suggested that the first step in HC-SCR over oxide catalysts involves the formation of strongly bound nitrites and nitrates. In addition, activation of the hydrocarbon takes place by partial oxidation to oxygenated compounds, such as acetates. Both nitrate and nitrite species as well as acetates have been detected in FTIR studies by several research groups. The ad-NO_x species are supposed to react with the adsorbed and partly oxidised hydrocarbon species on the catalyst surface to yield organo-nitrogen species [4 and references therein]. We have shown [6] that the HC-SCR mechanism over Ag/alumina involves a heterogeneous–homogeneous reaction network where part of the N_2 formation takes place in the gas phase. Components such as R-NO_2, R-NCO

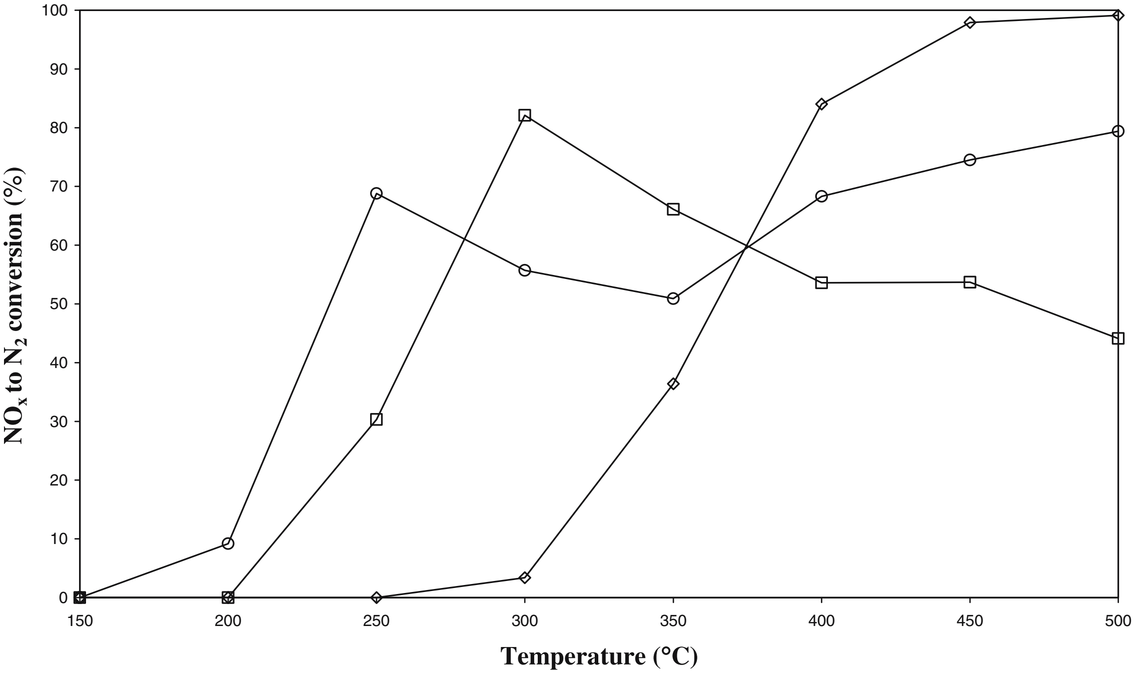


Figure 1. NO to N_2 conversion over Ag/alumina (◇), Cu-ZSM-5 (□) and Ag/alumina + Cu-ZSM-5 (○) catalysts. GHSV = 60,000 h^{-1}, gas mixture: 500 ppm NO, 375 ppm n-octane, 6 vol.% O_2, 350 ppm CO, 10 vol.% CO_2, 12 vol.% H_2O and He balance.

