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KINETICS, CATALYSIS, AND REACTION ENGINEERING

Reaction Mechanism and Microkinetic Model for the Binary Catalyst Combination of In/ZSM-5 and Pt/Al₂O₃ for NO_x Reduction by Methane under Lean Conditions

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A significantly enhanced activity in NO_x reduction by methane was observed when a small amount (5 wt %) of Pt/Al₂O₃ or Mn₂O₃ was mechanically mixed with In/ZSM-5 in both dry and wet lean conditions. The highest NO conversions to nitrogen were over 98% with these novel multifunctional catalysts at 500 °C in dry conditions. The same activity was not reached with bimetallic Pt–In/ZSM-5, which showed the benefit of macroscale separation of active compounds (In separated from Pt or Mn₂O₃) in CH₄-SCR. Neither Pd/Al₂O₃ nor Ir/Al₂O₃ was able to promote NO_x reduction as a mechanical mixture with In/ZSM-5. Based on the surface intermediate (FTIR) and kinetic studies, a reaction mechanism on the binary combination of In/ZSM-5 and Pt/Al₂O₃ was defined. The presence of NO₂ enhanced the formation of partially oxidized, nitrogen-free, and nitrogen-containing methane derivatives. In the key reaction, the adsorbed NH₂ (amine) and NO form N₂ on In/ZSM-5. Pt/Al₂O₃ enhanced NO₂ formation, methane oxidation, CO oxidation, and surprisingly the reduction step to nitrogen. The increased formation of N₂O in two-component reactors revealed that N₂ was formed on In/ZSM-5 by HC-SCR reactions but also on Pt/Al₂O₃ by NO decomposition. The microkinetic model, based on defined surface reactions on separated indium and platinum sites on different supports, was able to predict all observed reactant and product concentrations in steady-state CH₄-SCR.

Introduction

The world's known natural gas sources are much wider than crude oil ones, being utilized for energy and transport. The combustion of methane emits a low amount of particulates and SO_x, as opposed to oil and coal. If the nitrogen oxides emissions formed in lean combustion could be reduced by primary or secondary methods, power plants and vehicles fueled with natural gas are a solution to pass the future emission limits. NO_x reduction by hydrocarbons (HC-SCR) on zeolite and oxide-based catalysts in lean conditions was studied widely in the 1990s.^{1–3} Copper, cobalt, indium, iron, and cerium on zeolites have shown the highest activities.

Different types of catalysts are active in NO_x reduction by methane than by other hydrocarbons. Methane is particular among hydrocarbons, because it is difficult to activate and oxidize. Co/ZSM-5 was first introduced as a selective catalyst for NO_x reduction by methane.⁴ Pd/H-ZSM-5 also showed high activity in the same reaction in the presence of oxygen.⁵ Cooperation with protonic and Pd²⁺ sites and the stabilization of Pd by protons on ZSM-5 have been proposed to explain the high activity on these catalysts.^{6,7}

A bifunctional catalytic reaction with indium and gallium on H-ZSM-5 in NO reduction by methane was proposed by Kikuchi et al.^{8–10} The NO oxidation reaction was proposed to occur on zeolitic sites and NO reduction on Ga or In sites. InO⁺ has been found to be the active compound on ZSM-5 to catalyze NO reduction. The activity was enhanced by adding Ir or Pt on In/H-ZSM-5. These metals promoted the NO oxidation step to NO₂, which is generally accepted to be the main limiting step in NO_x reduction by hydrocarbons.^{11–13}

Two-component catalysts for NO_x reduction by various hydrocarbons have shown high activities as following combinations: Ce/ZSM-5 or Sn/ZSM-5 and Mn₂O₃, Au/Al₂O₃ and Mn₂O₃, and Al₂O₃ and Pt/SiO₂.^{14–16}

Bimetallic and two-component catalysts in CH₄-SCR have also been recently studied widely: In–Ce on ZSM-5 or mordenite,^{17–19} In–Fe₂O₃/H-ZSM-5,^{20,21} Pd–In/ZSM-5,²² Pt–In/Ferrierite,^{23,24} Co–Pt/ZSM-5,²⁵ Co–Pt/mordenite,²⁶ Pt–Co/Ferrierite,²⁷ Pd–Co on H-ZSM-5, H-mordenite, H-Beta or H-Ferrierite,^{28,29} Pt–H/Ga/ZSM-5,³⁰ Pd–Co/Ferrierite,³¹ Pt–Co/Ferrierite,³² In/H-ZSM-5+In₂O₃,³³ In/H-ZSM-5+Al₂O₃,³⁴ In/H-ZSM-5+CeO₂,³⁵ H-ZSM-5 or H–Y+Co/Al₂O₃,³⁶ and Co/NaX–CO.³⁷ Thus, the active compounds (Pt, Pd, Ir) to promote oxidation reactions have been usually added on the same zeolite supports with CH₄-SCR catalysts (In, Co, Pd) in the earlier studies.

In/ZSM-5 was found to be active in CH₄-SCR in our earlier study,³⁸ where the catalyst state in reaction conditions were examined in detail. A reaction mechanism-based kinetic model

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Table 1. Composition and Surface Area of the Catalysts

| catalyst | metal loading (wt %)/HR | surface area HR(m ² /g) |
|-----------------------------------|----------------------------|---------------------------------------|
| In/ZSM-5 | 7.2 | 269 |
| Pt-In/ZSM-5 | Pt 0.28+In 7.2 | 252 |
| Pt/Al ₂ O ₃ | 5.6 | 216 |
| Pd/Al ₂ O ₃ | 3.0 | 222 |
| Ir/Al ₂ O ₃ | 5.5 | 234 |
| In/Al ₂ O ₃ | 3.4 | 216 |
| Mn ₃ O ₄ | 99.9% oxide | 1.0 |

was introduced, and the actual reductant on In/ZSM-5 was proposed to contain N–C or N–H bonding. In the present study, NO_x reduction by methane has been examined by activity, surface characterization, and kinetic modeling studies using new types of combinations of In/ZSM-5 with second catalysts. Physical mixtures were studied to see if macroscale-separated active sites might promote reactions. The catalyst supports and active metals, which are known to possess particular abilities for CH₄ or NO activation, were investigated systematically to enhance the limiting steps in NO reduction to nitrogen (N₂) with In/ZSM-5.

Experimental Section

In/ZSM-5 (Tosoh, Si/Al₂ = 23) was prepared by an ion-exchange method, where washed, unprotonated ZSM-5 was ion exchanged in a 0.04 M In(NO₃)₃ solution for 24 h at 80–90 °C, dried, and calcined at 500 °C for 3 h.³⁸ The ion-exchange ratio of In³⁺ was calculated to be 140% on ZSM-5 by quantitative rf (Seiko Instruments SEA2010) and plasma analysis.

Alumina consisting mainly of high surface area γ -Al₂O₃ was prepared by the sol–gel method.³⁹ Platinum, palladium, iridium, and indium were impregnated by a pore-filling method using Pt(NH₃)₄Cl₂, Pd(NH₃)₄(NO₃)₂, IrCl₄·H₂O, and In(NO₃)₃·3H₂O as precursor salts in aqueous solutions. The molar ratio of Al/M (M = Pt, Pd, Ir, and In) was 65 in the samples. The catalysts were dried at 110 °C overnight and calcined at 600 °C for 3 h. The same impregnation method was also applied for the preparation of Pt–In/ZSM-5, where Pt was impregnated on In/ZSM-5 as described above. Mn₃O₄ was a commercial powder (Soekawa, 99.9%). Powder samples were screened to the particle size fraction below 250 μ m to homogenize powders and to decrease mass-transfer limitations in the experiments. The mixtures of In/ZSM-5 and an oxidation catalyst were prepared by mixing powders softly together. The composition and surface area (BET³⁸) of the catalysts are summarized in Table 1.

The steady-state activity of the powder catalysts was measured in a quartz flow reactor (diameter, 8 mm) using simulated exhaust gases containing ~1000 ppm NO_x (NO or NO₂), 1000 ppm methane, and 10% oxygen in helium at 200–600 °C. In a few experiments, 500 ppm N₂O also replaced NO_x and 8% water was present in the gas mixture. In these standard experiments, with one or two catalyst components, the total gas flow rate (*F*) was 66 mL/min and the amount of sample (*W*) was 0.2 g resulting in *F*/*W* of 20 dm³ h^{−1} g^{−1}. The composition of product gas (N₂, N₂O, NO, NO₂, CO₂, CO, and CH₄) was analyzed using two gas chromatographs (Shimadzu GC 8A with Porapak Q and Molecular sieve 5A columns) and a chemiluminescence NO_x/NO analyzer (Shimadzu NOA-305A).⁴⁰ In the kinetic experiments, the conditions were varied as follows: 500–1000 ppm NO, 500–2500 ppm CH₄, 4–10% O₂, and 20–240 dm³ h^{−1} g^{−1} *F*/*W*, which was varied by the amount of catalyst (*W*). The number of measurement points by temperature and concentrations was 63 for In/ZSM-5 and 61 for In/ZSM-5+Pt/Al₂O₃

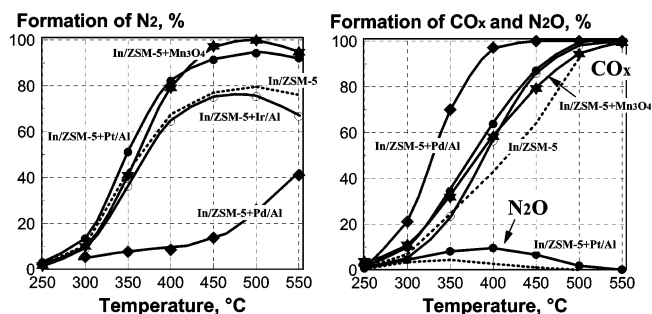


Figure 1. Activity of the physical mixture of In/ZSM-5 and the second compound in dry conditions. In/ZSM-5:Al₂O₃ = 19:1. (Feed: 1000 ppm NO, 1000 ppm CH₄, 10% O₂, balance He. *F*/*W* = 20 dm³ h^{−1} g^{−1}).

in the kinetic parameter evaluations. The deactivation had no role in these kinetic experiments, because the activity was the same in the standard experiment at the beginning and end of the activity experiments.

