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Promoted Fe / ZSM-5 catalysts prepared by sublimation: de-NO_x activity and durability in H_2O-rich streams

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Fe / ZSM-5 catalysts with an Fe / Al ratio ≈ 1.0, were prepared by sublimation of $FeCl_3$ into H / ZSM-5. They display high activity and durability for the selective catalytic reduction of NO_x to N_2, both in dry and wet gas flows. These catalysts have now been modified by exchanging a second cation into the zeolite. Mere neutralization of zeolite protons by Na^+ lowers the selectivity for NO_x reduction to N_2, but the cations Ce^{3+} and La^{3+} act as true catalyst promoters. With isobutane as the reductant in a simulated vehicular emission gas, almost 90% of NO_x is reduced to N_2 at 350°C over the La-promoted catalyst. The presence of 10% H_2O in the feed does not impair the catalyst performance at high temperature; in the temperature region below 350°C it even increases the N_2 yield. The beneficial effect of La is due to its lowering of the catalyst activity for the undesired combustion of the hydrocarbon. No signs of zeolite destruction are evident after 100 h TOS in a wet gas flow at 350°C. Carbonaceous deposits causing a slight deactivation are easily removed in an O_2 / He flow at 500°C; this in situ regeneration fully restores the original activity.

Keywords: de-NO_x in lean burn emissions, SCR of NO_x, promoted Fe / ZSM-5, catalyst durability

1. Introduction

Most zeolite-supported metal catalysts that are active in the selective reduction (SCR) of NO_x ($NO + NO_2$) to N_2 are known to lose much of their activity in the presence of water vapor. However, recent results show that certain Fe-based catalysts are remarkably stable against H_2O. Lunin et al. [1] report that the SCR activity of Fe/ montmorillonite catalysts actually increased slightly upon adding 1% H_2O to the feed. Feng and Hall [2,3] demonstrate a high SCR activity and durability for excessively exchanged Fe / ZSM-5 at 500°C. This catalyst was found to retain its activity in the presence of 20% H_2O and 150 ppm SO_2. In a 2500 h durability test at 500°C, it does not undergo dealumination or structural breakdown, only minimal loss of activity was observed.

In a recent paper [4], we showed that the combination of high activity and high durability also pertains to Fe/ ZSM-5 catalysts prepared by a novel method based on the sublimation of a volatile iron compound into the acid form of the zeolite. With $FeCl_3$ and H / ZSM-5 we succeeded to obtain Fe / ZSM-5 catalysts with an iron loading of ∼ 1 Fe per Al. An important advantage of the sublimation method is that high metal loadings are easily obtained with zeolites of different origin, whereas conventional ion exchange from aqueous solution does not lead to high exchange levels. Even when applying the special exchange technique described by Feng and Hall [3], with oxalate ions stabilizing $(FeOH)^+$ ions, we were unable to achieve high Fe / Al ratios by ion exchange. It is conceivable that subtle differences in the history of the zeolite are responsible for the poor reproducibility of this preparation method.

Characterization by TPR of Fe / ZSM-5 samples prepared by sublimation shows that the iron, which is present as Fe^{3+} after calcination, is easily reduced to Fe^{2+} with H_2 or CO at about 410°C [4]. Conditions of vehicular emission from personal cars using a lean fuel / air ratio have been simulated by using a feed containing 0.2% NO, 0.2% iso-C_4H_{10}, 3% O_2 and at a space velocity of 42,000 h^{-1}. Under these conditions the new catalysts reduce about 80% of NO to N_2 at 350°C. Addition of 10% H_2O to this feed does not impair the yield of N_2, at temperatures below the maximum yield temperature, the rate of NO_x SCR is actually significantly higher with the wet feed. This unique response to H_2O vapor distinguishes the Fe-based de-NO_x catalysts from the widely studied metal-exchanged zeolite catalysts Cu / ZSM-5, Co / ZSM-5, Pd / ZSM-5, Ga / ZSM-5 or In / ZSM-5. In our previous paper [4] we presented arguments that the active species in the Fe / ZSM-5 catalysts is presumably a binuclear $[HO–Fe–O–OH]^{2+}$ ion.

