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DME as Reductant for Continuous Lean Reduction of NO_x over ZSM-5 Catalysts

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Abstract Dimethyl ether (DME) is an interesting alternative fuel to diesel, but is not an efficient reductant in lean NO_x conversion over typical diesel HC-SCR catalysts. Comparatively high deNO_x activity was found over H-ZSM-5 in the presence of water, giving reduction of 28% NO and 37% NO_2 respectively with a DME/NO_x-ratio of 4.

Keywords Dimethyl ether · DME · NO_x reduction · ZSM-5 · NO_2 · Solid acid · Zeolite

1 Introduction

Concern for global climate change caused by increasing atmospheric CO_2 concentrations combined with limited fossil fuel resources and growing energy demand have increased the interest in research and investments in alternative fuels. Among these, dimethyl ether (DME) from biomass gasification is one of the most energy effective and low CO_2 emitting fuels according to recent well-to-wheel studies [1, 2]. In addition, with DME as a fuel current diesel engine technology and existing infrastructure for liquefied petroleum gas (LPG) can partly be used [3] facilitating the market introduction of DME as a fuel. Because of its high cetane number, DME is attractive as fuel for diesel engines [3] where it has the further advantage of producing very small amounts of soot [3–5]. This enables higher exhaust gas recirculation (EGR) rates, which lower the NO_x concentration in the exhaust. However, upcoming legislation limits for the emissions of NO_x and particulate matter from vehicles become increasingly challenging. To meet the most stringent demands, after-treatment technologies to minimize NO_x emissions will most likely be needed even with a DME-fuelled engine.

In a recent study it was found that a commercial Cu-ZSM-5 zeolite-based catalyst developed for hydrocarbon-assisted selective catalytic reduction (HC-SCR) of diesel exhaust showed virtually no NO_x reduction with DME as reducing agent in contrast to the high NO_x conversion found using DME and a commercial lean NO_x adsorber (LNA) catalyst [6]. However, out of the three main catalyst systems for lean NO_x reduction, the HC-SCR or lean NO_x catalyst (LNC) concept is the simplest one from a vehicle system viewpoint. Only few studies have been reported on HC-SCR using DME as reductant. Alam et al. studied HC-SCR catalysts supplied by catalyst manufacturers and reported a peak NO_x conversion of over 70% over a Co/Al_2O_3 catalyst in the absence of water but found formation of formaldehyde [7]. Masters and Chadwick, also performed their study without water and in a powder reactor and reported up to 75% NO_x conversion over a MoO_3/Al_2O_3 catalyst and 68% NO_x conversion over Al_2O_3 [8]. They detected formaldehyde when oxidizing DME with O_2 but not in the presence of NO_x. Finally, Masuda et al. found NO_x conversions below 20% over Ag-mordenite and Ag/Al_2O_3 with DME as reducing agent in real exhaust from a diesel engine [9].

In the present study, we investigate the NO_x reducing performance of the zeolites H-ZSM-5, Ag/H-ZSM-5 and Ag/Na-ZSM-5 for DME-SCR of NO and NO_2 in the

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absence and presence of water, and investigate some aspects of the reaction mechanism for NO_x reduction.

2 Experimental Methods

2.1 Catalyst Preparation

Zeolite H-ZSM-5 powder (batch number: 2125120, Akzo Nobel Catalysts BV) with a SiO_2/Al_2O_3 (SAR) molar ratio of 40 was used as received for the preparation of a H-ZSM-5 coated monolith catalyst. Additional properties of the H-ZSM-5 powder may be found elsewhere [10]. The H-ZSM-5 powder was also used to prepare Ag/H-ZSM-5 and Ag/Na-ZSM-5 through ion-exchange. First, the zeolite powder was calcined at 500 °C for 2 h in air. To obtain Ag/Na-ZSM-5 the H-form zeolite was then ion-exchanged to Na-ZSM-5 by mixing a 0.1 M NaOH-solution with a slurry of H-ZSM-5 and Milli-Q water at room temperature for 3 h keeping the pH below 10. The silver ion-exchange was conducted similarly for both Ag/H-ZSM-5 and Ag/Na-ZSM-5. Four grams zeolite were suspended in 400 mL 0.01 M $AgNO_3$-solution and stirred at room temperature for 22 h. The ion-exchange was repeated one and two more times for the Ag/Na-ZSM-5 and the Ag/H-ZSM-5, respectively. After the last ion-exchange the powder was washed 2 times with Milli-Q water and freeze-dried. The preparation was carried out in the dark. The resulting silver content was analyzed by SEM-EDX (Leo Ultra 55 FEG SEM) and found to be 4.9 wt% Ag and 6.7 wt% Ag, respectively, which correspond to 61% and 80% exchange of the counter ions by silver ions for the Ag/H-ZSM-5 and the Ag/Na-ZSM-5.