In situ static and dynamic FTIR studies were made for In/ZSM-5,³⁸ and In/Al₂O₃,⁴⁰ in our earlier study and the same methods were also applied for the pressed sample discs of catalyst combinations using NO–CH₄–O₂–He gas mixtures at 200–480 °C. The gas mixture in dynamic studies was the same as in the activity experiments, which enabled us to combine the analysis of gas and surface components during the reactions.

Results and Discussion

Catalytic Activities. (1) Single-Component Catalysts. The catalytic activities were compared by N₂ formation, not by NO_x measurement, which eliminates the effect of side products in activity comparisons. The unprotonated In/ZSM-5 showed a high activity in CH₄–SCR in our earlier studies³⁸ and was used as the base catalyst in the combinations.

The properties of alumina-based catalysts were examined for CH₄ and NO activations, since the purpose of this study was to combine these catalysts with In/ZSM-5 as a physical mixture, where another active metal was not supported on In/ZSM-5 but on separate Al₂O₃ particles. In/Al₂O₃ had a low activity in CH₄–SCR (maximum 8% of N₂ in dry mixture) and ZSM-5 was necessary to support indium active for NO_x reduction.

Pd/Al₂O₃ with a high Pd loading (3%) was completely a methane oxidation catalyst without any activity for NO_x reduction. Pd/Al₂O₃ did not have any activity for NO_x reduction by methane, even if NO₂ was in the feed gas instead of NO. The CH₄ light-off temperature (*T*₅₀) with Pd on sol–gel alumina was 290 °C in dry conditions. It was reported that alumina-based precious metal (Pd, Pt, Rh) catalysts are very efficient in NO reduction in the presence of methane in stoichiometric and rich conditions but not in lean conditions.⁴¹ Pd catalysts are very active in complete methane oxidation in lean conditions with the wide range of Pd loadings.⁴² The activity of Pt/Al₂O₃ in CH₄–SCR was not examined alone in this stage, but Pt catalysts are generally known to have a superior activity in oxidizing NO to NO₂.

(2) Two-Component Catalysts: In/ZSM-5 with Pt/Al₂O₃, Pd/Al₂O₃, Ir/Al₂O₃, and Mn₃O₄ in Dry Conditions. The mechanical mixtures of In/ZSM-5 with Pd/Al₂O₃, Ir/Al₂O₃, Pt/Al₂O₃, or pure Mn₃O₄ were examined to increase the NO_x efficiency by enhancing the limiting reaction steps (Figure 1). The combinations tried in this study differ from the known published combinations in HC–SCR (see Introduction). These good oxidation catalysts should increase NO oxidation to NO₂ (like Pt, Ir, and Mn₃O₄) and the oxidation of methane (like Pd)

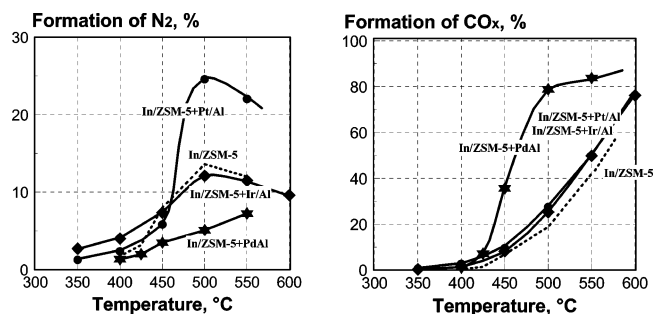


Figure 2. Activity of the physical mixture of In/ZSM-5 and the second compound in wet conditions. In/ZSM-5:M/Al₂O₃ = 19:1. (Feed: 1000 ppm NO, 1000 ppm CH₄, 10% O₂, 10% H₂O, balance He. *F/W* = 20 dm³ h⁻¹ g⁻¹).

in the reaction zone. However, NO reduction to nitrogen was expected to proceed mainly on In/ZSM-5.

The addition of a low amount (5%) of Pd/Al₂O₃ to In/ZSM-5 (mixing ratio 19:1) destroyed the NO_x reduction capability, because Pd/Al₂O₃ had an excessively high activity for methane oxidation in the absence of water. The addition of Ir/Al₂O₃ to In/ZSM-5 (19:1) had a slight negative effect on the NO_x conversion. The promoting second compound was found, the low-temperature CH₄ oxidation to CO₂ was avoided when 5% Pt/Al₂O₃ was mixed together with In/ZSM-5, and the maximum NO conversion to nitrogen was improved from 80 (In/ZSM-5 only) to 93%. Thus, very high activity compared to the known bimetallic concepts (i.e., Pt–In/ZSM-5) was found by dividing indium and platinum physically on separate carriers: 7.2% In on ZSM-5 and 5.6% Pt on sol–gel prepared Al₂O₃ with the mixing ratio of 19:1.

The highest measured NO conversion to nitrogen was 98% on In/ZSM-5+Mn₃O₄ (19:1). The presence of Mn₃O₄ promoted NO reduction to nitrogen even if the methane oxidation activity was similar, e.g., with the mixture of In/ZSM-5+Ir/alumina. Mn₃O₄ was attempted for CH₄-SCR because it was found as a promoting catalyst for propene-SCR in our earlier study.³⁹ Mn₂O₃ has shown similar promotion in other studies.⁴³ The use of Mn₃O₄ instead of other manganese oxides was based on our stability evaluations. According to the thermodynamic calculations, MnO₂ is stable up to 250 °C, Mn₂O₃ up to 450 °C, and Mn₃O₄ up to 750 °C in practical lean conditions (10% O₂). The irreversible phase change (Mn₂O₃ → Mn₃O₄) in reaction conditions is very probable, if Mn₂O₃ had been used in this application. Mn₃O₄ sufficiently catalyzed NO₂ formation, but did not excessively enhance the complete methane oxidation. Thus, the use of Mn₃O₄ with In/ZSM-5 resulted also in the two-component catalyst that showed even a higher activity than In/ZSM-5+Pt/Al₂O₃, and the thermal stability of Mn₃O₄ is better than other studied metal oxides (i.e., Mn₂O₃, CeO₂, and In₂O₃) in combinations.

(3) Two-Component Catalysts: In/ZSM-5 with Pt/Al₂O₃, Pd/Al₂O₃, and Ir/Al₂O₃ in Wet Conditions. In the presence of water, the physical mixture of In/ZSM-5 and Pt/Al₂O₃ (19:1) showed clearly higher NO reduction to nitrogen (24% at 500 °C) than In/ZSM-5 (Figure 2). No significant differences were detected between In/ZSM-5 and In/ZSM-5+Ir/Al₂O₃. The addition of Pd/Al₂O₃ with the mixing ratio of 19:1 clearly decreased NO conversion to nitrogen and also increased the methane oxidation rate in wet conditions in comparison to In/ZSM-5. The comparison between Pt and Pd catalysts with In/ZSM-5 showed that reactions other than methane activation itself are more important in reaching higher NO_x efficiencies.

(4) Effect of Pt Addition Method and Pt Amount. Kikuchi and Yogo¹⁰ successfully added Ir and Pt onto In/H-ZSM-5 to

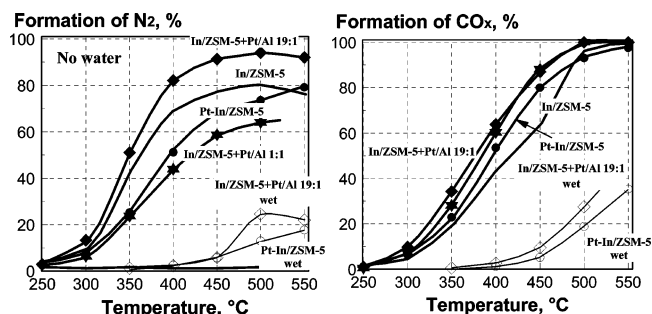


Figure 3. Effect of the Pt/Al₂O₃ amount in the mixture of In/ZSM-5+Pt/Al₂O₃ and the activity comparison of In/ZSM-5+Pt/Al₂O₃ with Pt–In/ZSM-5 in dry and wet conditions (Feed: 1000 ppm NO, 1000 ppm CH₄, 10% O₂, 0/10% water, balance He. *F/W* = 20 dm³ h⁻¹ g⁻¹).

enhance NO oxidation to NO₂. However, the activity of the original In/ZSM-5 decreased with the addition of platinum in our experiments (Figure 3), although the conversion to nitrogen with Pt–In/ZSM-5 increased continuously up to 550 °C (79%). Thus, Pt added on In/ZSM-5 was not able to increase the activity. The original state of zeolite (protonated in earlier and unprotonated in our study), different precursors, active metal loadings, preparation methods, and different reaction conditions are likely the explanations for the detected differences compared to earlier observations.¹⁰

Even if the ratio of In/Pt was the same (27) in Pt–In/ZSM-5 and in the mechanical mixture of In/ZSM-5 and Pt/Al₂O₃, the activities were different. The Pt addition both as Pt/Al₂O₃ and Pt–In/ZSM-5 enhanced methane oxidation compared to In/ZSM-5 at 350–550 °C. However, the presence of Pt/Al₂O₃ particles in the same catalyst bed with In/ZSM-5 particles significantly promoted NO reduction to nitrogen. The difference in NO₂ formation is not an explanation, because NO₂ formation should be roughly similar on both Pt/Al₂O₃ and Pt/ZSM-5 according to our experience.⁴⁴ In the catalyst bed, Pt is more homogeneously distributed in Pt–In/ZSM-5 than in the binary mixture.

When the weight ratio of In/ZSM-5:Pt/Al₂O₃ was 1:1 (50 wt % Pt/Al₂O₃ in the mixture), NO conversion to nitrogen was decreased compared to In/ZSM-5 (Figure 3). Even if almost no differences were detected in methane oxidation to CO_x, an excessive amount of Pt/Al₂O₃ had a negative effect on NO_x reduction. However, the lower amount of In/ZSM-5 (0.1 g) in the combination in the experiment compared to only In/ZSM-5 (0.2 g) was a reason for the activity decrease.

In the kinetic experiments, the highest NO conversions to N₂ (>99%) with the mixture of In/ZSM-5 and Pt/Al₂O₃ (19:1) were detected at 450–500 °C when CH₄/NO was highest (C₁/NO = 2500 ppm/500 ppm = 5). This maximum was significantly higher than with only In/ZSM-5 (maximum 90%). The promoting effect of increasing oxygen concentration was observed in the range of 4–10%.

