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Improved Automotive NO_x Aftertreatment System: Metal Ammine Complexes as NH_3 Source for SCR Using Fe-Containing Zeolite Catalysts

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Abstract Ammonia storage is a challenge in the selective catalytic reduction of NO_x in vehicles. We propose a new system, based on metal ammines as the ammonia source. In combination with iron containing zeolites as the SCR catalyst it should be possible to obtain a low temperature system for NO_x removal.

Keywords SCR · NO · Metal ammines · Ammonia storage · Fe-containing zeolites

1 Introduction

It has become increasingly important to reduce the emission of nitrogen oxides from both stationary and mobile combustion technologies in order to protect the environment from high level of NO_x pollution. High levels of NO_x can lead to problems such as acid rain, oxygen depletion, as well as forest and crops damage. Thus, it can be considered extremely harmful to the environment. Furthermore, the compounds are toxic for humans at inhalation. Nitrogen oxides are emitted with the exhaust gasses during the combustion of both fossil fuels and biofuels. This means that it is necessary to clean the exhaust gas in both stationary and automotive application [1].

Approximately 20% of all NO_x emissions originate from vehicles [2]. In vehicles, the problem with high exhaust levels of NO_x is especially seen for lean-burn vehicles (diesel and lean-burn gasoline). In a lean-burn engine, the ratio between air and fuel is higher than the stoichiometric ratio resulting in excess oxygen in the exhaust gas. For modern gasoline cars, the commercially used three-way catalyst only functions properly when the ratio is very close to stoichiometric fuel mixture. In a lean-burn vehicle, the oxidation of CO and hydrocarbons can still take place efficiently but the excess of oxygen simply prevents the reduction of nitrogen oxides. Lean-burn engine operation can be used in gasoline-driven cars to improve the fuel economy. Furthermore lean-burn combustion methods are used in diesel cars. Since the number of diesel cars is currently increasing significantly, it would be of major importance to develop a way to efficiently eliminate this source of NO_x pollution [3, 4].

The environmental concerns have resulted in a continually decrease in the allowed NO_x concentrations in countries such as Japan, Europe and US controlled by legislation. Therefore, the catalytic removal of NO using selective catalytic reduction (SCR) appears to become crucial for reducing the emissions from diesel cars and lean-burn cars as it appears to be the only viable technology to efficiently reduce the NO_x level to the required low levels, which can be expected to continually decrease. Recently, NO_x control by SCR in passenger diesel vehicles has begun to be implemented by a few OEMs, but it is expected to get much more widespread in the future. The advantage of this particular approach is that it allows the reduction of nitrogen oxides by using ammonia as the reductant, which is feasible even in oxygen-rich exhaust gases. The currently most studied alternative method for reducing the NO_x level is by an approach based on NO_x storage combined with catalytic removal—sometimes referred to as Lean NO_x Trap (LNT) [5]. However, due to

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disadvantages of LNT it is not very likely that the system will play a major role for the removal of NO_x in vehicles in the future.

Since the use of selective catalytic reduction of the nitrogen oxides by ammonia seems to be an attractive solution, we will go further into this reaction. The reaction can take place by one of the two following paths.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O\,(\text{fast SCR})$$

where the last reaction is known as fast SCR. To obtain fast reduction, it is most optimal that the ratio between NO and NO_2 in the exit gas is about 1:1, but even if there is less NO_2 present, the rate is still increased.

In SCR, two factors are very important, namely the use of a reductant and a catalyst. Here, we will consider the possibility of improving both of these and thereby obtain a new and improved SCR system. It has previously been shown that the best reductant for the process is ammonia. Direct use of liquid ammonia is possible for most stationary applications, where it is allowed to dose NH_3 directly from a liquid ammonia tank. However, the main problem by using a liquid ammonia tank is that it is considered too dangerous for automotives applications. Therefore, it has been necessary to try to find alternative methods of dosing ammonia for this purpose [6, 7]. The automotive industry has, so far, mainly considered urea as a safer—but indirect—method of storing and transporting the NO_x reductant for SCR. A schematic view of an SCR system based on urea as the ammonia source is shown in Fig. 1.