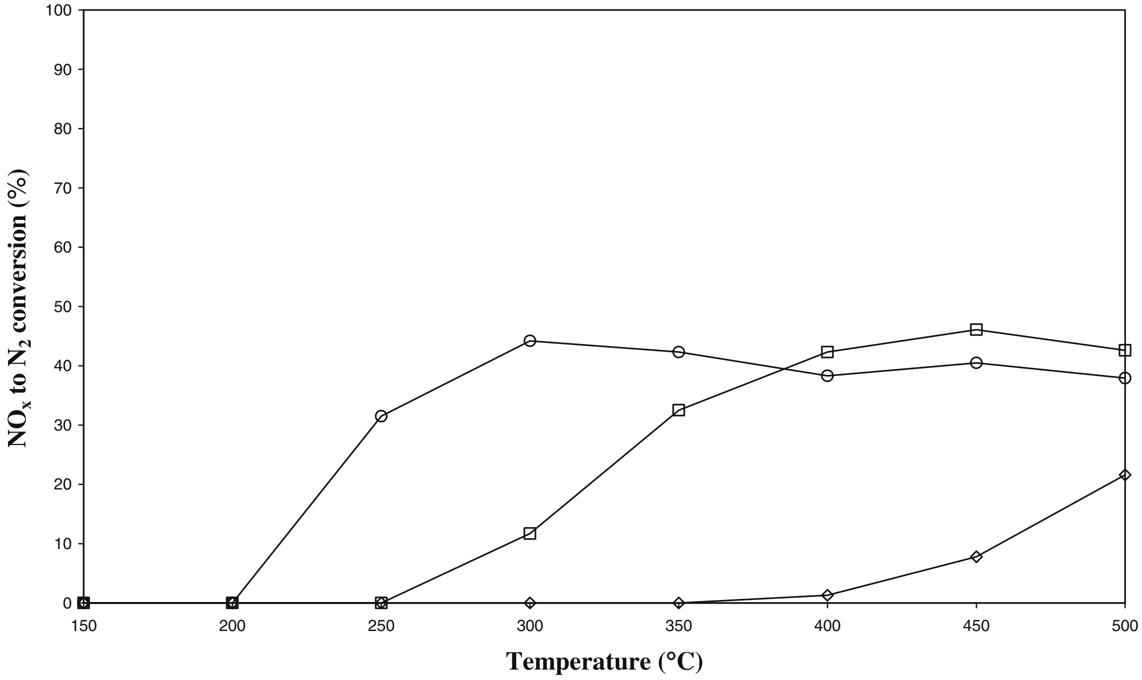


Figure 2. NO to N_2 conversion over Ag/alumina (◇), Cu-ZSM-5 (□) and Ag/alumina + Cu-ZSM-5 (○). GHSV = 60,000 h^{-1}, gas mixture: 500 ppm NO, 430 ppm toluene , 6 vol.% O_2, 350 ppm CO, 10 vol.% CO_2, 12 vol.% H_2O and He balance.

and R-CN formed through the reaction between oxygenates and ad-NO_x species over the Ag/alumina are intermediate species for the production of amines and ammonia for the last step of the HC-SCR reaction mechanism, which takes place both on the surface and in the gas phase behind the Ag/alumina catalyst [6]. This is also supported by the GC–MS experiments done for this study. However, the formation of N_2 in the gas phase over Ag/alumina does not occur at such a low temperature (200 °C) in the absence of hydrogen as N_2 formation over the cascade system. It means that the homogeneous reactions per se leading to the final formation of N_2 over Ag/alumina catalyst cannot fully explain the reaction mechanism over the cascade system due to the low temperature. The species formed over the Ag/alumina are obviously the same as described, but as no N_2 is formed over the Ag/alumina at low temperature, they further react over the Cu-ZSM-5.

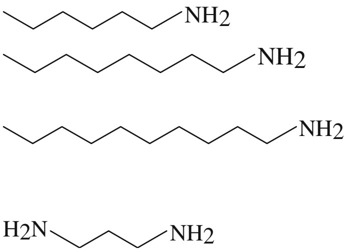
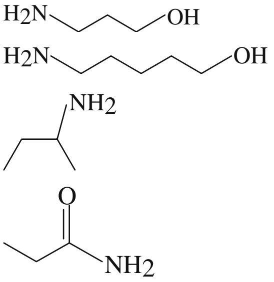
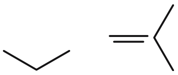
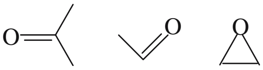
When toluene was used as a reducing agent totally different activity patterns were recorded over the two catalysts as well as over the cascade system (figure 2). Over the Ag/alumina catalyst the conversion of NO to N_2 remained almost non-existing up to 400 °C and resulted in a peak maximum of about 20% at 500 °C. The decrease in activity when toluene is used as a reducing agent for HC-SCR over Ag/Al_2O_3 is dramatic compared to octane leading to the conclusion that aromatic compounds in the diesel fuel are a major disadvantage for Ag/alumina catalysts. Compared to Ag/alumina catalyst Cu-ZSM-5 is by far not so sensitive towards poisoning due to the presence of aromatic compounds: NO to N_2 reduction is achieved in the temperature range of 300–500 °C at a considerable level. However, again the cascade concept of these two catalysts is superior compared to the activities over the single beds. The reduction activity between 200–300 °C over the cascade system is surprising as the Ag/alumina bed shows no activity below 400 °C and the Cu-ZSM-5 only minor activity below 300 °C in the presence of aromatic compounds. Thus it can be concluded that the application of these two beds has a synergetic effect on the conversion of NO to N_2. It seems that the gas mixture is transformed over the Ag/alumina bed to species, which are highly reactive over Cu-ZSM-5 to produce N_2.