In the present work, modification of the Fe / ZSM-5 catalysts by adding small amounts of a second metal has been studied. Our FTIR data [4] had shown that after sublimation of sufficient $FeCl_3$ vapor onto H / ZSM-5 all proton sites had disappeared. After washing, however, a small concentration of new protons was detected by their O–H band. Presumably they are the result of some hydrolysis of Fe ions or oxo-ions to neutral oxide particles and protons. It occurred to us that these protons could be used for a secondary ion exchange, which would enable us to incorporate small amounts of modifier cations into the catalyst.

A second objective of this work concerns the durability of the Fe/ZSM-5 catalysts. If they deactivate after extended times on stream, it will be of interest to know whether this deactivation is caused by an irreversible deterioration of the zeolite support or merely by deposition of a carbonaceous layer that can be easily volatilized by coke burn-off.

2. Experimental

The Fe/ZSM-5 catalyst was prepared by the method that was described in detail in our previous paper [4]. In brief, the parent ZSM-5 zeolite (UOP, lot#13923-60, Si/Al = 14.2, Na/Al = 0.67) was first transformed to H/ZSM-5 by conventional exchange with NH_4^+ ions, followed by calcination. $FeCl_3$ was then sublimed into the cavities of H/ZSM-5, where it reacts chemically with the acid sites according to the reaction: $H^+ + FeCl_3 = [FeCl_2]^+ + HCl\uparrow$. After all protons were replaced by $[FeCl_2]^+$, further $FeCl_3$ vapor passed through the zeolite without being retained. The $[FeCl_2]^+$ loaded sample was washed with water and calcined in flowing O_2 at 600°C. The finished Fe/ZSM-5 has an Fe^{3+} loading of 300%, i.e. Fe/Al = 1.

Modified samples, (Fe + M)/ZSM-5 (M = Na, Ce, La), were prepared by exchanging small amounts of a second cation into the Fe/ZSM-5. 2.0 g Fe/ZSM-5 was added to 200 ml 0.05 M $La(NO_3)_3\cdot 6H_2O$ (or 0.05 M $Ce(NO_3)_3\cdot 6H_2O$; or 0.5 M NaCl) solution. The slurry was stirred at room temperature overnight, vacuum filtered, washed, and air dried. The compositions of the (Fe + M)/ZSM-5 catalysts, as determined by ICP analysis, are given in table 1. One sample was prepared by neutralizing the residual protons in Fe/ZSM-5 with a pH = 10.0 NaOH solution. This sample will be labeled (Fe + Na)/ZSM-$5_{\text{alkal.}}$.

Selective catalytic reduction of NO with iso-C_4H_{10} was studied in a continuous flow reactor described previously [4,5]. A gas mixture of 0.2% NO, 0.2% iso-C_4H_{10}, 3% O_2 and when desired, 10% H_2O, was fed to 0.2 g of a catalyst at a rate of 280 ml/min, resulting in a gas hourly space velocity GHSV = 42,000 h^{-1}. The reaction temperature was increased stepwise from 250 to 500°C. The catalyst was preconditioned at each temperature for 30 min before products were analyzed by GC.

The yields of N_2, CO and CO_2 are defined as the percentages of reactant molecules (NO or isobutane) converted to these products; they have been calculated from the analysis of the gas phase effluent, disregarding any products retained by the catalyst. The "competitiveness factor" is defined in this paper as the molar consumption ratio of NO and isobutane.

H_2-TPR was used to characterize the state of the iron in the zeolite. Before the TPR runs, the samples were calcined in flowing O_2 at 600°C for 2 h. TPO was used to detect carbonaceous deposits on (Fe + La)/ZSM-5 after its use as a catalyst.

Table 1
Composition of (Fe + M)/ZSM-5 catalysts

Catalyst	M	M/Al	Fe/Al
Fe/ZSM-5	–	–	1.0
(Fe + Na)/ZSM-$5_{\text{alkal.}}$	Na	0.45	0.92
(Fe + Na)/ZSM-5	Na	0.04	0.95
(Fe + Ce)/ZSM-5	Ce	0.001	1.0
(Fe + La)/ZSM-5	La	0.003	1.0

3. Results

The yields of NO reduction to N_2 and of isobutane oxidation to CO and CO_2 in the absence of water vapor in the feed are shown in figure 1 as a function of temperature. All yields were identical for data collection at ascending or descending temperature. The temperature dependence of these yields is similar for all catalysts studied. First, the conversions increase with temperature, but when the iso-C_4H_{10} is nearly used up the yields of N_2 and CO pass through a maximum and further decrease with temperature. For most catalysts the maximum of the N_2 yield is achieved near 350°C. The CO_2 yield continues to increase with temperature while CO is oxidized in a secondary reaction.