However, urea has several distinct disadvantages. First, the low storage capacity requires a large storage volume and there is a possibility of uncontrolled decomposition, and also blockings in the system are likely (e.g., by freezing or undesired decomposition in supply lines). In stationary applications, the commonly used commercial catalyst is based on vanadia and tungsta supported on titania. However, this catalyst has several important disadvantages such as being toxic and showing high activity for oxidizing SO_2 to SO_3. Moreover, the catalyst is characterized by a relatively low activity at low temperature and a low selectivity at higher temperatures. Therefore, it does not, in a lower perspective, appear to be a viable option in automotive applications; most interest is therefore centered on various transition metal-containing zeolite-based catalysts.

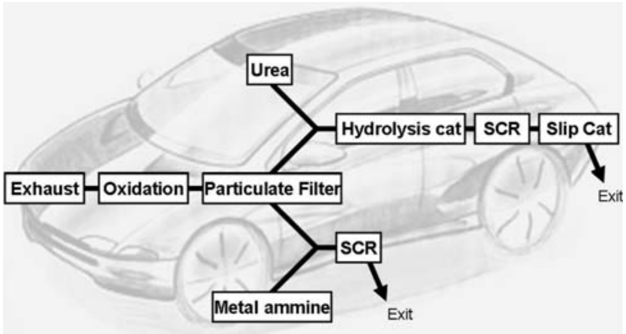


Fig. 1 SCR system in automotive application. After the particulate filter two different paths are shown. The upper path is the traditional urea based system while the lower part is based on metal ammines. It is clear that the metal ammine system is much simpler than the urea-based system

Thus, significant challenges within this field could be to find improved solutions for ammonia storage and to discover and develop improved SCR catalysts, since the technology is becoming more and more important in the future as the numbers of diesel cars are rapidly increasing, and the environmental concerns are growing as well.

1.1 Indirect Ammonia Storage Technologies

The best known reductant for SCR today is ammonia. Ammonia is produced by the Haber–Bosch reaction from hydrogen and nitrogen [8]. For commercial purposes, ammonia is transported as a liquid under pressure, which constitutes a safety risk in itself [9]. It is possible to handle liquid or aqueous ammonia directly for SCR in stationary application when taking appropriate precautions. In automotive applications, such as diesel or lean-burn gasoline cars, there is, however, an unacceptable risk connected with direct ammonia supply from a liquid tank. Since ammonia is generally considered too dangerous to use directly as reductant in SCR for automotive applications, other methods of storage need to be considered. This can for example be done using an indirect storage form.

The current method, which can be used to dose ammonia in automotive applications typically involve urea [7], as seen in Fig. 1. Compared to ammonia, urea is non-toxic, which makes it easier and safer to handle [10].

When urea is used as an ammonia source the following two reactions play an important role [2]:

$$(NH_2)_2CO \rightarrow NH_3 + HNCO\,(t > 160\,^{\circ}\mathrm{C})$$

$$HNO + H_2O \rightarrow NH_3 + CO_2\,(\text{hydrolysis catalyst}\, t \geq 200^{\circ})$$

The first of these reactions is the thermal decomposition of urea in which ammonia and isocyanic acid are formed. The decomposition reaction may also take place at lower rate in the storage tank if the temperature is higher than ~50 °C—but over the time span of months, this can lead to some ammonia formation directly in the storage tank itself. In the second reaction, the isocyanic acid is hydrolyzed to ammonia and carbon dioxide. For this reaction, a hydrolysis catalyst is needed as well [11] or the SCR catalyst has to be designed according to demands of carrying out hydrolysis as well as the desired SCR reaction. The conversion of isocyanic acid is well-studied and several catalysts have been investigated since it is of crucial importance for urea-SCR. It is well-known that several side reactions may take place in parallel during urea decomposition (i.e., the isocyanic acid undergoes a series of condensation reactions that lead to the formation of different solids), so the picture is far from as simple as expressed in the two reaction schemes above [12]. This leads to an uncertainty on the degree of conversion of urea to ammonia, which of course is undesirable since it is necessary to control the NH_3–NO_x ratio accurately.