For the activity tests, the zeolite powders were wash-coated on honeycomb structured cordierite monoliths (400 cpsi) in a weight ratio of 80:20 between zeolite powder and silica binder (Bindzil colloidal silica $30NH_3/200$, Eka Chemicals) with a total weight of the washcoat corresponding to 20% of the monolith weight. The monoliths were finally calcined in air at 550 °C for 2 h. Their BET-surface areas were 60 $m^2/g_{monolith}$ for the H-ZSM-5, 65 $m^2/g_{monolith}$ for the Ag/H-ZSM-5, and 45 $m^2/g_{monolith}$ for the Ag/Na-ZSM-5, which correspond to 355, 350 and 218 m^2/g for the zeolite powders, respectively.

2.2 Activity Tests

A horizontally mounted quartz-tube reactor was used for the catalytic activity tests. The reactor temperature was measured in the gas stream before the catalyst and inside a channel in the centre of the monolith. The effluent gases were mixed by a computerized multi component gas mixer (Environics 2000). Water was introduced to the system via a separate oven. The reactor exhaust gas composition was analyzed by a gas phase FTIR instrument (mks-instruments, MultiGas 2030) and a NO_x-detector (Eco Physics, CLD 799 EL ht).

Before each experiment, the catalysts were pre-treated in a gas stream of 8% O_2 in Ar at 550 °C for 30 min. Activity tests were performed either without water with a feed gas mixture of 1000 ppm NO, 500 ppm DME and 8% O_2 balanced in Ar or with 5% water in a feed gas mixture of 475 ppm NO_x (NO or NO_2); 475, 950, 1425 or 1900 ppm DME; and 7.6% O_2 balanced in Ar. All tests were performed as steady state experiments at temperatures between 500 °C and 200 °C. Starting at 500 °C with a DME/NO_x-ratio of 1, the DME inlet concentration was stepwise increased, dwelling 15 min at each step. After the step with the highest DME concentration, the catalyst was cooled in Ar to the next reaction temperature, and the procedure was repeated. All experiments and the pre-treatment were performed with a space velocity of 33,400 h^{-1} based on the monolith volume.

For the catalyst evaluation, NO_x conversion is defined as $(1-[NO_{x,out}]/[NO_{x,in}]) \cdot 100\%$ and DME conversion as $(1-[DME_{out}]/[DME_{in}]) \cdot 100\%$. Yield of methanol, CO_2, CO and formaldehyde is defined as $[X_{out}]/2[DME_{in}] \cdot 100\%$.

3 Results and Discussion

3.1 NO_x Reduction Over H-ZSM-5

There is only a limited number of studies on DME-SCR and in particular only two studies on DME-SCR with water in the feed gas that we can relate our study to [6, 9]. While most earlier reports on DME-SCR have been performed in the absence of water, important differences in NO_x reduction with hydrocarbons have been reported upon introduction of water [11]. In Fig. 1 the effect of water on the NO_x conversion over H-ZSM-5 is shown for a DME/NO_x-ration of 1 and with NO as NO_x source. In the absence of water, the NO_x conversion increases with increasing temperature, reaching a maximum of 20% at 500 °C. In the presence of water, NO_x conversion is observed at lower temperatures and reaches a maximum of only 8% at 350 °C. In our study, the presence of water thus lowers the maximum NO_x conversion but lowers and broadens the temperature window where the catalyst is active. Below 400 °C, a significant formation of methanol is observed in the presence of water with a clear maximum at 300 °C, while only minor amounts of methanol are formed in the absence of water. Furthermore, DME conversion starts at lower temperatures and reaches total DME conversion at lower temperatures than without water. This earlier DME conversion in the presence of water is partly due to the