Besides these common elements there are marked differences between individual modified catalysts. Whereas the temperature profiles of the iso-C_4H_{10} conversion are identical for Fe/ZSM-5 and (Fe + Na)/ZSM-5, the N_2 yield is distinctly lower over (Fe + Na)/ZSM-5. Since yields are defined as products of conversion and selectivity, it follows that the (Fe + Na)/ZSM-5 catalyst displays a lower SCR selectivity and thus a higher selectivity for the combustion of iso-C_4H_{10} with O_2, especially at high temperature. Over the neutralized sample, (Fe + Na)/ZSM-$5_{\text{alkal.}}$, the conversion of iso-C_4H_{10} is low and the N_2 yield is very low. Also the CO yield is lower over this than any other catalyst of this series.

The maximum N_2 yield is about the same over (Fe + Ce)/ZSM-5 and unmodified Fe/ZSM-5, however, the temperature at which this maximum is achieved over (Fe + Ce)/ZSM-5, 325°C, is 25°C lower than over Fe/ZSM-5. Likewise, the isobutane combustion profile over (Fe + Ce)/ZSM-5 is shifted to lower temperature. In contrast, over (Fe + La)/ZSM-5 the isobutane conversion profile is shifted to higher temperatures, and the CO_2 yield at any given temperature below 450°C is lower than for all other catalysts. Accordingly, a higher N_2 yield is achieved over this catalyst; it reaches its maximum value at 375°C.

