Interaction of CH_4 with NO and NO_2 over Pt-ZSM-5 in the absence of O_2

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The reduction of NO and NO_2 with CH_4 to form N_2 catalyzed by Pt-ZSM-5 has been investigated. For both reactions the dependence of conversion on temperature is similar to that of CH_4 combustion catalyzed by Pt. The conversion increases slowly before a sharp increase at the ignition temperature ($\sim$300 °C for NO + CH_4 and $\sim$475 °C for NO_2 + CH_4). Based on results in which the mole ratios and partial pressures of NO_x and CH_4 were varied, it is suggested that the oxygen surface coverage determines the catalytic activity of Pt-ZSM-5. It is postulated that NO_2 rapidly dissociates on Pt, covering the surface with oxygen adatoms. The interaction of oxygen adatoms with the Pt surface is sufficiently strong that CH_4 cannot compete for adsorption sites. Thus, the catalytic activity is low at temperatures less than 475 °C, where oxygen desorption from the surface is unfavorable. However, NO has a lower sticking probability, and the slower rate of N–O bond dissociation results in a lower steady state oxygen coverage and, in turn, a higher activity in the NO + CH_4 reaction. Experiments in which the CH_4 + NO_2 reaction temperature was cycled from 350 to 500 °C and back to 350 °C provides evidence that overstoichiometric CH_4 dissociation on the Pt surface can occur, and the surface carbon that is formed enhances NO_2 reduction to N_2.

KEY WORDS: Pt-ZSM-5; selective catalytic reduction; nitrogen oxides; methane; reaction kinetics

1. Introduction

For many years the catalytic conversion of nitrogen oxides has dictated the air/fuel ratio in automotive engines. The current three-way catalytic converters are effective only for NO_x removal at approximately the stoichiometric air/fuel ratio and more fuel-rich conditions [1–3]. Higher engine efficiency is obtained as the air/fuel ratio is increased; therefore, technology is required to selectively reduce NO_x under lean conditions. Methane is a desirable reductant, but only a few catalytic systems form N_2 selectively from a $NO_x + CH_4 + O_2$ mixture [4–10]. However, certain applications warrant considering the catalytic reduction (SCR) of NO_x with CH_4 at low oxygen partial pressures and in the absence of oxygen. Natural gas engines, for example, operate at approximately the stoichiometric air/fuel ratio [11].

The reduction of NO with CH_4 to form N_2 in the absence of O_2 is catalyzed by many materials. Both Cu- and Co-ZSM-5 catalyze the reaction with Cu-ZSM-5 showing a higher activity [4,9,12–15]. The NO + CH_4 reaction proceeds readily on Li-doped MgO catalysts and it appears that activation of CH_4, rather than NO, is the rate-determining step [16]. The activation of methane by a C–H bond cleavage was also suggested as the rate-determining step of the NO + CH_4 reaction catalyzed by alumina-supported Rh [17] and Pt [18,19]. Further, the reaction requires relatively large ensembles and occurs preferentially on flat planes exhibited by large Pt particles, as shown by catalytic experiments with Pt/γ-Al_2O_3 and Pt–Au/γ-Al_2O_3 [20].

Many researchers have concluded that nitrogen dioxide is a key intermediate in the NO_x SCR with hydrocarbons catalyzed by transition metal ion exchanged zeolites [4,5,13,21–30]; hence, the direct reduction of NO_2 with CH_4 on this family of catalysts has been extensively studied [12,13,25,26]. However, much less is known about the NO_2 + CH_4 reaction catalyzed by noble-metal-containing zeolites. The objective of the present research was to understand the molecular level chemistry dictating the NO + CH_4 and NO_2 + CH_4 reactions catalyzed by Pt-ZSM-5. This was accomplished by comparing the macroscopic performance of Pt-ZSM-5 in these reactions to the unselective behavior of Pt-ZSM-5 for NO_x SCR with CH_4 when O_2 is present [9].

2. Experimental

The Pt-ZSM-5 used in this investigation was supplied by Sandia National Laboratories. The catalyst composition was analyzed by ICP (Pt, Na, Si and Al) at Galbraith Laboratories. The Si/Al ratio (22.8) and the ion exchange level (14% based on Pt^{2+}/2Al ratio) were calculated from the weight percentages. The catalyst contained < 0.06 wt% Na, suggesting that the remaining charge was balanced by H^+.