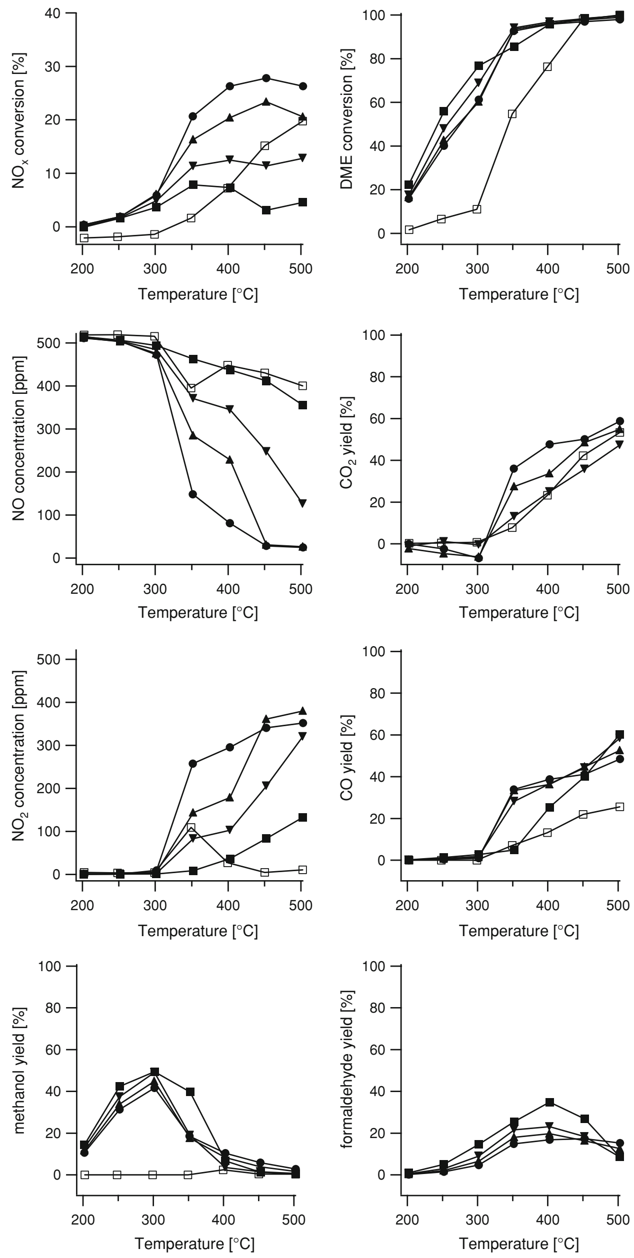

Fig. 1 Conversion, yield and concentration of gases during DME-SCR of NO over H-ZSM-5 as a function of temperature in the absence of water with DME/NO_x = 1 (☐) and in the presence of 5% water (filled symbols). Gas mixture: 1000 ppm NO, 8% O_2 and 1000 ppm DME (☐), and 475 ppm NO, 7.6% O_2, 5% H_2O and 475 ppm DME (■), 950 ppm DME (▼), 1425 ppm DME (▲) and 1900 ppm DME (●)

formation of methanol. It has been reported for H-ZSM-5 catalysts, that NO_x adsorbs on the acidic sites forming NO^+ ions [10, 12], which are believed to be intermediates in NO_x reduction. Since water is reported to adsorb on the same acidic sites as NO^+ [12] it is likely that there is a competition for the adsorption sites between NO an water. Furthermore, NO^+ is reported to be unstable in the presence of water forming NO and NO_2 [12, 13]. These two reasons can explain the decrease in NO_x reduction in the presence of water. Thus, the presence of water clearly changes the conditions on the catalyst affecting the conversion of both NO_x and hydrocarbons.

The remaining experiments in this study were carried out in the presence of about 5% water to better mimic realistic conditions of engine out emissions. An increasing DME/NO_x-ratio results in an increased conversion of NO_x reaching a maximum of 28% at a DME/NO_x-ratio of 4 and an increase in optimal temperature to 450 °C. Detection of only minor amounts of N_2O (not shown) together with semi-quantitative N_2 measurements in the introductory study indicate a high selectivity to N_2 in the entire temperature range and for all DME/NO_x-ratios studied. At temperatures above 300 °C, the NO_2 concentration increases with increasing DME/NO_x-ratio and temperature, while the NO concentration decreases (Fig. 1). The conversion of DME also increases with temperature and reaches almost total conversion at 350 °C and above for all DME/NO_x-ratios studied. Formaldehyde is formed above 200 °C with a maximum around 400 °C and acetaldehyde is detected in the same temperature range, albeit in smaller amounts (results not shown). The yields of CO_2 and CO start to increase above 300 °C mimicking the NO_x reduction curves. The CO_2 yield for the DME/NO_x-ratio of 1 in the presence of water is not shown because the values obtained were near the detection limit of the instrument.