3.2. *GC–MS*

In [12] we made a preliminary identification of the species in the gas phase behind the Ag/alumina catalyst by argon matrix isolation combined with EPR and FT-IR techniques. Moreover, Eränen *et al.* [6] have shown that activation of NO over Ag/alumina catalyst is a crucial step in the reaction mechanism leading to a high reduction of NO and it is enhanced by hydrogen. Based on these studies [6,12] it is reasonable to assume that also in the cascade reactor system the reacting media is not in the same state when it reaches Cu-ZSM-5 as it is prior to the silver catalyst.

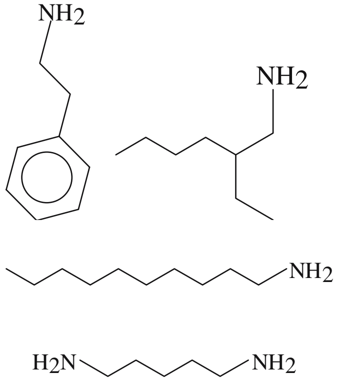
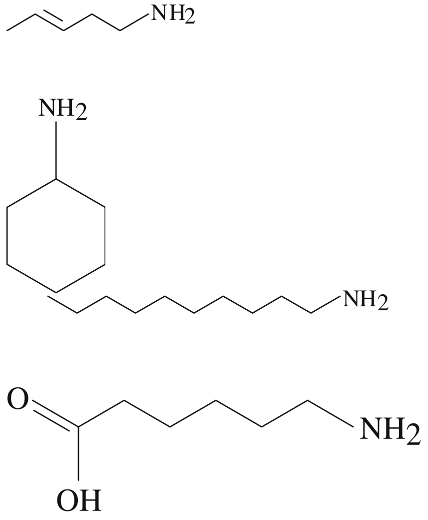
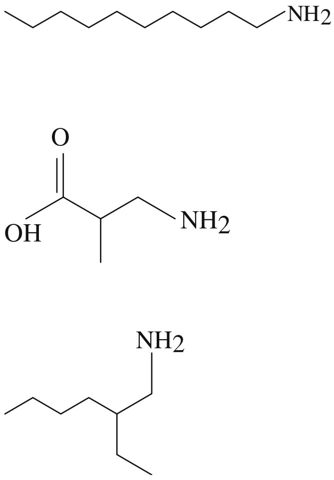
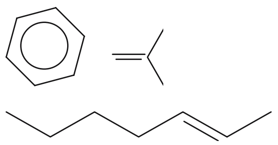
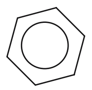
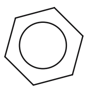
When the effluent coming from the Ag/alumina was analysed by GC–MS, the following species were detected: unburned hydrocarbons, various amines, N-containing hydrocarbons and oxygenates depending on the temperature and the reducing agent used (tables 1 and 2). As shown, some amines were formed already at 200 °C with both octane and toluene. The results also showed that the oxidation of octane over Ag/alumina starts already at 250 °C whereas the oxidation of toluene did not occur at all at 300 °C (figure 3). In fact the noticeable decrease of the toluene peak in the GC–MS spectra started above 400 °C, e.g. at the same temperature where the NO to N_2 conversion starts over Ag/alumina when toluene is used. This indicates that the HC-SCR activity over Ag/alumina is strongly dependent on the ability to oxidise the hydrocarbon chain. Thus, the logical explanation for the increased activity over the whole system is formation of reactive species (amines + oxygenates) over the first bed, which are then fed to the Cu-ZSM-5 catalyst. As N_2 is

Table 1
Typical species found in the gas phase using octane as reducing agent

Temperature	200 °C	300 °C	400 °C
Amines and N-containing hydrocarbons[*]			– –
Unburned hydrocarbons[**]			–
Oxygenates[***]			

[*] and [**] = detected at 200–300 °C, [***] = detected at 200–400 °C.