Based on their stabilities and particle sizes, it is assumed that In/ZSM-5 and Pt/Al₂O₃ will not disturb each other chemically or sterically in mixtures. Therefore, the combination of In/ZSM-5 and Pt/Al₂O₃ (19:1) was selected for further surface and kinetic studies.

Reaction Experiments with Possible Intermediates. Reactivities of NO₂ and N₂O. The activity of In/ZSM-5 was improved near to the same level with In/ZSM-5+Pt/Al₂O₃ (19:1), when NO was changed to NO₂ in feed (Figures 1 and 4). Thus, NO oxidation was a limiting reaction on In/ZSM-5. The change from NO to NO₂ in feed had no effect on NO_x conversion in the case of In/ZSM-5+Pt/Al₂O₃ (19:1), which

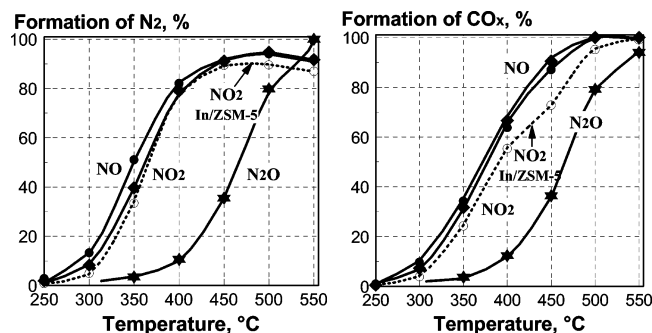


Figure 4. Reduction of 1000 ppm NO, 1000 ppm NO₂ and 500 ppm N₂O to nitrogen by 1000 ppm methane on the catalyst mixture of In/ZSM-5 + 5.6% Pt/Al₂O₃ (19:1) in the presence of 10% oxygen in dry conditions. In/ZSM-5 with NO₂ as a reference (dotted line).

confirmed that NO oxidation was no more a limiting step, when the amount of Pt/Al₂O₃ was adequate.

Nitrous oxide (N₂O) was not decomposed but preferably reduced by methane to nitrogen on In/ZSM-5³⁸ or In/ZSM-5+Pt/Al₂O₃ ($T_{50} = 470$ °C). The low amount of Pt/Al₂O₃ with In/ZSM-5 did not enhance N₂O removal. Pt/Al₂O₃ alone was poorer in N₂O decomposition ($T_{50} > 500$ °C) and reduction than In/ZSM-5. N₂O removal was complete on these catalysts above 600 °C. It is clear that the N₂O route is not a key to the enhanced activity in these catalyst mixtures. To decompose NO to nitrogen in the absence of oxygen, the temperature had to be over 600 °C on In/ZSM-5.³⁸ Therefore, oxygen and lean conditions are needed to oxidize methane partially to intermediates and NO to NO₂, which operates as a reactive oxidizer in the methane activation.

The formation of nitrous oxide was 2–3 times higher on In/ZSM-5+Pt/Al₂O₃ (19:1) than on In/ZSM-5, when NO or NO₂ reacted with CH₄ in lean feed gases (Figure 1). The presence of 10% water in the feed gas slightly suppressed the selectivity to form N₂O. The increase in N₂O formation was significant, even if Pt is well-known as a catalyst to dissociate NO and produce N₂O in lean NO_x reduction.⁴⁵ This observation supports the theory that NO was not reduced only on In/ZSM-5 but also on Pt/Al₂O₃, because nitrogen and nitrous oxide are produced simultaneously when adsorbed N reacts with adsorbed N or NO.⁴⁶ Thus, a mixture of N₂ and N₂O is always formed on Pt catalysts in HC- and NH₃-SCR. The N₂O decomposition studies showed that formed N₂O is hardly removed below 450 °C. N₂O might be formed in the sequential surface reactions, where reducing intermediates were formed on In/ZSM-5 sites, and drifted on Pt/Al₂O₃, where N₂ and N₂O were formed. Because

of the rare physical contact points between separate active sites, the intermediates could reach the Pt sites by short-lived gas-phase compounds or surface migration.

The NO₂ formation rate was higher on In/ZSM-5+Pt/Al₂O₃ than on In/ZSM-5 in dry and particularly in wet conditions, which was expected due to the high NO₂ formation activity of Pt/Al₂O₃. The highest NO₂ concentrations in outlet were detected at low temperatures, where consequent reactions of NO₂ were not yet initiated or completed. Alumina support has a role in the reactions, because it has a higher capacity than zeolites for nitrate adsorption at low temperatures. Ren et al.³⁴ found that Al₂O₃ promoted NO₂ formation and methane activation on In/H-ZSM-5+Al₂O₃ (~2:1). The presence of Pt/Al₂O₃ with In/ZSM-5 also catalyzed NO₂ reaction back to NO, and the equilibrium in respect to the NO/NO₂ ratio was reached at lower temperatures. Thermodynamically, NO₂ is the main nitrogen oxide at 250–350 °C in lean conditions. No NO₂ was formed when N₂O was in the feed gas, which proved that N₂O is not able to react to NO and NO₂ in these conditions. This transformation (N₂O → NO_x) needs high temperatures (>1000 °C) analogous to how NO is originally formed thermally in combustion.

No CO was detected in outlet gases in the presence of Pt/Al₂O₃, which is known as a very efficient CO oxidation catalyst. CO is not an important gas-phase intermediate in HC-SCR reactions,³ but it could inhibit the adsorption of other reactants. Pt catalyst might promote CH₄-SCR by preventing CO inhibition.

Characterization of Binary Catalyst Compositions and Surface Compounds. (1) State of Indium and Surface Area. Based on our earlier studies with In/ZSM-5, InO⁺ and In₂O₃ were detected (XRD, XPS) and proposed to be present on In/ZSM-5 in reaction conditions.³⁸ Because the ion-exchange ratio in In/ZSM-5 was 140%, the presence of free In₂O₃ on ZSM-5 was evident. The addition of Pt on In/ZSM-5 slightly decreased the surface area.

(2) Surface Species by Dynamic FTIR Studies. FTIR responses were detected in the reaction chamber having a mixture of In/ZSM-5+Pt/Al₂O₃ (19:1) in flowing NO–CH₄–O₂–He, CH₄–O₂–He, and He gas mixtures in a heating ramp from 200 °C up to 480 °C. The difference spectra were calculated by subtracting these single spectra from each other. This was a method of eliminating the effect of rising temperature (desorptions) and finding the intermediates. The difference spectra showed that the presence of NO with CH₄, O₂, and He generated new, observable peaks, which can be designated as

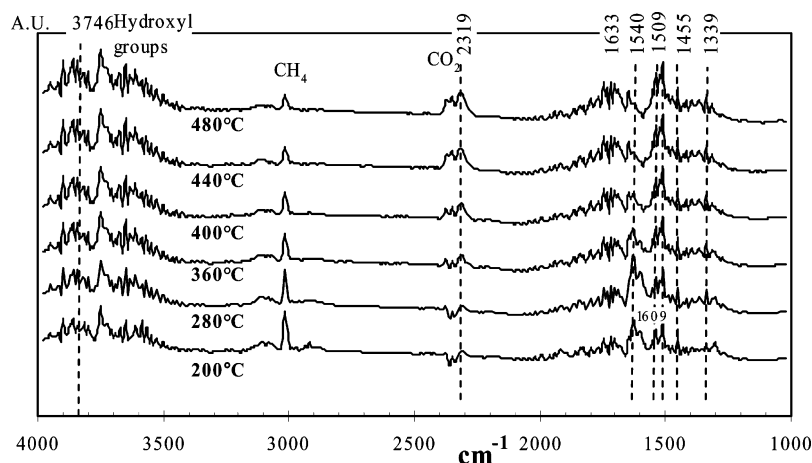


Figure 5. Difference spectra NO–CH₄–O₂–He minus He on In/ZSM-5 + Pt/Al₂O₃ (19:1) in flowing gas at 200–480 °C.

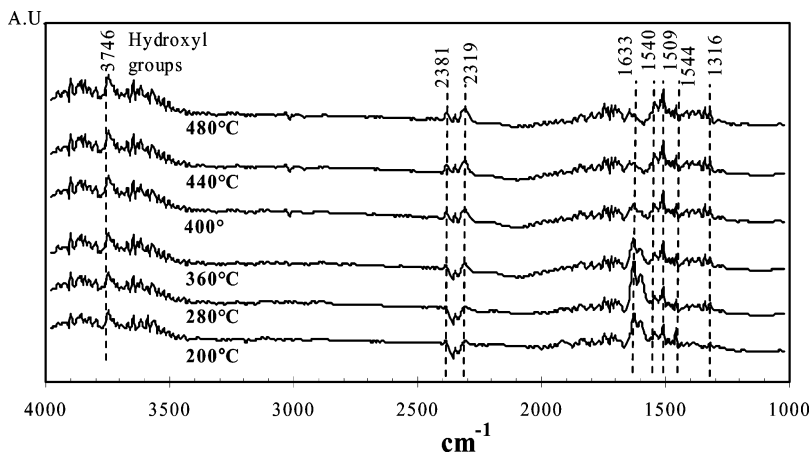


Figure 6. Difference spectra $\text{NO}-\text{CH}_4-\text{O}_2-\text{He}$ minus $\text{CH}_4-\text{O}_2-\text{He}$ on $\text{In/ZSM-5} + \text{Pt/Al}_2\text{O}_3$ (19:1) in flowing gas at 200–480 °C. (A) NRO mechanism (the experimental data set explained by the model with the R^2 value of 96%). (B) NH_2 mechanism (the experimental data set explained by the model with the R^2 value of 99%).

nitrogen-free and nitrogen-containing carbonaceous compounds (Figures 5 and 6). Thus, the presence of NO_x activates CH_4 to form $\text{H}-\text{C}-\text{O}$ compounds, whose FTIR intensities were much weaker in the $\text{CH}_4-\text{O}_2-\text{He}$ flow. Many bridged carbonaceous compounds possibly also containing nitrogen can be present at 1600–1450 cm^{-1} .³⁸ The presence of NO_x was also required to modify hydroxyl groups in the range of 3600–3900 cm^{-1} . The hydroxyl groups can be bridged to Si or Al. Hydrophobic, Brønsted acid sites depend on these hydroxyl groups and are important in activating hydrocarbons to HC-SCR reactions.^{47–49}