The NO and NO_2 (each 1% in He, 99.5% purity), CH_4 (1% in He, 99.97% purity; the higher hydrocarbon impurity was <1% of CH_4), O_2 (10% in He, 99.994% purity) and He (99.999% purity) were obtained from Praxair and were used as received. Analyses by gas chromatography showed no

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detectable impurities in the NO_2 tank; the NO tank contained impurities of CO_2 (~0.0075%) and N_2O (~0.01%).

Prior to each experiment, the catalyst sample was pretreated *in situ* with 2.5% O_2 (balance He) flowing at 75 cm^3/min (GHSV $\approx$ 42 000 h^{-1}). During this pretreatment, the temperature was increased to 500 °C at 4 °C/min and stabilized at that temperature for 14 h before cooling to room temperature.

Methane oxidation with NO or NO_2 was conducted in the temperature range of 200–550 ± 1 °C. A stainless-steel gas line supplied a continuous flow to the quartz U-tube reactor (4 mm i.d.) that contained 50 mg of catalyst. The steady state conversion at each temperature was defined by consecutive measurements in which the standard deviation in CH_4 concentration was less than 0.6% of the average value. Unless otherwise specified, a mixture of 2000 ppm CH_4 and 2000 ppm NO (or NO_2) in He at atmospheric pressure was introduced into the reactor at a flow rate of 75 ml/min. When the feed gas composition was varied, this was done at 500 °C by switching from one feed gas composition to a He flow (~40 cm^3/min) for 10 min and then to the other feed gas composition.

The effluent from the reactor was analyzed by gas chromatography (Varian GC 3300). An Alltech 6′ CTR I column connected to a TCD was used to quantify N_2, N_2O, O_2, CO and CO_2, and a Supelco 30′ Chromosorb P AW column connected to a FID was used to quantify hydrocarbons. However, no N_2O, O_2, CO and hydrocarbons other than CH_4 were detected. Only N_2 and CO_2 were formed during all reactions.

X-ray powder patterns were recorded with a Diano XRD-5 diffractometer equipped with a receiving graphite monochromator to obtain Cu $K_{\alpha 1}$ radiation and with a scintillation detector. The scans were performed at a rate of 0.2°/min. The average Pt particle size was determined from the broadening of the [111] X-ray line, as described elsewhere [31].

3. Results

The conversion of both CH_4 and NO_2 depended strongly on temperature (figure 1). For CH_4 conversion the behavior was similar to that of CH_4 combustion by O_2 catalyzed by Pt supported on silica or alumina. There was a very slow increase in conversion with temperature, followed by a rapid increase when the ignition temperature was reached [11]. The CH_4 conversion in the $CH_4 + NO_2$ reaction was $<1\%$ at temperatures below the light-off temperature of 374 °C, but increased from ~12% at 475 °C to ~56% at 500 °C (figure 1). Correspondingly, the conversion of NO_2 was $<1\%$ at temperatures below 385 °C and $\leqslant 5\%$ at temperatures below 475 °C. Thereafter, the NO_2 conversion increased to approximately 85% as the temperature increased to 500 °C.

The oxidation of CH_4 by NO_2 to form N_2 and CO_2 follows the stoichiometry:

$$CH_4 + 2NO_2 \rightarrow N_2 + CO_2 + 2H_2O \qquad (1)$$

For the equimolar feed composition, the limiting reagent is NO_2 and the theoretical limit for CH_4 conversion is 50%. However, the actual CH_4 conversion at 500 °C was 56%, ~13% higher than expected for NO_2 conversion into N_2 of 86% according to the stoichiometry of reaction (1) (figure 1). The CH_4 conversion decreased to ~50% after about 1 h time on stream at 500 °C.