There are several other challenges with indirect ammonia storage in form of urea. Normally, an aqueous solution containing 32.5 wt% urea (i.e., AdBlue®) is used. Such a solution is a corrosive liquid with high creeping capability and it has a high conductivity, which enables corrosion of a less noble "alloy" in fluid contact with a more "noble" alloy. Furthermore, a liquid solution as that described above has a freezing point of −11 °C. This can present a problem in cold areas in wintertime when the vehicle needs to be started up, since the frozen urea solution needs to be heated to above the melting point before the system is ready to operate. In order to make the urea solution work in the system, it needs to be injected into the exhaust by spraying it into the exhaust as an aerosol [13, 14]. It has been observed that it can be difficult to obtain a high mixing efficiency and furthermore solid deposits are often observed. This means that particles/solids, which can cause clogging are formed inside the system. Dosing limitations at low exhaust temperature have also been observed since incomplete urea conversion is seen below 200 °C. The exhaust gas temperature is reduced when using aqueous urea simply because of the required evaporation of water. As seen in Fig. 1 two extra catalysts are needed. It is necessary to use a hydrolysis catalyst (or a larger volume of SCR catalyst if the SCR also has to conduct the decomposition of isocyanic acid). Also, a slip catalyst may be needed in addition to the SCR catalyst as bursts of ammonia may form if solid deposits are released form the walls of the exhaust line when there is a sudden increase in exhaust temperature during acceleration. This catalyst is typically quite expensive due to the high metal prices of Pd and Pt, which are the most used for the other catalytic reactions.

In order to be of commercial interest, the effectiveness for removal of NO_x must be carefully considered. The $DeNO_x$ effectiveness versus the temperature is shown in Fig. 2, comparing NH_3-SCR, urea-SCR and LNT.

The LNT has a narrower operating window than the SCR system. The SCR catalyst may be active below 200 °C provided that the catalyst is not vanadia-based since these catalysts are already considered highly optimized and not appropriate for low temperature applications. The conversion of isocyanic acid over a hydrolysis catalyst (or the first part of the SCR catalyst) does not take place below 200 °C, which is problematic since passenger car or light-duty vehicles typically have exhaust gas temperatures below 200 °C during urban driving or stop-and-go traffic. Thus, SCR based on ammonia and not urea provides an opportunity to expand the $DeNO_x$ regime into lower temperatures than what is possible with the present urea-SCR solution. That would obviously increase the demand on the SCR catalyst as well as the ammonia source.

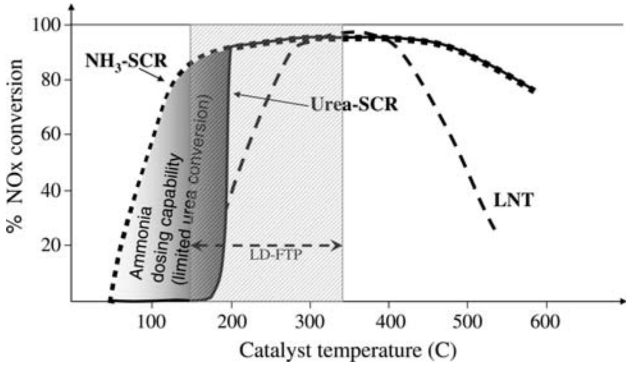


Fig. 2 $DeNO_x$ effectiveness vs. temperature (LNT and SCR curves adapted from: C. Lambert (DEER-2006) http://www.cemamerica.com/doeevents/DEER/Presentations/Thursday/TS5%20Emission%20Control%20Tech,%20Part%202/2006_DEER_Lambert.pdf