The peak pair at 1601 and 1632 cm^{-1} matched to the intense peaks caused by gaseous NO_2 . The peak of 2319 cm^{-1} matched also to the satellite peak of gaseous NO_2 , but the peak height was increased as a function of temperature and thus the peak of 2319 cm^{-1} might also be related to other compounds. These peaks were not observed in the $\text{CH}_4-\text{O}_2-\text{He}$ flow or on evacuated samples. These peaks disappeared at higher temperatures, and the peaks of 1509 and 1540 cm^{-1} became dominant. Gaseous NO_2 was observed as higher peak intensity on $\text{In/ZSM-5} + \text{Pt/Al}_2\text{O}_3$ than by an earlier study on In/ZSM-5 .³⁸ The surface NO_x species were not easily detectable because gaseous NO_2 was present at the same range of 1600–1630 cm^{-1} with them.⁵⁰ Nitrates are most probably present at 1540 cm^{-1} by our single gas and other FTIR experiments.³⁸ NCO- and CN-type intermediates on In, ZSM-5 or $\text{Pt/Al}_2\text{O}_3$ can be present at 2319 cm^{-1} .⁹ The spectra were about the same with pure In/ZSM-5 and the $\text{In/ZSM-5} + \text{Pt/Al}_2\text{O}_3$, and the surface species were located mainly on In/ZSM-5 , whose weight covered 95% of the catalyst mixture. Thus, most of the observed peaks on $\text{In/ZSM-5} + \text{Pt/Al}_2\text{O}_3$ were already found by our earlier detailed FTIR studies with In/ZSM-5 .³⁸ It was found by FTIR studies that $\text{Pt/Al}_2\text{O}_3$ catalyzed the formation of NO_2 , which enhanced methane reactions to oxygenated compounds.

Reaction Mechanism. The reaction mechanisms for NO_x reduction by methane were proposed on In/ZSM-5 and In/ZSM-5 with $\text{Pt/Al}_2\text{O}_3$ based on the observations in this and earlier studies,^{38–40,51,52} with high-temperature HC-SCR catalysts using various hydrocarbons as reductants. The addition of $\text{Pt/Al}_2\text{O}_3$ enhances certain limiting steps, which will be added in reaction mechanisms recently presented for In/ZSM-5 by us.³⁸

The methane activation and oxidation to oxygenated intermediates includes a stepwise dehydrogenation with subsequent water and CO_2 release.⁵³ The abstraction of a hydrogen atom from methane is known to demand a high activation energy and to be the rate-limiting step.⁵⁴ The partially oxidized methane

derivates are accumulated on In sites in the presence of oxygen and NO_2 , the promotion of which is included in the mechanism. Other parallel reaction pathways and chemical surface intermediates than presented might exist and explain as well the methane oxidation, but the defined mechanisms cover the observations and chemical mass balances in gas and surface phases. When an intermediate containing N–H or N–C bonding is formed from these oxygenated carbonaceous compounds, nitrogen formation is possible by reaction with one of the defined potential reductants (H_2NCO , HNCO , NCO , NH , NH_2) and NO . Thus, several N–C- or N–H-containing intermediates (amides, amine, isocyanides) are probable, and the dominating reducing compound depends on the conditions (temperature, concentrations). The most reactive nitrogen species to reduce NO have the oxidation state of –III (CNO , NCO , NH_2), opposite to species with high oxidation states (nitrogen oxides). However, the simplest chemical compounds of these intermediates are most plausible in the final (elementary) reaction to form N_2 . Nitro species are known precursors, which form first amides and then amines in reducing conditions.⁵⁵ In lean conditions, hydrocarbons and their derivates form locally reducing conditions, which cause the formation of surface reductants on HC-SCR catalysts. Beutel et al.⁵⁶ also found nitrosopropane and its amide- and amine-type hydrolysis products on Cu/ZSM-5 in propane-SCR studies. The final step in HC-SCR was found to be the NH_3 -SCR reaction also in several earlier studies, and HCN , HNCO , and nitromethane are known to react to NH_3 compounds in the presence of water and oxygen.^{57–60} Sowade et al.^{18,19} proposed that methane may be activated by NO_2 on Ce-In/ZSM-5 , forms mobile intermediates containing both carbon and nitrogen, and results in N_2 formation over acidic sites. Therefore, the formation of these reducing compounds from oxygenated hydrocarbons and nitro species is the generally accepted mechanism in HC-SCR on various catalysts.

The formation of ammonium compounds is obvious on acidic zeolites at lower temperatures, but the ammonium nitrite ($\text{NH}_4\text{-NO}_2$) route to N_2 is related more to NH_3 -SCR reactions⁶¹ and lower temperatures than to CH_4 -SCR, where no ammonia is in the feed and the main reactions proceed at higher temperature. Even if adsorbed ammonium nitrite existed at certain conditions, it should react to nitrogen by the released water ($\text{NH}_4\text{NO}_2 \rightarrow \text{NH}_2 + \text{NO} + \text{H}_2\text{O} \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$) as elementary reactions. This scheme results in the same final step that we present. The earlier findings are mostly not in conflict with our mechanisms, but the net reactions have been divided here into elementary

reactions to derive microkinetic models for CH₄-SCR. In the following kinetic model, the adsorbed NH₂ (amine) was assumed to be the actual reductant and a representative for the N-containing reducing compounds.

NO₂ has a crucial role in activating CH₄ to oxygenated compounds. NO₂ is a more efficient oxidant than molecular oxygen in adding reactive oxygen (adsorbed O) on the surface and thus keeping the oxidation sequence in progress. NO₂ is able to keep the catalyst surface free from blocking carbonaceous material, which can terminate the reaction sequence in NO reduction in long-term use.⁵⁶ Nitro species, detected in many other studies, are not able to react directly to N₂ but are reactive oxygen sources in carbonaceous precursors to form reducing intermediates. Even if methane is adsorbed in the initiation step as an oxygen-containing compound like CH₄O on the surface, additional reactive oxygen is necessary to continue the reaction sequence. The role of NO₂ in NO_x reduction with methane is probably more important than with other hydrocarbons, because methane is difficult to activate and the catalysts are easily deactivated in lean conditions. The difference in NO_x reduction and NO₂ formation temperatures might be a problem in real conditions, because thermodynamically NO₂ formation is low above 500 °C.

Acid sites on ZSM-5 are also able to catalyze NO₂ formation but are not alone stable in the usual reaction conditions. Therefore, the In and Pt sites are defined to be the active sites in reactions. Thermodynamically, platinum can be cycling between metallic (Pt) and different oxide forms (PtO₂, PtO) in reaction conditions. If the support–metal interactions are lumped together, two different active sites can be proposed to cover the observed catalytic properties: Indium site (*) and platinum site (#), whose denominations will be used in the equations. In fact, these sites are chemically usually oxides (PtO_x, InO_x) or hydroxides in lean conditions.

The following reactions can be proposed for the binary catalyst system. The main routes and surface species are the same as presented for In/ZSM-5 in the last study,³⁸ but certain reactions may proceed also on Pt sites.

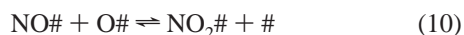
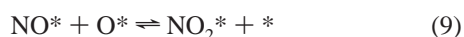
adsorptions on In sites:



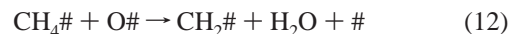
adsorptions on Pt sites:



Nitrogen dioxide is formed reversibly on both sites,



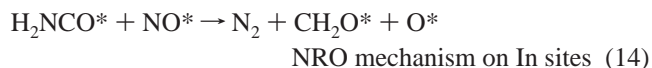
The oxidative agent for methane can be adsorbed oxygen on In or Pt sites.



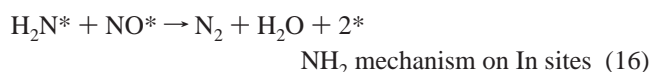
In fact, adsorbed CH₄O and CH₄ can be understood to be the same compound (chemically adsorbed methane or methanol), but sites are defined differently by oxygen balance. Similarly, CH₂O* and CH₂# can be understood as adsorbed formaldehyde or methylene compounds. These dehydrogenation reactions best match to known hydrocarbon oxidation mechanisms and are used to prepare a quantitative kinetic model. On a catalyst surface, OH groups might act as an oxidizing compound instead of adsorbed O or NO₂ but that alternative was neglected. The reaction rates on In sites are increased by enhanced NO₂ formation on Pt sites, because NO₂ is a source for O*. According to reaction experiments, the activity of In/ZSM-5 to form N₂ increased near to the same level with In/ZSM-5+Pt/Al₂O₃ (19:1) when NO was replaced by NO₂ in the feed. The reaction between adsorbed CH₄O and NO₂ will create the unpaired N-containing carbonaceous intermediates (H₂NCO = NRO, where R = CH₂).



This reaction emphasizes the role of NO₂ to form reducing intermediates on the catalyst surface. Carbonaceous nitro compounds might be precursors in this reaction step. H₂NCO (amide) is proposed to react with NO to N₂ in the first reduction mechanism.

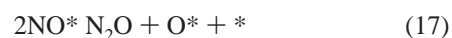


or dissociate to adsorbed NH₂, which reacts in an elementary surface reaction with NO to N₂ in the second reduction mechanism,⁶²



The reaction between NRO and NO is more a net reaction, which can be used in kinetic modeling, but which will proceed at least by two elementary reaction steps such as by eqs 15 and 16. The proposed reduction mechanism is also very well-known as a selective NO reduction step in NH₃-SCR by the Langmuir–Hinshelwood mechanism, e.g., on CuO/alumina,⁶³ and vanadia/titania.⁶⁴ However, the Eley–Rideal mechanism has earlier been proposed for NH₃-SCR in the case of vanadia/titania-based NH₃-SCR catalysts.⁶⁵

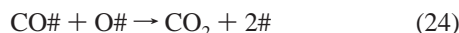
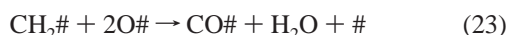
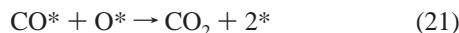
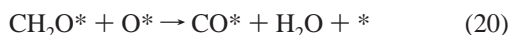
N₂O formation proceeds by the dissociation of the other adsorbed NO molecule by the net reaction



The experimental results lead us to also consider the role of Pt/Al₂O₃ in the reducing steps. A high N₂O formation in the presence of Pt/Al₂O₃ was a clue that NO dissociation is evident in catalyst mixtures. Therefore, the enhanced NO₂ formation and activation of methane were not the only promotions, but Pt/Al₂O₃ played a part in the reduction steps. A generally accepted reaction mechanism particularly for the Pt catalysts

in HC-SCR is the NO decomposition route by NO dissociation.⁵⁰ Thus, we propose that NO is also reduced to N₂ and N₂O by NO dissociation by the following surface reaction on Pt/Al₂O₃:

The carbonaceous intermediates are oxidized to CO_x on In or Pt sites.