Typically, NO_x conversion in HC-SCR is volcano shaped as a function of temperature. The initial rise in conversion with temperature is due to faster reaction kinetics. Above the optimum temperature conversion decreases typically as selectivity decreases and more reductant is unselectively oxidized by oxygen. In this study, NO conversion reaches a maximum over H-ZSM-5 at 350 °C for a DME/NO_x-ratio of 1 (Fig. 1). Increasing the DME/NO_x-ratio increases the conversion above 250 °C and shifts the maximum conversion to 450 °C. This shift is due to faster reactions at higher temperatures enabled by the higher concentration of reductant available at higher DME/NO_x-ratios.

The observed increase in NO_2 concentration above 350 °C is due to gas phase reactions in the presence of NO and DME as evident from reactor experiments without catalyst (results not shown). However, no NO_x reduction was observed without catalyst, emphasizing that NO_x reduction takes place at the catalyst surface. One common view is that the first step of NO_x reduction over zeolite catalysts is the oxidation of NO to NO_2. In Fig. 1 it can be seen that NO_x reduction starts over H-ZSM-5 at the same temperature as NO_2 is formed in the gas phase. The H-ZSM-5 sample itself is not particularly active for NO oxidation forming only minor amounts of NO_2 in the presence of only NO and O_2 (results not shown). This observation is in good agreement with previous work on the enhancement of selective NO oxidation activity of zeolite catalysts [14, 15]. In DME-SCR, the gas phase formation of NO_2 apparently compensates for the lack of NO oxidation capability of H-ZSM-5.

3.2 NO_2 Reduction Over H-ZSM-5

To assess whether NO oxidation is limiting NO_x reduction in DME-SCR over H-ZSM-5 experiments were carried out with NO_2 in the feed with results shown in Fig. 2. NO_x reduction increases with increasing DME/NO_x-ratio and increasing temperature reaching a maximum of 37% at 500 °C and a DME/NO_x-ratio of 4. Below 300 °C, the remaining NO_x was mainly in the form of NO; whereas at higher temperatures and especially with increasing DME/NO_x-ratio, mainly NO_2 was detected. The conversion of DME was almost complete at and above 350 °C independent of the DME/NO_x-ratio. Also the formation of CO, CO_2, methanol, formaldehyde and acetaldehyde was very similar to that observed with NO as NO_x source (results not shown). The only differences were somewhat lower methanol formation and higher formaldehyde formation, especially below 300 °C when using NO_2 as NO_x source. However, NO_x conversions are in general higher with NO_2 than with NO, for a given DME/NO_x-ratio. This difference is expected despite the large amounts of NO_2 formed from NO in the gas phase at high DME/NO_x-ratios and temperatures. At low temperatures, the NO_x reduction is higher with NO_2 in the feed since NO_2 is more active and the gas phase NO oxidation reactions are too slow. At high temperatures the higher NO_x conversion observed can be explained by a higher concentration of reducing agent being available for NO_x reduction with NO_2 than with NO as NO_x source since some of the DME is consumed in the gas phase reaction with NO yielding NO_2. This fraction of the DME is subsequently not available for NO_x reduction on the catalyst.