1.2 Solid Ammine Salts as a Source of Ammonia for SCR

As mentioned in the Introduction, it is important for the SCR reaction to find a safe and easy-to-handle reductant. Since ammonia has turned out to be the best reductant for the process it is necessary to find a simple and safe way to handle and dose it. Work has been done trying to establish ways to use urea for ammonia supply instead, but as described above this is far from optimal. In this section, we will focus on a new approach. Several requirements need to be met in order to develop a new and useful ammonia storage technology. In order for a system to become commercially important it is of crucial importance that the cost of the system can be kept low and that the safety at the same time can be kept high. Furthermore, it is important that the ammonia source has a high volumetric and gravimetric ammonia capacity, and that it is possible to carefully control the ammonia release, both regarding the release dynamics according to unpredictable driving patterns and to minimize the amount of "free" ammonia gas at a any given time. The fuel penalty should also be reasonable, which means that the operating power of the system should be kept low.

Another way to supply ammonia to the exhaust system, which has recently been suggested, is by using ammonia containing complexes, metal ammines, as the storage medium [15]. Such metal ammines have been known for a long time, and in many cases their synthetic paths are well-described, and their properties are well-characterized in the literature [16]. Examples of such metal ammines are $Mg(NH_3)_6Cl_2$, $Ca(NH_3)_8Cl_2$ and $Sr(NH_3)_8Cl_2$. As a powder, these complexes can be synthesised by a simple reaction of anhydrous metal chlorides with ammonia and the raw material is non-toxic and widely available salts.The following reversible absorption/desorption reactions and corresponding enthalpies describes the fundamental properties of $Mg(NH_3)_6Cl_2$ [15]:

$$MgCl_2(s) + NH_3(g) \rightarrow Mg(NH_3)Cl_2(s); \quad \Delta_f H = -87.0 kJ/mol\, NH_3$$

$$Mg(NH_3)Cl_2(s) + NH_3(g) \rightarrow Mg(NH_3)_2Cl_2(s); \quad \Delta_f H = -74.9 kJ/mol\, NH_3$$

$$Mg(NH_3)_2Cl_2(s) + 4NH_3(g) \rightarrow Mg(NH_3)_6Cl_2(s); \quad \Delta_f H = -55.6 kJ/mol\, NH_3$$

From these reaction schemes it is clear that the ammonia adsorption is exothermic while the release of ammonia from a safe storage cartridge is endothermic. In order to get a suitable degree of safety when using a metal ammine, the vapor pressure is an important parameter to examine. The vapor pressure over a given ammine salt can be determined experimentally or by calculations using the van't Hoff relationship.

$$\ln(p) = -\Delta H_{des}/RT + \Delta S_{des}/R$$

A low vapor pressure, and thereby a high degree of safety, at ambient temperatures is linked to a certain level of ammonia release energy. In order for a given metal ammine to be considered safe, the vapor pressure should at least be lower than 1 bar at room temperature. As an example, the complex $Mg(NH_3)_6Cl_2(s)$ has a vapor pressure of only 2.2 mbar at 300 K, which makes it extremely safe—almost 30.000 times less volatile than liquid ammonia [17]. The calcium and strontium salts also provide a desorption pressure lower than one bar at room temperature but releases the ammonia during operation at a temperature level lower than for the magnesium-based salt. Thus, the choice of salt is based on a compromise between desired operating temperature and power consumption. Using $Sr(NH_3)_8Cl_2$ enables the use of warm engine (80–90 °C) coolant to extract seven out of eight stored ammonia molecules.

The desorption of ammonia from metal ammines has been shown not to be limited by diffusion or to the presence of an activation energy but only the thermodynamic equilibrium and heat transportation.