The mechanism includes five overall reactions: methane oxidation, reduction of NO by methane producing nitrogen, partial reduction of NO by methane producing nitrous oxide, reversible NO oxidation to nitrogen dioxide, and reduction of nitrogen dioxide by methane producing nitrogen. Pt/Al₂O₃ enhances CO oxidation, and no gaseous CO was detected in reaction conditions. The deactivating effect of water can be explained by the decreased amount of active sites (InO⁺). Otherwise the mechanisms are the same in dry and wet mixtures.

Kinetic Model by NH₂ Mechanism for In/ZSM-5. Kinetic parameters were estimated by data from both the In/ZSM-5 and In/ZSM-5+Pt/Al₂O₃ (19:1 and 1:1) experiments. The same experimental data as in our earlier publication³⁸ were used to estimate parameters by the new reaction mechanism where H₂N* replaces H₂NCO* as the final, actual reductant. It is important that the mechanisms are able to show the dynamic reaction rates in the usual conditions.

The NRO and NH₂ mechanisms were first compared by data obtained with the In/ZSM-5 catalyst. The prediction of data and simulations with that NRO mechanism can be found in detail in our previous paper.³⁸ Steady-state rate equations were derived for the NH₂ mechanism on In sites. The rate of the nitrogen formation depended on partial pressures as follows:

$$r_{\text{N}_2}(\text{NH}_2) = \frac{k_{13}k_4p_{\text{CH}_4}p_{\text{O}_2}^{(1/2)}p_{\text{NO}_2}}{(\text{denom})^2\text{ads}} + \frac{k_{13}k_9p_{\text{CH}_4}p_{\text{O}_2}p_{\text{NO}}}{(\text{denom})^3\text{ads}} \quad (26)$$

where

$$\text{ads} = 1 + \frac{k_{9,4} + k_{13}p_{\text{CH}_4}p_{\text{O}_2}^{(1/2)}}{\text{denom}} \quad (27)$$

$$\begin{aligned} \text{denom} = & 1 + K_{\text{NO}}p_{\text{NO}} + K_{\text{O}_2}^{(1/2)}p_{\text{O}_2}^{(1/2)} + K'_{\text{CH}_4}p_{\text{CH}_4}p_{\text{O}_2}^{(1/2)} + \\ & k_4p_{\text{NO}_2} + k_{13}k_4p_{\text{CH}_4}p_{\text{O}_2}^{(1/2)}p_{\text{NO}_2} + \frac{k_9p_{\text{NO}}p_{\text{O}_2}^{(1/2)} + k_9k_{13}p_{\text{CH}_4}p_{\text{NO}}p_{\text{O}_2}}{k_{9,4} + k_{13}p_{\text{CH}_4}p_{\text{O}_2}^{(1/2)}} \end{aligned} \quad (28)$$

The production rates for the other gaseous compounds, i.e., NO, NO₂, N₂O, CO₂, CO, H₂O, and CH₄, were calculated in the kinetic modeling but not shown there, except N₂O in Figure 1

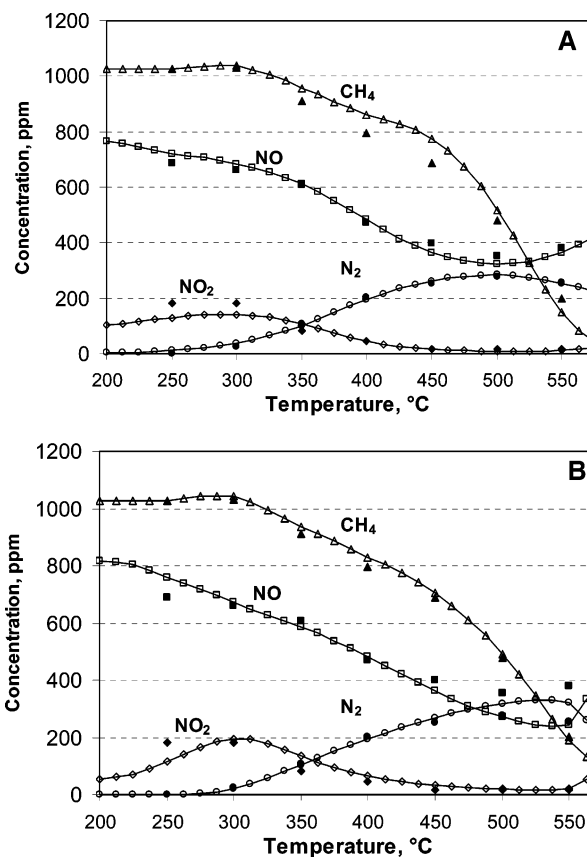
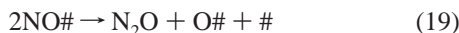


Figure 7. Measured (filled points) and simulated (lines) gas-phase compositions in In/ZSM-5 reactor outlet as a function of temperature by (A) NRO and (B) NH₂ mechanisms (1000 ppm NO, 1000 ppm CH₄, 10% O₂, $F/W = 60 \text{ dm}^3 \text{ h}^{-1} \text{ g}^{-1}$). (A) One site by NH₂ mechanism (parameters modified by In/ZSM-5+Pt/Al₂O₃ data). (B) Two-sites (In and Pt) mechanism.

and the sum of CO₂ and CO shown as CO_x (=unreactive carbon compounds). All concentrations of these gaseous species except water content were measured and used in parameter estimation. A small amount of CO was observed, but CO formation was neglected in the model. In the derivation of kinetic rate equations, adsorption steps 1–3 and 5–7 were assumed to be quasi-equilibrium and steps 4 and 8–10 were proposed to be rate-controlled, reversible reactions. Other reactions were assumed to be rate-controlled irreversible steps. The reactor was assumed to behave as an ideal plug flow reactor. The reactor model becomes system of ODEs, which was solved by stiff ODE solver LSODE. The parameters were estimated by the Levenberg–Marquard algorithm.

The NH₂ mechanism on In sites was able to predict even better than the NRO mechanism the observed activity results in the different conditions (Figure 7). Visually it is not easy to see the differences in a single experiment, but the overall R^2 value for all experimental data sets was 96% for NRO and 99% for the NH₂ mechanism.

Kinetic Model for the Catalyst Mixture of In/ZSM-5+Pt/Al₂O₃. In the next step, the experimental data for the catalyst mixture of In/ZSM-5 and Pt/Al₂O₃ (19:1 and 1:1) were analyzed by the same principles as for In/ZSM-5. First was assumed single, arbitrary In+Pt sites to replace the In active sites in the model by the NH₂ mechanism (Figure 8A). The new kinetic parameters were found, and the reaction simulations were carried out. Significant changes were found only for three kinetic parameters. The rate parameter k_{13} related to the rate of reactions 13, 15, and 16 was in the presence of Pt/Al₂O₃ 2.2 times, and the parameter $k_{9,4}$ related to NO₂ adsorption was in the presence

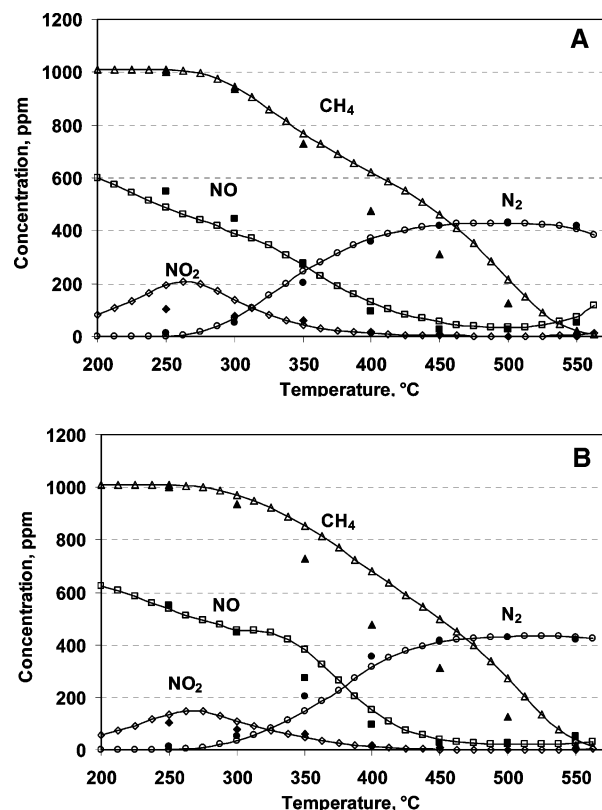


Figure 8. Measured (filled points) and simulated (lines) gas-phase compositions in In/ZSM-5+Pt/Al₂O₃ (19:1) reactor outlet as a function of temperature by (A) one (NH₂ mechanism) and (B) two active sites (NH₂ and N mechanisms) (1000 ppm NO, 1000 ppm CH₄, 10% O₂, $F/W = 60 \text{ dm}^3 \text{ h}^{-1} \text{ g}^{-1}$).