Table 2
Typical species found in the gas phase using toluene as reducing agent

Temperature	200 °C	300 °C	400 °C
Amines and N-containing hydrocarbons			
Unburned hydrocarbons			
Oxygenates	–	–	–

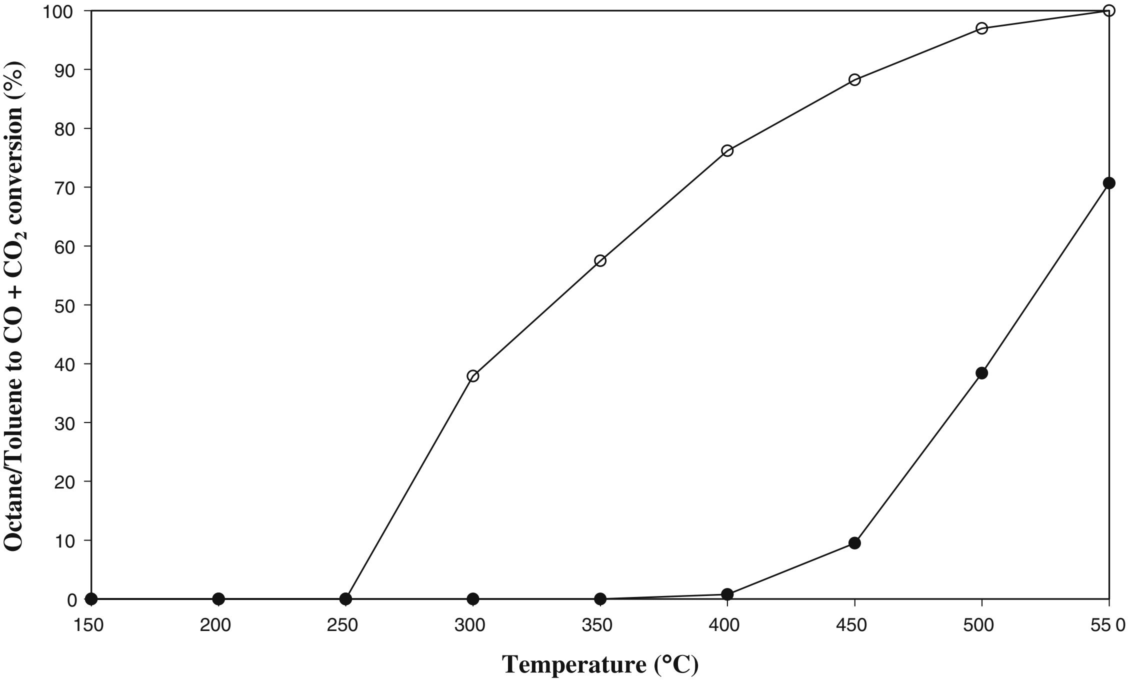


Figure 3. Octane (○) versus toluene (●) oxidation to $CO + CO_2$ over Ag/alumina catalyst. GHSV = 60,000 h^{-1}, gas mixture: 500 ppm NO, 12 vol.% H_2O, 375 ppm n-octane or 430 ppm toluene and He balance.

not detected over the Ag/alumina alone, it seems that NO activation does not take place probably due to the low temperature. If NO would be activated then N_2 should be formed by reaction with amines in the gas phase as shown in [6]. At these low temperatures (< 250 °C) the activation of NO is probably taking place over Cu-ZSM-5 resulting in species reacting further with the amines formed over Ag/alumina. Activation of NO to NO^+ over Mordienite and H-ZSM-5 has been shown previously [13,14].

4. Conclusions

A cascade reactor concept consisting of a Ag/alumina and a Cu-ZSM-5 bed was tested for lean HC-SCR. The performance of the combination of these two catalysts was found to be superior compared to either of the catalysts alone in the temperature range 150–500 °C applying both straight alkane and aromatic compound. With GC–MS measurements from the effluent between the beds, e.g. behind the Ag/alumina catalyst, it was shown that the cascade system has a synergetic reaction mechanism, which is not just a combination of the reaction mechanism over the single beds. This difference is due to the formation of amines and functionalisation of hydrocarbons used as reducing agents to different oxygenates.

Acknowledgments

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