Under normal conditions, the metal ammine complexes are polycrystalline powders with a low bulk density [18], and is as such difficult to handle. In order to use it in automotive application, it is important to minimize the required storage volume. It has been shown that the material can be compacted into solid units with a density similar to that of a non-porous, single crystal. Preparation of large units (1 kg or more) can be made with similar high density (AdAmmine, c.f. www.amminex.com). Dense units have the advantage that it forms nano-pores during desorption, which facilitates the complete desorption of ammonia from a large storage unit [19]. This is a very important factor because it means that the ammonia molecules can leave a solid "rod" without first having to travel through a long solid state diffusion path. The advantage of a system based on dense metal ammines is that it is safe and easy to handle, it does not take up much room and does not weigh much, relatively to the amount of ammonia that it is possible to generate from it. It has a well-defined capacity of ammonia and it is inexpensive. Furthermore, the only thing released from the complex when used in an automotive application is ammonia gas, meaning that blocking of the system which could be problematic in cases when urea is used, does not take place here. If comparing the properties of the storage units with liquid ammonia and urea several things can be noted. A 100 g $Mg(NH_3)_6Cl_2$ metal ammine block of approximately 80 mL in size can store 51.7 g NH_3, which equals 74 L of ammonia gas at 20 °C and 1 bar. The equivalent ammonia gas pressure to this would be almost 900 bars. If we compare the ammonia capacity of metal ammines and urea, a 3.1 times higher storage volume and 2.8 times higher mass is needed when using the latter. The demonstrated capacity is above 600 g NH_3 per liter storage volume. For comparison, liquid ammonia at 8–9 bar pressure at room temperature is 610 g/L. The AdBlue solution has an equivalent ammonia capacity of 200 g ammonia per liter.

For a normal mid-size passenger car, some 5 kg of NH_3 may be needed to last for one service interval of 25.000–30.000 km. This would require approx. 25 L (27.4 kg) AdBlue or 8 L (9.7 kg) of AdAmmine.

These data along with Fig. 1 show clearly that the metal ammines have a high potential as a direct source of ammonia for SCR in automotive applications.

1.3 Using Iron-Based Zeolites as SCR Catalysts

The most common commercially used catalyst for SCR today in stationary applications is based on vanadium. This catalyst works effectively at high temperature, but at low temperature the activity is relatively low in accordance with the needs in the stationary applications. At the same time it can be noted that the selectivity of the vanadium-based catalysts at high temperatures is low due to competitive ammonia oxidation, and the catalyst also shows some activity in the oxidation of sulfur dioxide to sulfur trioxide. These features alone make it interesting to develop and design a tailored catalysts e.g., for the novel system described above that features direct ammonia dosing. Furthermore, the vanadium-based catalyst is toxic, which can be a serious issue in automotive applications. Thus, there have been intense efforts to develop alternative SCR catalysts that have properties that are more suitable for automotive applications. In particular, it has been shown that transition metal containing zeolites can be used as efficient SCR catalysts and that they are in fact promising alternatives in vehicles [20–23]. Significant efforts have been devoted to investigating catalysts based on over-exchange Fe-ZSM-5, and this has indeed led to improved performances by using different experimental approaches [24–27]. Recently, it was shown that the reaction rate rates in these systems can be limited by the rate of diffusion in the zeolites. It was shown that introducing a mesoporous structure in the iron-containing zeolites can be a possible solution to this problem [28, 29]. In these hierarchical zeolite catalysts, the zeolite crystals features both the conventional microporous structure and in addition also a mesoporous structure. This both improves the accessibility of the active sites and makes it possible to achieve a better metal dispersion than the conventional systems, which can also be of significant importance [30].

2 Experimental

Experiments have been done in our laboratories with conventional ZSM-5, ZSM-12 [11] and BEA zeolites as well as mesoporous ZSM-5 and ZSM-12 zeolites. The major difference between ZSM-5 and ZSM-12 zeolites is that ZSM-5 has both straight and sinusoidal channels while ZSM-12 only has straight channels. Moreover, ZSM-5 has smaller pores than ZSM-12. BEA has a slightly more open porosity than ZSM-5 and a tridirectional pore network. This is expected to enhange the diffusion for BEA compared to the other zeolites.

2.1 Catalyst Preparation

The conventional zeolites can be prepared by standard methods and numerous different recipes are available both for zeolite synthesis and for iron incorporation. The mesoporous zeolites can be prepared using crystallization methods involving an auxiliary carbon matrix, which can be removed afterwards by combustion [31–33]. The iron can then be introduced onto the zeolites using simple incipient wetness impregnation techniques with an aqueous solution of iron salt, in our case iron(III) nitrate. After the impregnation step the samples were dried and then calcined. After the preparation the catalytic activity for DeNO$_x$ could be investigated.