Table 2. Kinetic Parameters for In/ZSM-5 and the Combination of In/ZSM-5 and Pt/Al₂O₃ Catalysts in Single-Site Model^a

| parameter ^b | In/ZSM-5 | In/ZSM-5 + Pt/Al ₂ O ₃ | dimension |
|------------------------|----------------------|---|---|
| k_4 | 0.63 | 0.64 | $\text{m}^3 \text{ g}^{-1} \text{ h}^{-1}$ |
| E_{a4} | 81.2 | 81.1 | kJ mol^{-1} |
| k_{-4} | 6.3×10^{-4} | 6.7×10^{-4} | $\text{mol g}^{-1} \text{ h}^{-1}$ |
| E_{a-4} | 143 | 143 | kJ mol^{-1} |
| $k_{9,4}$ | 4.6 | 4.1 | $\text{mol g}^{-1} \text{ h}^{-1}$ |
| $E_{a9,4}$ | 124 | 127 | kJ mol^{-1} |
| k_9 | 535 | 596 | $\text{m}^{4.5} \text{ g}^{-1} \text{ h}^{-1} \text{ mol}^{-0.5}$ |
| E_{a9} | 32.7 | 33.7 | kJ mol^{-1} |
| k_{11} | 8.3×10^{-4} | 8.6×10^{-4} | $\text{m}^{4.5} \text{ g}^{-1} \text{ h}^{-1} \text{ mol}^{-0.5}$ |
| E_{a11} | 125 | 125 | kJ mol^{-1} |
| k_{13} | 4.7×10^{-2} | 1.0×10^{-1} | $\text{m}^{4.5} \text{ g}^{-1} \text{ h}^{-1} \text{ mol}^{-0.5}$ |
| E_{a13} | 27.4 | 27.4 | kJ mol^{-1} |
| K'_{H_4} | 9.0 | 9.0 | $\text{m}^{4.5} \text{ mol}^{-1.5}$ |
| H'_{H_4} | 20.3 | 20.4 | kJ mol^{-1} |
| K_{O_2} | 2.4×10^{-4} | 2.3×10^{-4} | $\text{m}^3 \text{ mol}^{-1}$ |
| K_{NO} | na ^c | 4.6×10^{-2} | $\text{m}^3 \text{ mol}^{-1}$ |

^a $k_{9,4} = k_{-9}/k_{-4}$; $K'_{\text{CH}_4} = K_{\text{CH}_4}(1 + k_{11}(k_{20})^{-1} + k_{13}(k_{15})^{-1})$. ^b k_i and K_i values are at 350 °C. ^c na, not available.

of Pt/Al₂O₃ 0.9 times value with only In/ZSM-5. The last change resulted in the higher surface coverage of NO₂ in the presence of Pt/Al₂O₃ at the same amount of uncovered surface sites. The NO adsorption equilibrium constant K_{NO} was identified as a small but nonzero value in the presence of Pt/Al₂O₃ contrary to unblended In/ZSM-5. Although every parameter was freely adjustable in estimation, the other parameters, except these three were unchanged within their trust regions. There are six temperature-dependent rate parameters both for In/ZSM-5 only and In/ZSM-5+Pt/Al₂O₃ (Table 2). The numbers of these parameters and overall reactions are the same, as a reversible reaction is counted as two reactions. In addition, a few

Table 3. Kinetic Parameters for Pt/Al₂O₃ in Catalyst Combination^a

| parameter ^b | value | dimension |
|-------------------------------|----------------------|---|
| k_8 | 1.7 | $\text{m}^3 \text{ g}^{-1} \text{ h}^{-1}$ |
| E_{a8} | 0 | kJ mol^{-1} |
| k_{-8} | 4.4 | $\text{mol g}^{-1} \text{ h}^{-1}$ |
| E_{a-8} | 21.7 | kJ mol^{-1} |
| k_{10} | 8.1 | $\text{m}^{4.5} \text{ g}^{-1} \text{ h}^{-1} \text{ mol}^{-0.5}$ |
| E_{a10} | 33.0 | kJ mol^{-1} |
| k_{12} | 0.21 | $\text{m}^{4.5} \text{ g}^{-1} \text{ h}^{-1} \text{ mol}^{-0.5}$ |
| E_{a12} | 134 | kJ mol^{-1} |
| k_{18} | 26 | $\text{m}^6 \text{ g}^{-1} \text{ h}^{-1} \text{ mol}^{-1}$ |
| E_{a18} | 199 | kJ mol^{-1} |
| k_{19} | 21 | $\text{m}^6 \text{ g}^{-1} \text{ h}^{-1} \text{ mol}^{-1}$ |
| E_{a19} | 76.6 | kJ mol^{-1} |
| $K'_{\text{CH}_4, \text{Pt}}$ | 22 | mol m^{-3} |
| $H'_{\text{CH}_4, \text{Pt}}$ | 77.4 | kJ/mol |
| $K_{\text{O}_2, \text{Pt}}$ | 2.8×10^{-3} | mol m^{-3} |

^a $K'_{\text{CH}_4, \text{Pt}} = K_{\text{CH}_4, \text{Pt}}(1 + k_{12}(k_{23})^{-1})$, ^b k_i and K_i values are at 350 °C.

adsorption parameters were used. The estimated relative standard error of the parameters was between 6 and 25%.

Even if the one-site mechanism with the modified parameters was able to explain rather well the promotion and the dynamics with the catalyst combination, a new two-site kinetic model was derived based on the presented reactions on In(NH₂ mechanism) and Pt sites (NO decomposition mechanism), where N₂ can be formed on both sites, and in addition, Pt sites have a promoting effect on NO₂ formation, CH₄ oxidation, and CO oxidation. NO decomposition is known as the particular mechanism of Pt catalysts in HC-SCR.⁶⁶

The rate equation for nitrogen formation was derived to be a combination by two mechanisms:

$$r_{\text{N}_2}(\text{InNH}_2 - \text{Pt}) = r_{\text{N}_2}(\text{NH}_2) + r_{\text{N}_2, \text{pt}} \quad (29)$$

$$r_{\text{N}_2, \text{pt}} = \frac{k_{18} p_{\text{NO}}^2}{(\text{denom}_{\text{pt}})^2} \quad (30)$$

where

$$\text{denom}_{\text{pt}} = 1 + K_{\text{O}_2}^{(1/2)} p_{\text{O}_2}^{(1/2)} + K_{\text{CH}_4, \text{pt}}' p_{\text{CH}_4} + \frac{k_8}{k_{-8}} p_{\text{NO}_2} + k_{10} p_{\text{NO}} p_{\text{O}_2}^{(1/2)} \quad (31)$$

A graphical comparison between one- and two-site mechanisms with In/ZSM-5+Pt/Al₂O₃ (19:1) is seen in Figure 8. In addition, the goodness of fit was quantified by R^2 values, which were 99.9% for the arbitrary one site and 98% for the two-site mechanism. Estimated parameters for Pt/Al₂O₃ catalyst are shown in Table 3. Six temperature-dependent rate parameters, one temperature-independent adsorption parameter, and one temperature-dependent adsorption parameter were used in the estimation. The results obtained for the mixture of In/ZSM-5+Pt/Al₂O₃ were only used to estimate the parameters for the Pt/Al₂O₃ model. The model for unblended In/ZSM-5 described above was applied without any re-estimation for In sites.

The effect of temperature on N₂ formation and CH₄ consumption was simulated with a low space velocity as a function of the catalyst bed length (Figure 9). This type of simulation can be used as a tool to design the catalyst. The simulation clearly showed that a larger reactor is required for a low-temperature range such as at 350 °C, but much smaller reactors (dimensionless length of 0.2–0.4 or $F/W \sim 50\text{--}100 \text{ dm}^3 \text{ h}^{-1} \text{ g}^{-1}$) are efficient enough at 450–550 °C with N₂ formation above 80% in dry conditions. The reactor volume can clearly

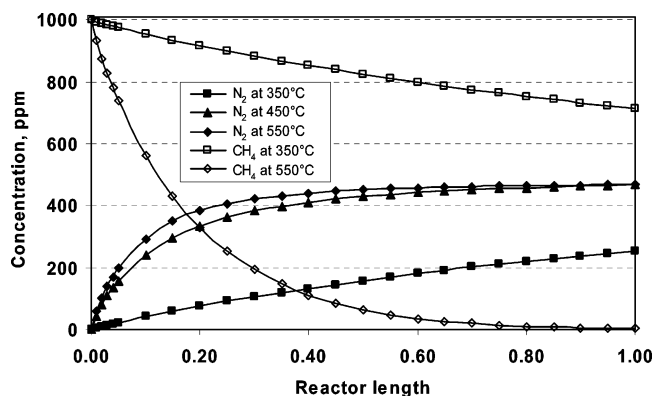


Figure 9. Simulated concentrations of N_2 and CH_4 as a function of a length on In/ZSM-5+Pt/ Al_2O_3 (19:1) catalyst reactor at 350, 450, and 550 °C (Inlet: 1000 ppm NO, 1000 ppm CH_4 , 10% O_2 , up to $F/W = 20 \text{ dm}^3 \text{ h}^{-1} \text{ g}^{-1}$ corresponding to the dimensionless length of 1.00).

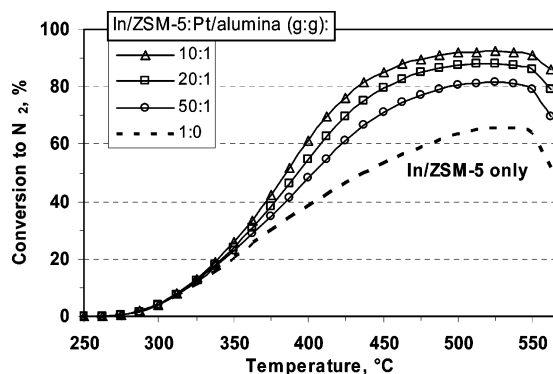


Figure 10. Simulated N_2 formation with In/ZSM-5+Pt/ Al_2O_3 by the amount of Pt/ Al_2O_3 in the mixture according to two sites with NH_2 mechanism and NO decomposition (1000 ppm NO, 1000 ppm CH_4 , 10% O_2 , $F/W = 60 \text{ dm}^3 \text{ h}^{-1} \text{ g}^{-1}$, 0.067 g OF In/ZSM-5).

be smaller with this catalyst combination keeping the same conversions to N_2 than with In/ZSM-5 only.

The simulations were applied to evaluate the effect of the ratio of In/ZSM-5 and Pt/ Al_2O_3 on performance. If the amount of In/ZSM-5 was fixed and the amount of Pt/ Al_2O_3 was increased, N_2 formation was increased (Figure 10). It was possible for the kinetic model to simulate the enhanced activity by the catalyst ratios in the range of 1:0–10:1 (0–9% Pt/ Al_2O_3 in bed). However, the model was based on the limited data about the catalyst ratios and the model should not be extended to higher Pt/ Al_2O_3 amounts, where the methane oxidation reactions can be faster on Pt catalysts and whose range was not adequately covered in activity experiments.