The factors associated with the higher CH_4 conversion were explored further. Figure 2 shows the carbon balance for the $CH_4 + NO_2$ reaction to form CO_2 (CO was not detected). In the temperature range of 250–475 °C the carbon balance closed within 2%. However, the conversion of CH_4 to CO_2 at 500 °C was still below 50% even though the total

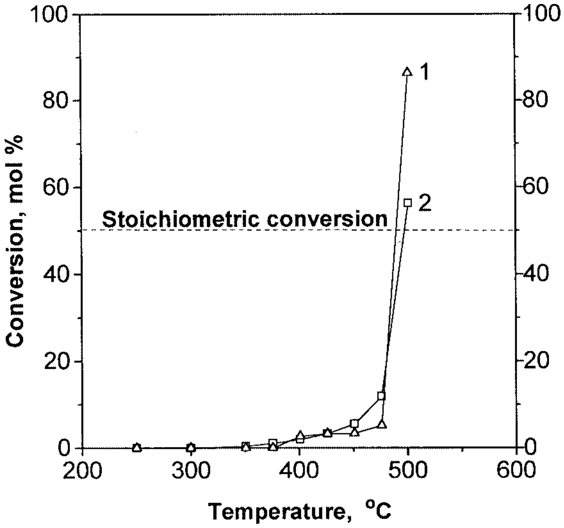

Figure 1. Methane oxidation with NO_2 catalyzed by Pt-ZSM-5: curve (1) the conversion of NO_2 to N_2 and curve (2) the conversion of CH_4. The dotted line represents the upper limit of CH_4 conversion to CO_2 for the CH_4/NO_2 ratio of 1 according to the stoichiometry of reaction (1).

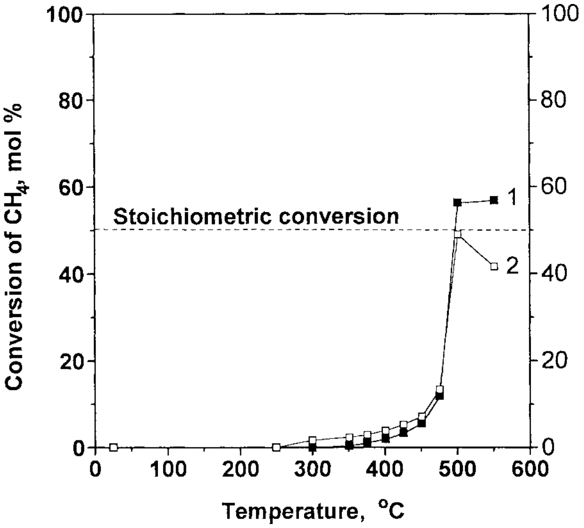

Figure 2. Carbon balance for CH_4 oxidation by NO_2: curve (1) the total conversion of CH_4 and curve (2) the conversion of CH_4 to CO_2. The dotted line represents the upper limit of CH_4 conversion to CO_2 for the CH_4/NO_2 ratio of 1 according to the stoichiometry of reaction (1).

CH_4 conversion was ~56%. The conversion of CH_4 to CO_2 was 41% at 550 °C while the total CH_4 conversion was 54%.

The light-off temperature for the CH_4 + NO reaction was 175 °C lower than for the CH_4 + NO_2 reaction. Figure 3 shows that the conversions of NO and CH_4 were <1% and <5%, respectively, at 300 °C. The NO conversion to N_2 and the CH_4 conversion increased with increasing temperature up to 400 °C. At temperatures greater than 400 °C the conversion of CH_4 and NO toward N_2 remained constant at ~23 and 77%, respectively. Over the entire temperature range the CH_4 conversion exceeded the stoichiometric limit of the following reaction:

$$CH_4 + 4NO \rightarrow CO_2 + 2N_2 + 2H_2O \tag{2}$$

The influence of feed gas composition on catalyst performance was explored. Table 1 shows the catalytic activity expressed in terms of conversion for four different feed gas compositions at 500 and 550 °C: 2000 ppm CH_4/4000 ppm NO_2, 2000 ppm CH_4/4000 ppm NO, 1000 ppm CH_4/2000 ppm NO_2, and 2000 ppm CH_4/2000 ppm NO_2. The results for each composition are described below.