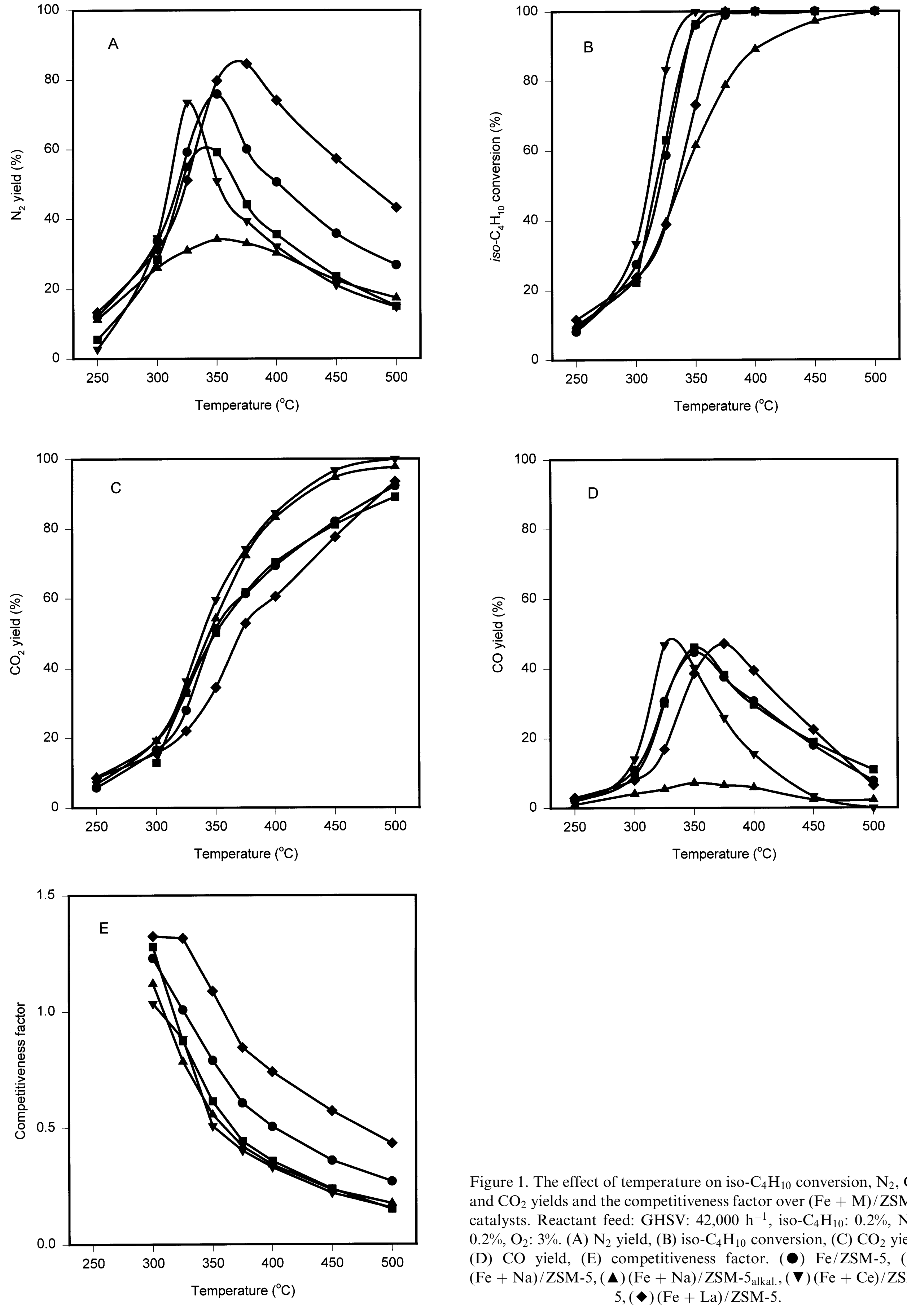

Figure 1. The effect of temperature on iso-C_4H_{10} conversion, N_2, CO and CO_2 yields and the competitiveness factor over (Fe + M)/ZSM-5 catalysts. Reactant feed: GHSV: 42,000 h^{-1}, iso-C_4H_{10}: 0.2%, NO: 0.2%, O_2: 3%. (A) N_2 yield, (B) iso-C_4H_{10} conversion, (C) CO_2 yield, (D) CO yield, (E) competitiveness factor. (●) Fe/ZSM-5, (■) (Fe + Na)/ZSM-5, (▲) (Fe + Na)/ZSM-$5_{\text{alkal.}}$, (▼) (Fe + Ce)/ZSM-5, (◆) (Fe + La)/ZSM-5.

Figure 1 also shows the competitiveness factor which decreases with temperature for all catalysts. (Fe + La)/ZSM-5 shows the highest value in the whole temperature region, indicating that this catalyst has the highest selectivity for NO reduction.

Figure 2 shows the H_2-TPR profiles of these catalysts. With one exception they all show one main reduction peak at about 420°C followed by several shoulders at high temperature; however, (Fe + Ce)/ZSM-5 has only one broad reduction peak. The H_2 consumption peak over Fe/ZSM-5, (Fe + Ce)/ZSM-5, and (Fe + La)/ZSM-5 under the main reduction peak gives a ratio of $H_2/Fe = 0.5$ indicating reduction of Fe^{3+} to Fe^{2+}. With these catalysts this first reduction step, clearly, has a lower activation energy than further reduction to Fe^0. However for (Fe + Na)/ZSM-5 and (Fe + Na)/ZSM-$5_{alkal.}$, the reduction steps are not discretely separated; when the reduction was stopped at 780°C, the signal had not returned to the base line, though the H_2/Fe ratio significantly exceeded the value of 0.5.

Figure 3 shows the selective catalytic reduction of NO in the presence of 10% H_2O over (Fe + La)/ZSM-5. Remarkably, the presence of 10% H_2O does not suppress the SCR activity, actually the presence of water vapor *enhances* the SCR of NO to N_2 in the temperature range below the maximum at 350°C. Likewise, the hydrocarbon conversion in this temperature region is increased by the presence of H_2O. At temperatures above 375°C the SCR of NO_x to N_2 is identical for the dry and the wet feed. However, the secondary oxidation of CO to CO_2 is suppressed by the presence of water.

A durability test was carried out over (Fe + La)/ZSM-5, as shown in figure 4. In the presence of 10% H_2O, this catalyst is quite stable during the 100 h of this test. Although the N_2 yield is ~ 10% lower after 100 h, this deactivation is not permanent. Upon exposing the used catalyst to an O_2/He flow at 500°C for 2 h, it fully regains its original activity. This indicates that some carbonaceous deposit is formed over the catalyst during its normal use. This assumption is confirmed by the TPO results of figure 5. The TPO profile of (Fe + La)/ZSM-5 after use for 10 h at 350°C with a wet feed shows a CO_2 evolution peak at 600°C.