A microkinetic model was derived for CH_4 -SCR reactions with a two-component system, which was seen to be valuable itself. The number of parameters was slightly higher than in the case of power law equations, but a key point is the catalyst modeling based solely on the surface reaction mechanism. Empirical and microkinetic models both result in equations that depend on the concentrations or partial pressures of reactants (NO, CH_4 , O_2 , and possibly NO_2), but the microkinetic model enables us to have more correct dependencies, which might be impossible by empirical models based on power law fittings.^{19,21,54} The microkinetic modeling adds to the real understanding of how the catalytic reactions proceed and depend on the conditions. These reaction models simulated that certain key intermediates (amines, amides) disappeared immediately after they formed and thus they were not found in FTIR studies. Surface intermediate characterizations can be misleading if

observed compounds are thought of as the only intermediates in NO reduction to N_2 . The existence of many fast-reacting intermediates also simplified the rate equations. In the future, it might be possible to simplify these microkinetic models based on further observations.

Conclusions

NO_x reduction by methane was significantly enhanced both in dry and wet gas mixtures when a small amount (5 wt %) of Pt/ Al_2O_3 or Mn_3O_4 was mechanically mixed with In/ZSM-5. The highest conversions were as high as 98% with Mn_3O_4 and 95% with Pt/ Al_2O_3 at 500 °C with $\text{CH}_4/\text{NO} = 1$. The addition of platinum directly into In/ZSM-5 with the same concentration did not increase the activity. Pd/ Al_2O_3 had excessive methane oxidation activity, which caused the collapse in the CH_4 -SCR activity in the mixture with In/ZSM-5.

The combination of In/ZSM-5 and Pt/ Al_2O_3 was studied more to find reaction mechanism and kinetics. The reactions were proposed to initiate by the formation of NO_2 on In/ZSM-5 or Pt/ Al_2O_3 . The partial oxidation of methane and the formation of nitrogen-containing carbonaceous intermediates were enhanced by NO_2 , which is a source of reactive oxygen. The fast methane oxidation to CO_x was a limiting factor for the CH_4 -SCR activity at higher temperatures (>550 °C). In general, the fixation of nitrogen can be accomplished with the reaction between NO and an actual reductant containing N–H or N–C bondings (amides, isocyanides, amines). Adsorbed H_2NCO and its decomposition product NH_2 were compared as the final reductants on In/ZSM-5. The reaction between adsorbed NH_2 and NO is the most plausible as the elementary reaction to form N_2 . The reaction studies revealed that NO decomposition (dissociation) on Pt/ Al_2O_3 enhanced N_2 and as well joint N_2O formation in the mixture of In/ZSM-5 and Pt/ Al_2O_3 . A kinetic model based on defined surface reactions was derived by assuming two macroscale-separated catalytic compounds and sites, where NO is reduced by two paths ($\text{NH}_2 + \text{NO}$ reaction on In sites and NO decomposition on Pt sites). In addition, the Pt sites were proposed for catalyzing the NO, CH_4 , and CO oxidation reactions. The measurements were explained well with this model, and simulations in untested conditions were applied for reactor design. Altogether, the main results of this CH_4 -SCR study are the multifunctional catalyst mixtures with high activity, the role of the second catalyst in N_2 formation, and complete microkinetic models by one- or two-site mechanisms.

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Literature Cited

- Held, W.; Koenig, A.; Richter, T.; Puppe, L. Catalytic reduction of NO_x in net oxidizing exhaust gas. *SAE Pap.* **1990**, 900496.
- Hamada, H.; Kintaichi, Y.; Sasaki, M.; Itoh, Y.; Tabata, M. Highly selective reduction of nitrogen oxides with hydrocarbons over H-form zeolite catalysts in oxygen-rich atmosphere. *Appl. Catal.* **1990**, 64, L1.
- Iwamoto, M.; Hamada, H. Removal of nitrogen monoxide from exhaust gases through novel catalytic processes. *Catal. Today* **1991**, 10, 57.
- Li, Y.; Armor, J. N. Catalytic reduction of nitrogen oxides with methane in the presence of excess oxygen. *Appl. Catal. B* **1992**, 1, L31.