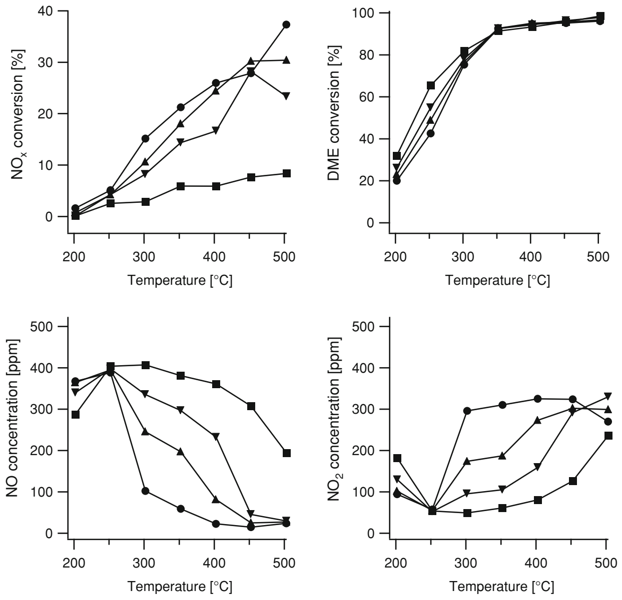

Fig. 2 Conversion and concentration of gases during DME-SCR of NO_2 over H-ZSM-5 as a function of temperature with different DME/NO_x-ratios. Gas mixture 475 ppm NO_2, 7.6% O_2, 5% H_2O and 475 ppm DME (■), 950 ppm DME (▼), 1425 ppm DME (▲) and 1900 ppm DME (●)

3.3 NO_x Reduction with DME Over Ion-Exchanged ZSM-5

The activity for NO reduction and DME oxidation of the Ag/H-ZSM-5 and Ag/Na-ZSM-5 catalysts is shown in Fig. 3. The NO_x reduction is lower over both these catalysts than over H-ZSM-5, showing maximum conversions of 10% and 11% at 500 °C, respectively. Above 300 °C at a DME/NO_x-ratio of 1, the NO_2 concentration increases at higher temperatures also for the Ag/H-ZSM-5 and the Ag/Na-ZSM-5 samples. At higher DME/NO_x-ratios, however, a peak in NO_2 concentration occurs at 350 °C over Ag/H-ZSM-5 and at 300 °C over Ag/Na-ZSM-5, followed by a more moderate increase in NO_2 formation at higher temperatures (Fig. 3). Methanol, formaldehyde and acetaldehyde formation are generally lower over the silver exchanged zeolites than over H-ZSM-5, but the formaldehyde/methanol ratio is higher over Ag/Na-ZSM-5. Carbon monoxide and carbon dioxide are detected above 300 °C over the Ag/H-ZSM-5 and Ag/Na-ZSM-5 catalysts, similar to over the H-ZSM-5 catalyst. However, over the Ag/H-ZSM-5 catalyst more CO_2 than CO is always formed while over the H-ZSM-5 the opposite is observed. Even more CO_2 is formed and less CO over the Ag/Na-ZSM-5 catalyst compared to Ag/H-ZSM-5. The CO_2 yields for a DME/NO_x-ratio of 1 are not shown because the values obtained are near the detection limit of the instrument. Both silver containing catalysts show slightly better NO_x conversion with NO_2 than with NO as NO_x source (results not shown), although still lower than the NO_x conversion found over H-ZSM-5. Maximum conversion is found at 300 °C for DME/NO_x-ratios larger than 1. In comparison to NO_2 reduction over H-ZSM-5, less NO is formed at lower temperatures and more NO at higher temperatures at DME/NO_x-ratios over 1 for both silver containing catalysts.

Comparing Figs. 1 and 3, it is apparent that the NO_x reducing activity and the formation of methanol and formaldehyde decrease in the order H-ZSM-5 > Ag/H-ZSM-5 >Ag/Na-ZSM-5, while the CO_2/CO ratio increases in the same order. Summarized, the oxidizing activity is lower and the selectivity towards partially oxidized carbon