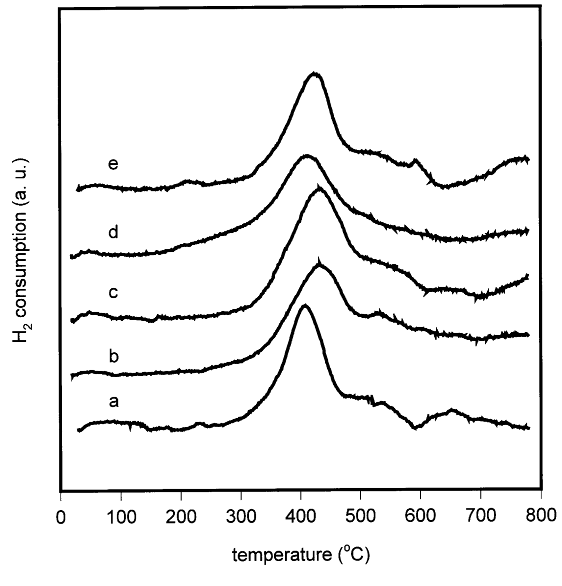

Figure 2. H_2-TPR profiles of calcined (Fe + M)/ZSM-5. (a) Fe/ZSM-5, (b) (Fe + Na)/ZSM-$5_{alkal.}$, (c) (Fe + Na)/ZSM-5, (d) (Fe + Ce)/ZSM-5, (e) (Fe + La)/ZSM-5 (5% H_2/Ar 30 ml/min, ramp rate 8°C/min).

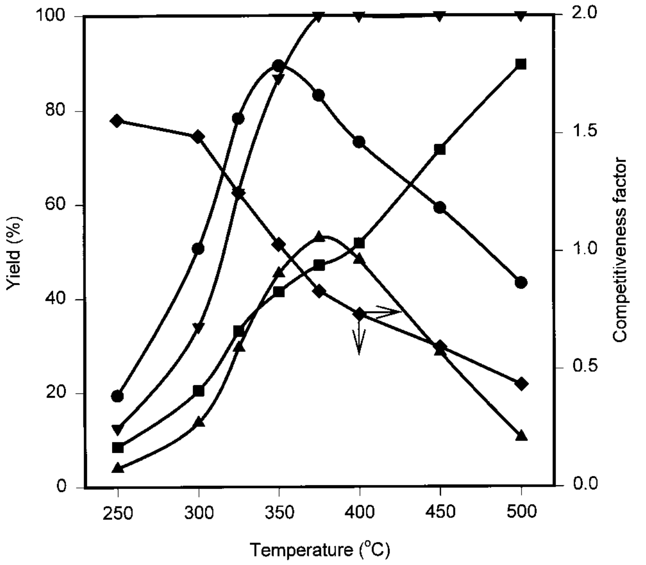

Figure 3. The effect of temperature on iso-C_4H_{10} conversion, N_2, CO and CO_2 yields and the competitiveness factor over (Fe + La)/ZSM-5 in the presence of H_2O. Reactant feed: GHSV: 42,000 h^{-1}, iso-C_4H_{10}: 0.2%, NO: 0.2%, O_2: 3%, H_2O: 10%. (●) N_2 yield, (■) CO_2 yield, (▲) CO yield, (▼) sum of CO_2 and CO yields, (◆) competitiveness factor.

4. Discussion

In our previous paper [4] an oxygen-bridged binuclear iron complex $[HO–Fe–O–Fe–OH]^{2+}$ was shown to be a plausible candidate for the active species in Fe/ZSM-5. It is consistent with two crucial findings:

(1) The Fe/Al ratio is 1, while all Fe is Fe^{3+}. Clearly, oxo- or hydroxo Fe complexes compensate the zeolite lattice charge.

(2) Reduction with CO, which is unable to reduce naked metal ions, leads to the same change in Fe valency from Fe^{3+} to Fe^{2+} as reduction with H_2. In our model, this means that the pair of iron ions loses their bridging oxygen atom during reduction with either H_2 or CO.