2.2 Activity Test

The activity tests were carried out in a fix-bed reactor using 50 mg of the catalyst in each test. The tests were performed with a flow of 300 mL/min of a gas mixture consisting of 1,000 ppm NO, 1,100 ppm NH_3, 3.5% O_2 and 3% H_2O in N_2. The NO concentration was determined using a chemiluminescent NO–NO$_x$ gas analyzer [34, 35].

3 Results and Discussion

3.1 Catalytic Activity

Experiments have been done comparing the activity of otherwise similar mesoporous zeolites and conventional zeolites of ZSM-5 and ZSM-12 at different temperatures and the trend is clear in all cases—the activity is higher for the mesoporous zeolites than for the conventional. These results are published elsewhere [34, 35].

Another series of experiments have been done trying to establish the optimal iron content in the zeolite. The activity increases until it reaches a maximum and after that the activity decreases again. This trend can be seen in Fig. 3 for ZSM-5 and ZSM-12 [30, 35].

For the conventional ZSM-5 zeolite this maximum is found to be approximately 2.5 wt% while it for the mesoporous is about 7 wt%. Similarly for ZSM-12 the highest activity obtained at 4 wt% Fe for the conventional zeolite versus 6 wt% for the mesoporous zeolite.

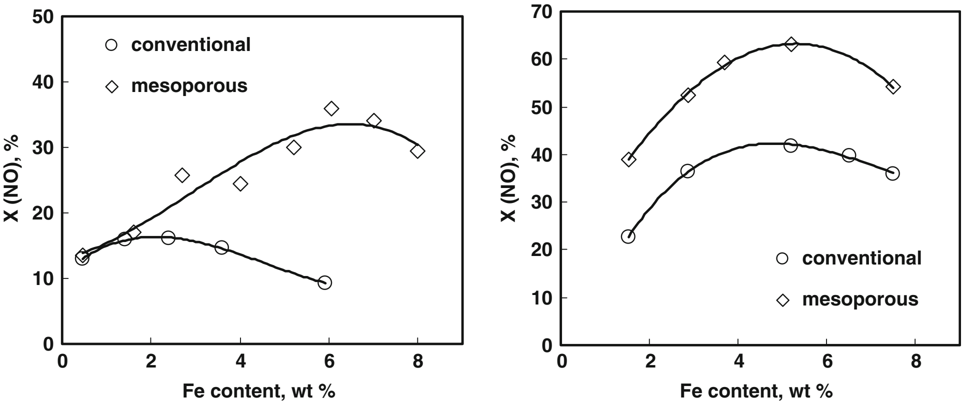
This difference in activity between conventionally and mesoporous zeolites can be ascribed to a better accessibility of the active sites in the mesoporous catalyst and/or to an improved dispersion or the iron-species made possible by the larger external surface area available. For the conventional BEA zeolite, the iron content seems to play a less important role. A small maximum in activity is found for loadings around 2.5–30 wt%.

vvIn our most recent experiments, we have tried to elucidate the influence of the zeolite structure type on the catalytic activity. For this, iron-containing BEA catalysts have been synthesised and compared with the analogous ZSM-5 and ZSM-12 catalysts. It is very clear that the activity of the conventional BEA catalyst is significant higher than the activity of ZSM-5 and ZSM-12 as shown in Fig. 4 [36].

Based on the work done by mesoporous ZSM-5 and ZSM-12 it might be possible to enhance the activity of BEA by introducing mesopores.