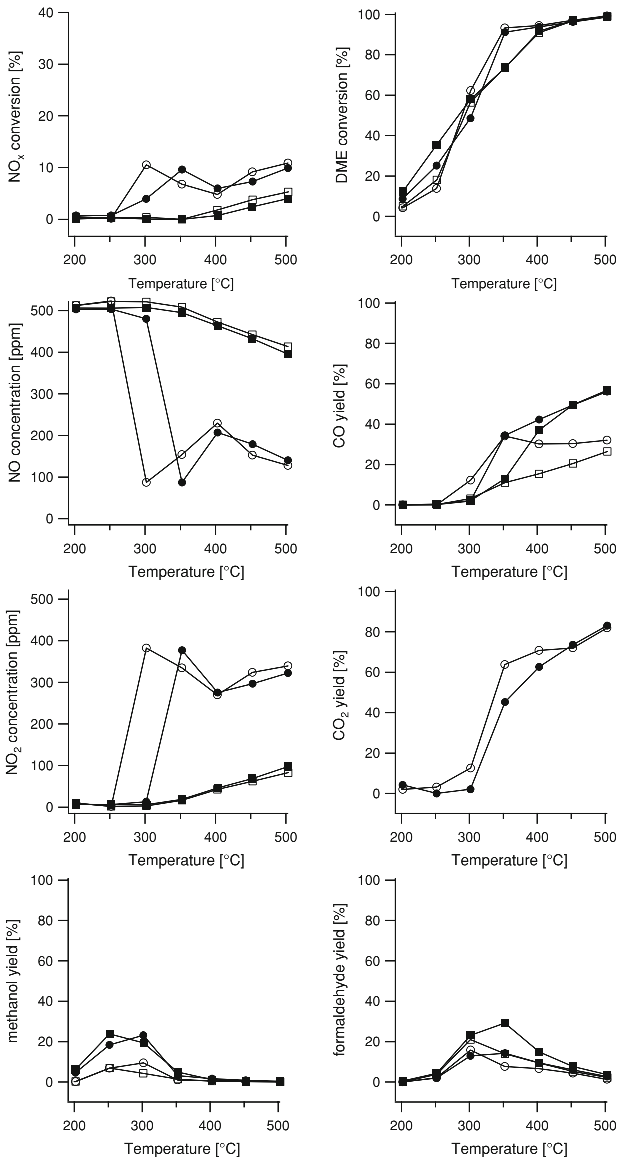

Fig. 3 Conversion, yield and concentration of gases during DME-SCR of NO over Ag/H-ZSM-5 (■,●) and Ag/Na-ZSM-5 (□,○) as a function of temperature with two different DME/NO_x-ratios. Gas mixture 475 ppm NO, 7.6% O_2, 5% H_2O and 475 ppm DME (■,□) respectively 1900 ppm DME (●,○)

containing products is higher for H-ZSM-5 than for Ag/H-ZSM-5 and Ag/Na-ZSM-5 in the presence of water. In an introductory study (results not shown), H-ZSM-5 zeolites with five different silica–alumina ratios (SAR) were tested. The zeolite with the lowest SAR, being at the same time the most acidic one, showed the highest NO_x reduction activity. This is in accordance with the findings from Masters and Chadwick, who showed that the most acidic γ-alumina catalyst was most active for NO reduction with DME [8]. Furthermore, Erkfeldt et al. found in a recent study [6] that a commercial Cu-ZSM-5 catalyst did not show any significant activity for DME-SCR. These findings, together with our own results support the hypothesis that the acidic sites of the H-ZSM-5 zeolite are active sites for DME-SCR.

According to Park et al. a good SCR-catalyst needs three different functions: (i) ability to oxidize NO to NO_2, (ii) activation of hydrocarbon, and (iii) reduction of NO_x to N_2 and oxidation to CO_2 [16]. The ability to oxidize NO to NO_2 (function i) is likely less important for DME-SCR, since NO is oxidized to NO_2 in the gas phase. Higher amounts of methanol and formaldehyde, less CO_2 and higher NO_x conversion have been observed over H-ZSM-5 than over Ag/H-ZSM-5 and Ag/Na-ZSM-5. This observation indicates that weaker oxidation sites are more favourable for DME-SCR. Whether the DME is activated in the gas phase reaction with NO or on the catalyst (function ii), cannot be deduced from the data presented here. Finally, protons seem to promote the conversion of NO to N_2 (for function iii) possibly through the formation of NO^+ ions as suggested by Hadjiivanov [12]. It may thus be suggested that H-ZSM-5 is a better NO_x reduction catalyst with DME than Ag/H-ZSM-5 and Ag/Na-ZSM-5 in the presence of water due to differences in either activity and selectivity for partial DME oxidation or to better selectivity for hydrocarbon oxidation with NO_x than with oxygen.

4 Conclusions

Comparatively high conversion of NO_x was achieved in the presence of water over H-ZSM-5, reaching 28% NO conversion at 450 °C and 37% NO_2 conversion at 500 °C at a DME/NO_x-ratio of 4. But considerable amounts of methanol, formaldehyde and acetaldehyde were observed. A comparison of the H-ZSM-5 catalyst with less active Ag/H-ZSM-5 and Ag/Na-ZSM-5 catalysts suggests that the acidic Brønsted sites are crucial in DME-SCR over ZSM-5 catalysts. During DME-SCR high yields of NO_2 were observed due to reactions between DME and NO in the gas phase.

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