The binuclear complex ion is thought to be formed by hydrolysis of $FeCl_2^+$ ions or their dimers, when the sample is washed with water or exposed to H_2O vapor. Two exchange sites of the zeolite matrix are required to balance the charge of the bipositive $[HO–Fe–O–Fe–OH]^{2+}$ ion. The geometric conditions for the existence of

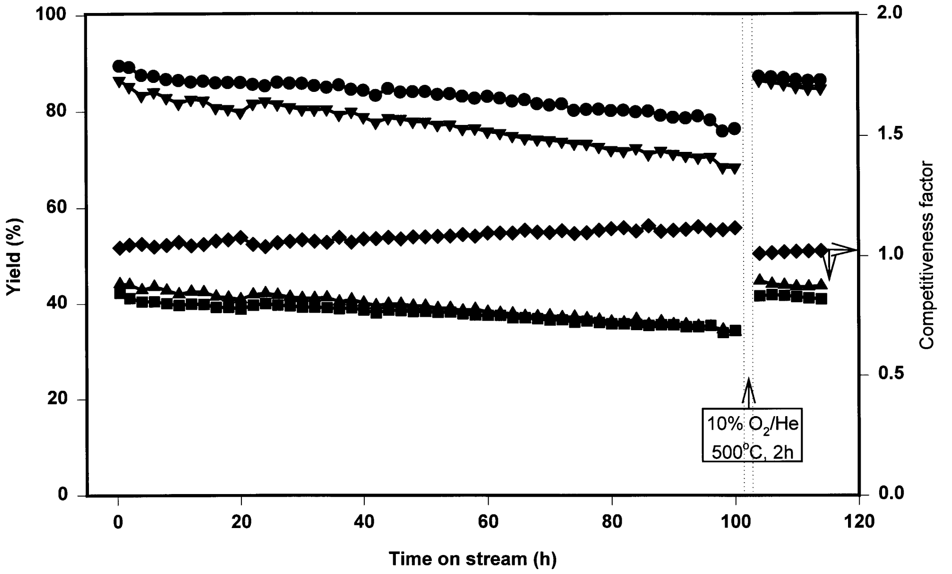

Figure 4. Stability and in situ regenerability of (Fe + La)/ZSM-5. Reaction conditions: temperature 350°C, other parameters as in figure 3. (●) N_2 yield, (■) CO_2 yield, (▲) CO yield, (▼) sum of CO and CO_2 yields, (◆) competitiveness factor.

two Al-centered tetrahedra in appropriate proximity inside ZSM-5 were analyzed by Feng and Hall [6]. These conditions are met for the Si/Al ratio of the zeolites used in the present work. The formation of $[HO–Fe–O–Fe–OH]^{2+}$ ions will also depend on the pH. At high pH, hydrolysis will result in more highly condensed species and colloidal gels or even precipitation of gelatinous FeOOH [7], whereas at low pH dissolution into Fe^{3+} ions is preferred.

After neutralizing Fe/ZSM-5 with NaOH at pH = 10.0, the ICP results in table 1 show that a considerable amount of sodium is present in the catalyst while only a small fraction of the iron has been replaced. As the sample was thoroughly washed, the Na^+ ions will be located at exchange sites and part of the Fe will be present as neutral iron (hydr-)oxide clusters. The TPR profile of (Fe + Na)/ZSM-$5_{alkal.}$ does not display the typical reduction peak of any of the known bulk iron oxides. This suggests that very small iron (hydr-)oxide clusters are formed in the cavities of the zeolite. Reduction of these clusters to Fe metal has been reported to require high temperature [8,9]. These clusters are not active for SCR reaction [9]. As was shown previously for Pd/ZSM-5, oxide clusters catalyze the combustion of the alkane with oxygen [10]. Iron oxide clusters are also likely to be active catalysts for the oxidation of CO to CO_2; indeed less CO is formed over (Fe + Na)/ZSM-$5_{alkal.}$. Formation of such clusters will not only lower the selectivity for the reduction of NO to N_2, but these clusters may also lower the conversion by blocking zeolite pores. As a result the N_2 yield will be very low, as found.