If we summarize the results we see that the zeolites are highly active at high temperatures compared to the

Fig. 3 Catalytic activities in the SCR of NO as a function of the iron content for respectively, Fe/HZSM-5 (*left*) and Fe/HZSM-12 (*right*). In the testing 50 mg catalyst is placed in a gas flow of 300 mL/min of a gas containing 1,000 ppm NO, 1,100 ppm NH_3, 3.5%O_2 and 3%H_2O in N_2 at 350 °C (adopted from ref. [11])



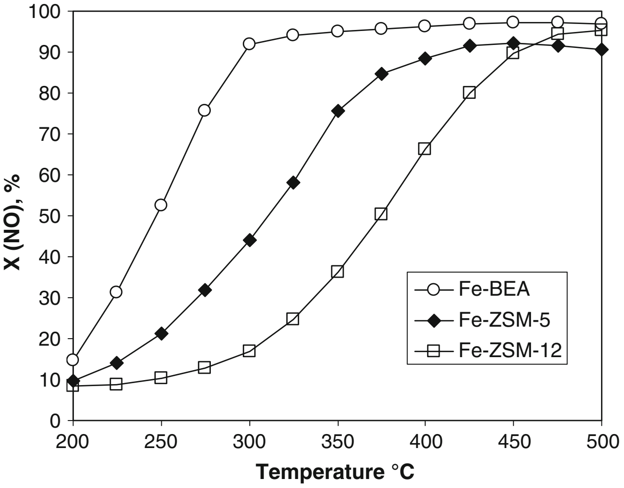


Fig. 4 Comparison of the catalytic activity of iron containing BEA, ZSM-5 and ZSM-12. In the testing 50 mg catalyst is placed in a gas flow of 300 mL/min of a gas containing 1,000 ppm NO, 1,100 ppm NH_3, 3.5%O_2 and 3%H_2O in N_2 and the conversion is measured at different temperatures

commercially used 3% vanadium on titania based catalysts and at the same time this type of zeolite catalysts are very stable. At temperatures as low as 400 °C the best of the mesoporous zeolites have activities in the same range as the commercial vanadium catalyst and the conventional BEA are even better than this. This means that these types of Fe-zeolite catalyst are very interesting commercially as catalysts in automotive applications in the future since the catalyst performance is improved at the same time as the poisonous vanadium is avoided. Furthermore it is possible to optimize the catalyst for NH_3 SCR to convert both NO and NO_2 in the exhaust stream, and the SCR rate is expected to increase if NO_2 is present as mentioned in the introduction.

NO might be converted to NO_2 as the first step in the SCR process. This step where NO is converted to NO_2 is the first step in the suggested mechanism and furthermore it is supposed to be the rate determining step [37, 38]. This is accomplished rather easy by leading the NO containing exhaust gas over an oxidation catalyst, using the excess oxygen from the exhaust from the diesel vehicle to the oxidation. The formed NO_2 can then be converted by the iron containing catalyst at even lower temperature with high activity. It has been shown that zeolites with narrow pores such as ZSM-5 are very good in the oxidation process of NO to NO_2 meaning that it is might be possible to use the same catalyst for both processes and therefore for the overall SCR of NO [39].

Further improvement of the catalyst can in some cases be performed by pre-treatment of the catalysts. It has previously been found that activation in a 1% NH_3 in N_2 at 500 °C for ZSM-5 and 600 °C for ZSM-12 can make the catalytic activity twice as big as without pre-treatment [34]. This can be explained by a reorganization of the iron oxide particles in the zeolite, where smaller and more active particles are formed. Besides, it is possible that the Fe^{3+} can be reduced to Fe^{2+} during the activation process, followed by a migration of the Fe^{2+} to ion-exchange position where it might be more active. However, there might are also other possible reasons. Finally, it is noted that all the iron-containing zeolites are highly active and selective at high temperatures compared to the commercially used catalysts based on vanadium and tungsta on titania.

3.2 A New System for Automotive SCR

As suggested in the previously paragraphs, it is possible to design a new system for the automotive SCR by combining solid-state ammonia storage with the use of an iron-containing zeolite catalyst as shown in Fig. 1. This system has several advantages such as safe handling of direct and precisely dosed ammonia as reductant from the metal ammine complex, high storage capacity, low cost of the metal ammines, and the simplicity of the system combined with a non-toxic catalyst and at the same time a significantly improved activity and selectivity. This new system is much simpler than the urea-based system, which has so far attracted most attention.

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