- (5) Nishizaka, Y.; Misono, M. Catalytic reduction of nitrogen monoxide by methane over palladium-loaded zeolites in the presence of oxygen. *Chem. Lett.* **1993**, 1295.
- (6) Adelman, B. J.; Sachtler, W. M. H. The effect of zeolitic protons on NO_x reduction over Pd/ZSM-5 catalysts. *Appl. Catal. B* **1997**, *14*, 1.
- (7) Lobree, L. J.; Aylor, A. W.; Reimer, J. A.; Bell, A. T. NO reduction by CH₄ in the presence of O₂ over Pd-H-ZSM-5. *J. Catal.* **1999**, *181*, 189.
- (8) Yogo, K.; Tanaka, S.; Ihara, M.; Hishiki T.; Kikuchi, E. Selective reduction on NO with propane on gallium ion-exchanged zeolites. *Chem. Lett.* **1992**, 1025.
- (9) Yogo, K.; Ihara, M.; Terasaki, I.; Kikuchi, E. Adsorption properties of oxygen and methane on Ga-ZSM-5: the origin of the selectivity of NO_x reduction using methane. *Appl. Catal. B* **1993**, *2*, L1.
- (10) Kikuchi, E.; Yogo, K. Selective catalytic reduction of nitrogen monoxide by methane on zeolite catalysts in an oxygen-rich atmosphere. *Catal. Today* **1994**, *22*, 73.
- (11) Kikuchi, E.; Ogura, M. Selective reduction of nitric oxide with methane on In/H-ZSM-5 based catalysts. *Catal. Surv. Jpn.* **1997**, *1*, 227.
- (12) Ogura, M.; Hayashi, M.; Kikuchi, E. Role of zeolite structure on reduction of NO_x with methane over In- and Pd-based catalysts. *Catal. Today* **1998**, *45*, 139.
- (13) Ogura, M.; Hiromoto, S.; Kikuchi, E. Precious metal loaded In/H-ZSM-5 for low concentration NO reduction with methane in the presence of water vapor. *Chem. Lett.* **1995**, *12*, 1135.
- (14) Misono, M. Catalytic reduction of nitrogen oxides by bifunctional catalysts. *Cattech* **1998**, *1*, 53.
- (15) Inaba, M.; Kintaichi, Y.; Hamada, H. Cooperative effect of platinum and alumina for the selective reduction of nitrogen monoxide with propane. *Catal. Lett.* **1996**, *36*, 223.
- (16) Hamada, H. Cooperation of catalytic species for the selective reduction of nitrogen monoxide with hydrocarbons. *Catal. Surv. Jpn.* **1996**, *1*, 53.
- (17) Berndt, H.; Schütze, F. W.; Richter, M.; Sowade, T.; Grünert, W. Selective catalytic reduction of NO under lean conditions by methane and propane over indium/cerium-promoted zeolites. *Appl. Catal. B* **2003**, *40*, 51.
- (18) Sowade, T.; Schmidt, C.; Schütze, F.-W.; Bernt, H.; Grünert, W. Relations between structure and catalytic activity of Ce-In-ZSM-5 catalysts for the selective reduction of NO by methane. I. The In-ZSM-5 system. *J. Catal.* **2003**, *214*, 100.
- (19) Sowade, T.; Liese, T.; Schmidt, C.; Schütze, F.-W.; Yu, X.; Bernt, H.; Grünert, W. Relations between structure and catalytic activity of Ce-In-ZSM-5 catalysts for the selective reduction of NO by methane. II. Interplay between the CeO₂ promoter and different indium sites. *J. Catal.* **2004**, *225*, 105.
- (20) Wang, X.; Zhao, X.; Shen, J.; Sun, X.; Zhang, T.; Lin, L. A Mössbauer study of In-Fe₂O₃/HZSM-5 catalysts for the selective catalytic reduction of NO by methane. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2846.
- (21) Wang, X.; W. Liu, T.; Zhao, X.; Sun, D.; Liang, L.; Lin, L. Kinetics of the selective reduction of NO with CH₄ over an In-Fe₂O₃/HZSM-5 catalyst. *React. Kinet. Catal. Lett.* **2000**, *69*, 299.
- (22) Heinisch, R.; Jahn, M.; Yalams, C. Reduction of nitrogen oxide with methane: Activity and methane conversion on In-HZSM-5 and PdIn-HZSM-5 honeycomb catalysts. *Chem. Eng. Technol.* **1999**, *22*, 4 337.
- (23) Ramallo-Lopez, J. M.; Requejo, F. G.; Gutierrez, L. B.; Miro, E. E. EXAFS, TDPAC and TPR characterization of PtIn/Ferrierite. The role of surface species in the SCR of NO_x with CH₄. *Appl. Catal. B* **2001**, *29*, 35.
- (24) Gutierrez, L. B.; Ramallo-Lopez, J. M.; Irusta, S.; Miro, E. E.; Requejo, F. G. J. Promotional effect of reduction treatments of PtIn(ferrierite) on its activity in the SCR of NO with methane. Kinetics and novel characterization studies. *Phys. Chem. B* **2001**, *105*, 9514.
- (25) Maisuls, S. E.; Seshan, K.; Feast, S.; Lercher, J. A. Selective catalytic reduction of NO_x to nitrogen over Co-Pt/ZSM-5 Part A. Characterization and kinetic studies. *Appl. Catal. B* **2001**, *29*, 69.
- (26) Gutierrez, L. B.; Boix, A. V.; Lombardo, E. A.; Fierro, J. L. G. Study of the Co-Pt synergism for the selective catalytic reduction of NO with CH₄. *J. Catal.* **2001**, *199*, 60.
- (27) Boix, A.; Mariscal, R.; Fierro, J. L. G. In situ DRIFTS study of NO reduction with CH₄ over PtCo-ferrierite catalysts. *Catal. Lett.* **2000**, *68*, 169.
- (28) Ogura, M.; Sugiura, Y.; Hayashi, M.; Kikuchi, E. Reduction of nitric oxide with methane on Pd/Co/H-ZSM-5 catalysts: cooperative effects of Pd and Co. *Catal. Lett.* **1996**, *42*, 185.
- (29) Pieterse, J. A. Z.; van den Brink, R. W.; Booneveld, S.; de Bruijn, F. A. Influence of zeolite structure on the activity and durability of Co-Pd-zeolite catalysts in the reduction of NO_x with methane. *Appl. Catal. B* **2003**, *46*, 239.
- (30) Melo, L.; Diaz, Y.; Mediavilla, M.; Albornoz A.; Brito, J. L. Effect of the supported Pt on the migration of structural ga toward the surface of catalysts of the Pt/H[Ga]ZSM-5 type. *Catal. Lett.* **2004**, *97* (1–2), 105.
- (31) Lee, T. J.; Nam, I.-S.; Ham, S.-W.; Baek, Y.-S.; Shin, K.-H. Effect of Pd on the water tolerance of Co-ferrierite catalyst for NO reduction by CH₄. *Appl. Catal. B* **2003**, *41*, 115.
- (32) Boix, A. V.; Zamaro, J. M.; Lombardo, E. A.; Miro, E. E. The beneficial effect of silica on the activity and thermal stability of PtCoFerrierite-washcoat cordierite monoliths for the SCR of NO_x with CH₄. *Appl. Catal. B* **2003**, *46*, 121.
- (33) Ren, L.; Zhang, T.; Xu C.; Lin, L. The remarkable effect of In₂O₃ on the catalytic activity of In/HZSM-5 for the reduction of NO with CH₄. *Top. Catal.* **2004**, *30/31*, 55.
- (34) Ren, L.; Zhang, T.; Tang, J.; Zhao, J.; Li, N.; Lin, L. Promotional effect of colloidal alumina on the activity of the In/ZSM-5 catalyst for the selective reduction of NO with methane. *Appl. Catal. B* **2003**, *41*, 129.
- (35) Sowade, T.; Schütze, F.-W.; Berndt H.; Grünert, W. Kinetic reaction models for the selective reduction of NO by methane over multifunctional zeolite-based redox catalysts. *Chem. Eng. Technol.* **2004**, *27* (12), 1277.
- (36) Yan, J.-Y.; Kung, H. H.; Sachtler, W. M. H.; Kung, M. C. Synergistic effects in lean NO_x reduction by CH₄ over Co/Al₂O₃ and H-zeolite catalysts. *J. Catal.* **1998**, *175*, 294.
- (37) Lee, J.-H.; Kim, J.-G.; Lee, J.-K.; Kim, J.-H. NO removal by CH₄ on Co-NaX-CO and Ag-NaX catalysts in a dual-bed system. *Catal. Today* **2003**, *87*, 35.
- (38) Maunula, T.; Ahola, J.; Hamada, H. Reaction mechanism and kinetics of NO_x reduction by CH₄ on In-ZSM-5 in lean conditions. *Appl. Catal. B* **2006**, *64*, 13.
- (39) Maunula, T.; Kintaichi, Y.; Inaba, M.; Haneda, M.; Sato, K.; Hamada, H. Enhanced activity on In and Ga-supported sol-gel alumina catalysts for NO reduction by hydrocarbons in lean conditions. *Appl. Catal. B* **1998**, *15*, 291.
- (40) Maunula, T.; Kintaichi, Y.; Haneda, M.; Hamada, H. Preparation and reaction mechanistic characterization of sol-gel indium/alumina catalysts developed for NO_x reduction by propene in lean conditions. *Catal. Lett.* **1999**, *61*, 121.
- (41) Burch, R.; Scire, S. Selective catalytic reduction of nitric oxide with ethane and methane on some metal exchanged ZSM-5 zeolites. *Appl. Catal. B* **1994**, *3*, 295.
- (42) Kumthekar, M. W.; Ozkan, U. S. Nitric oxide reduction with methane over Pd/TiO₂ catalysts. *J. Catal.* **1997**, *171*, 45.
- (43) Shelef, M. Selective catalytic reduction of NO_x with N-free reductants. *Chem. Rev.* **1995**, *95*, 209.
- (44) Maunula, T.; Lylykangas, R.; Lievonen A.; Härkönen, M. NO_x reduction by urea in the presence of NO₂ on metal substrated SCR catalysts for heavy-duty vehicles. *SAE Pap.* **2003**, 2003-01-20031863.
- (45) Vaccaro, A. R.; Perez-Ramirez, J.; Garcia-Cortes, J. M.; Salinas-Martinez de Lecea, C.; Kapteijn, F.; Moulijn, J. A. Dual-bed catalytic system for removal of NO-N₂O in lean-burn engine exhausts. Environmental Challenges and greenhouse gas control for fossil fuel utilization in the 21st century, ACS Meeting, San Diego, CA, April 1–5, 2001.
- (46) Maunula, T.; Ahola, J.; Salmi, T.; Haario, H.; Härkönen, M.; Luoma, M.; Pohjola, V. J. Investigation of CO oxidation and NO reduction on three-way catalysts with transient response techniques. *Appl. Catal. B* **1997**, *12*, 287.
- (47) Määttä, T. M.Sc. Thesis, Reduction of nitrogen oxides by hydrocarbons: characterization of Pt-zeolite catalysts and adsorption of hydrocarbons, Oulu University, 2002.
- (48) Yang, C.; Xu, Q. State of aluminium in zeolite β and influence of acidic or basic medium. *Zeolites* **1997**, *16*, 404.
- (49) Bolish, V.; Vedrine, J. C.; van de Berg, J. P.; Wolthuizen, J. P.; Derouane, E. Adsorption and activation of ethane by zeolite-H-ZSM-5. *J. Chem. Soc., Faraday Trans.* **1980**, *76*, 1606.
- (50) Zawadzki, J.; Wisniewski, M.; Skowronska, K. Adsorption and catalytic reduction of NO with methanol over carbon and carbon-supported catalysts. *Appl. Catal. B* **2002**, *35*, 255.
- (51) Maunula, T. Stability of deNO_x Catalyst Materials in Diesel and Lean Burn Gasoline Conditions. Oral presentation at the 3rd EU–Japan Workshop Meeting of Fundamental Aspects of Catalysis for DeNO_x and Combustion, Reading, UK, 1997.
- (52) Maunula, T.; Ahola, J.; Hamada, H. Reaction mechanism and kinetics of NO_x reduction by propene on Co/alumina catalysts in lean conditions. *Appl. Catal. B* **2000**, *26*, 173.
- (53) Pinaeva, L. G.; Sadovskaya, E. M.; Suknev, A. P.; Goncharov, V. B.; Sadykov, V. A.; Balzhinimaev, B. S.; Decamp, T.; Mirodatos, C. On the oxygen effect in nitric oxide reduction by methane over Co/ZSM-5. *Chem. Eng. Sci.* **1999**, *54*, 4327.

- (54) Cowan, A. D.; Dumpelmann, R.; Cant, N. W. The rate-determining step in the selective catalytic reduction of nitric oxide by methane over a Co-ZSM-5 catalyst in the presence of oxygen. *J. Catal.* **1995**, *151*, 356.
- (55) Morrison, R. T.; Boyd, R. N. *Organic chemistry*, 6th ed.; Prentice Hall Int.: Upper Saddle River, NJ, 1992.
- (56) Beutel, T.; Adelman, B.; Sachtler, W. M. H. Potential reaction paths in NO_x reduction over Cu/ZSM-5. *Catal. Lett.* **1996**, *37*, 125.
- (57) Liu, I. O. Y.; Cant, N. W.; Haynes, B. S.; Nelson, P. F. The formation of methyl isocyanate during the reaction of nitroethane over Cu-MFI under hydrocarbon-selective catalytic reduction conditions. *J. Catal.* **2001**, *203*, 487.
- (58) Radtke, F.; Koeppel, R. A.; Baiker, A. Hydrogen cyanide formation in selective catalytic reduction of nitrogen oxides over Cu/ZSM-5. *Appl. Catal.* **1994**, *104*, L125.
- (59) Sadykov, V. A.; Lunin, V. V.; Matyshak, V. A.; Paukshtis, E. A.; Rozovskii, A. Y.; Bugakov, N. N.; Ross, J. R. H. The reaction mechanism of selective catalytic reduction of nitrogen oxides by hydrocarbons in excess oxygen: Intermediates, their reactivity and routes of transformation. *Kin. Catal.* **2003**, *44*, No 3, 379.
- (60) Meunier, F. C.; Zuzaniuk, V.; Breen, J. P.; Olsson, M.; Ross, J. R. H. Mechanistic differences in the selective reduction of NO by propene over cobalt- and silver-promoted alumina catalysts: kinetic and in situ DRIFTS study. *Catal. Today* **2000**, *59*, 287.
- (61) Sun, Q.; Gao, Z.-X.; Chen, H.-Y.; Sachtler, W. M. H. Reduction of NO_x with ammonia over Fe/MFI: Reaction mechanism based on isotopic labeling. *J. Catal.* **2001**, *201*, 89.
- (62) Ukisu, Y.; Miyadera, T.; Abe, A.; Yoshida, K. Infrared study of catalytic reduction of lean NO_x with alcohols over alumina-supported silver catalysts. *Catal. Lett.* **1996**, *39*, 265.
- (63) Otto, K.; Shelef, M. Studies of surface reactions of nitric oxide by isotope labelling. IV: The reaction between nitric oxide and ammonia over copper surfaces at 150–200°C. *J. Phys. Chem.* **1972**, *76*, 37.
- (64) Topsoe, N.-Y.; Dumesic, J. A.; Topsoe, H. Vanadia/titania catalysts for selective reduction of nitric oxide by ammonia. II Studies of active sites and formulation of catalytic cycles. *J. Catal.* **1995**, *151*, 241.
- (65) Inomata, M.; Miyamoto, A.; Murakami, Y. Mechanism of the reaction of NO and NH₃ on vanadium oxide catalyst in the presence of oxygen under dilute gas conditions. *J. Catal.* **1980**, *62*, 140.
- (66) Burch, R.; Fornasiero, P.; Watling, T. C. Kinetics and mechanism of the reduction of NO by n-octane over Pt/Al₂O₃ under lean-burn conditions. *J. Catal.* **1998**, *176*, 204.

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