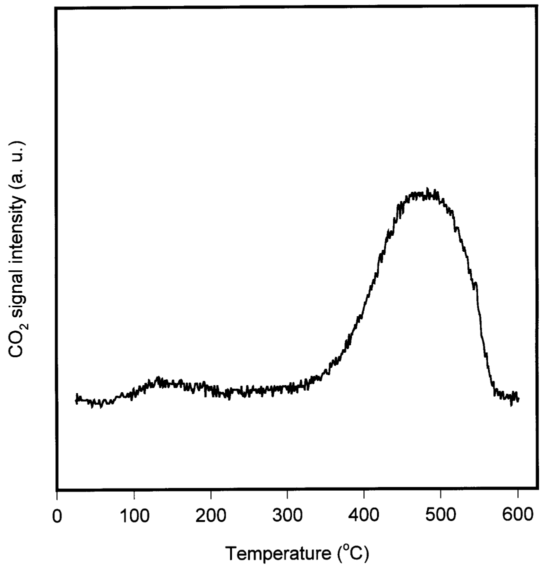

Figure 5. TPO of (Fe + La)/ZSM-5 catalyst after use with a wet feed for 10 h at 350°C. (5% O_2/Ar 60 ml/min, ramp rate 8°C/min).

When Fe/ZSM-5 is exchanged with NaCl, some iron will be displaced from the exchange sites, by consequence, the SCR activity is also found lowered. Although the exchange level is not very high, it may change the iron distribution on the zeolite as shown by its TPR profile.

With the preparation technique used here, the Ce or La content of the catalyst is very low, because only a small number of zeolite protons is available for exchange. Still, the effect of these modifiers on the catalytic activity is quite significant.

Ce^{3+} cations are likely to undergo hydrolysis and react with O_2 to form CeO_2 during calcination [11,12]. CeO_2 is well known for its oxygen storage and release capacity. The redox couple $2CeO_2 \rightleftharpoons Ce_2O_3 + \frac{1}{2}O_2$ may contribute to the SCR reaction, thus shifting the temperature of the N_2 yield maximum to a lower value. Ce^{3+} and CeO_2 have both been reported to enhance the SCR activity [13,14]. On the other hand, CeO_2 also catalyzes the reaction of hydrocarbons with O_2, thus lowering the SCR selectivity. Accordingly, (Fe + Ce)/ZSM-5 displays the lowest competitiveness factor among the catalysts studied here.

Among the modifiers studied in the present work, only lanthanum causes a marked increase in N_2 yield. Lanthanum addition is often used to improve the hydrothermal stability of zeolites, especially for zeolite Y. A binuclear $[La–(OH)_2–La]^{4+}$ complex ion is believed to be responsible for this improvement [15]. As La does not change its valency as easily as Fe does, one would expect that a small concentration of $[La–(OH)_2–La]^{4+}$ ions would have little effect on the catalytic action of the $[HO–Fe–O–Fe–OH]^{2+}$ ions. However, if the latter ions coexist with small Fe oxide clusters inside the zeolite, as was concluded above from the evidence for hydrolysis, it seems conceivable that La addition will result in the formation of mixed oxide clusters, containing both La and Fe ions. Such mixed oxides will have a lower oxidizing ability and thus be less active in catalyzing the oxidation of hydrocarbons and of CO to CO_2. Indeed, the present results show that the combustion activity of (Fe + La)/ZSM-5 is lower than that of Fe/ZSM-5. It appears, therefore, that the main action of La is to increase the selectivity of the SCR process by lowering the rate of the competitive combustion reaction between hydrocarbon and O_2.

The SCR activity of (Fe + La)/ZSM-5 is fully maintained in the presence of water vapor. At low temperatures, water vapor even enhances the reaction rate. This catalyst also shows good hydrothermal stability. The conclusion that La mainly lowers the catalytic activity for oxidizing hydrocarbons is in agreement with the observation that a carbonaceous deposit can form on these catalysts, as shown by TPO subsequent to the long duration test. Previously it was argued that the superiority of Fe/ZSM-5 over Cu/ZSM-5 in SCR can largely be contributed to the lower oxidation activity of Fe/ZSM-5; it is therefore not surprising that further attenuation of the undesired catalytic combustion leads to further improvement of the catalyst performance.

5. Conclusions

The catalytic activity of Fe/ZSM-5 is promoted by adding Ce^{3+} or La^{3+} to the catalyst. Notably a (Fe + La)/ZSM-5 catalyst with low La content shows high activity, selectivity and durability for the reduction of NO to N_2, even in the presence of 10% H_2O. Attenuated oxidation activity results in increased SCR selectivity and slight deactivation by carbonaceous deposits in 100 h TOS tests. The SCR activity can be fully restored by oxidative volatilization of this deposit, as the zeolite matrix apparently remains completely intact.

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