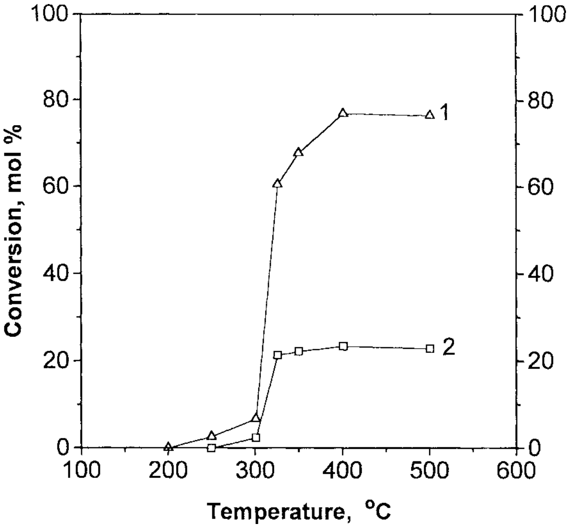

Figure 3. Methane oxidation with NO catalyzed by Pt-ZSM-5: curve (1) the conversion of NO to N_2 and curve (2) the conversion of CH_4.

2000 ppm CH_4/4000 ppm NO_2. Upon switching the feed gas composition of 2000 ppm CH_4/2000 ppm NO_2 to 2000 ppm CH_4/4000 ppm NO_2, the conversion of NO_2 to N_2 decreased rapidly from ~87 (figure 1) to 6.5%. The conversion continued to decrease with time to about 2.5% at 500 °C in ~20 min and increased to 3.6% when the reaction temperature was increased to 550 °C. The CH_4 conversion decreased from 28.3 to 19.1% during ~20 min at 500 °C. The conversion then increased to 43.5% when the reaction temperature was increased to 550 °C (table 1). The carbon balance between the CH_4 conversion and CO_2 production closed within 2% at this feed condition.

2000 ppm CH_4/4000 ppm NO. Quite different results were obtained when using 4000 ppm of NO instead of NO_2. The NO conversion to N_2 remained high (~82% at 500 °C) and it decreased to 73.1% when the temperature was increased to 550 °C. The CH_4 conversion with 4000 ppm NO was 54.0% initially at 500 °C and then decreased to 48.4% as the temperature was increased to 550 °C (table 1). The CO_2 production was 10–20% lower.

1000 ppm CH_4/2000 ppm NO_2. The NO_x conversion to N_2 decreased to 54.4% when the feed mixture was switched from 2000 ppm CH_4/4000 ppm NO to 1000 ppm CH_4/2000 ppm NO_2. The conversion was not stable and decreased to about 28% during the next ~20 min on stream. At the same time the CH_4 conversion decreased from ~72% initially to 47.3% at 500 °C (table 1). The CO_2 production was 10% higher than the CH_4 conversion.

2000 ppm CH_4/2000 ppm NO_2. When the standard feed (2000 ppm CH_4 and 2000 ppm NO_2 in He) was resumed, the conversion of NO_2 to N_2 increased to 95.3%, approximately 10% higher than that obtained initially (see figure 1). For the CH_4 conversion, the same initial activity was obtained, ~56% conversion at 500 °C (table 1, figure 1).

After the reaction of 2000 ppm CH_4 and 2000 ppm NO_2 catalyzed by Pt-ZSM-5 at 500 °C reached steady state in the experiment represented in table 1, the reaction temperature was decreased in steps from 500 to 350 °C. A positive hysteresis was observed for both the NO_x conversion to N_2 and CH_4 conversion as compared with the results obtained when the reaction temperature was increased from 350 to 500 °C (figure 4). The behavior at 450 °C was time dependent, as

Table 1

Conversion of NO_x and CH_4 during CH_4 oxidation with NO_x catalyzed by Pt-ZSM-5 with varying feed gas compositions.[a]

Feed gas composition[b]	Temperature (°C)	Conversion[c] (mol%)	
		NO_x to N_2	CH_4
2000 ppm CH_4 and 4000 ppm NO_2	500	6.5(2.5)	28.3(19.1)
	550	3.6	43.5
2000 ppm CH_4 and 4000 ppm NO	500	83.8(81.6)	54.0(48.4)
	550	73.1(71.5)	47.6(45.5)
1000 ppm CH_4 and 2000 ppm NO_2	500	54.4(28.4)	71.5(47.3)
2000 ppm CH_4 and 2000 ppm NO_2	500	95.3(91.9)	55.5(58.2)

[a] The feed gas composition was changed at 500 °C by switching from one feed gas composition to a He flow (~40 cm^3/min) for 10 min and then to the other feed gas composition.

[b] Balance He.

[c] In parentheses the conversion in 20 min on stream after the previous analysis.

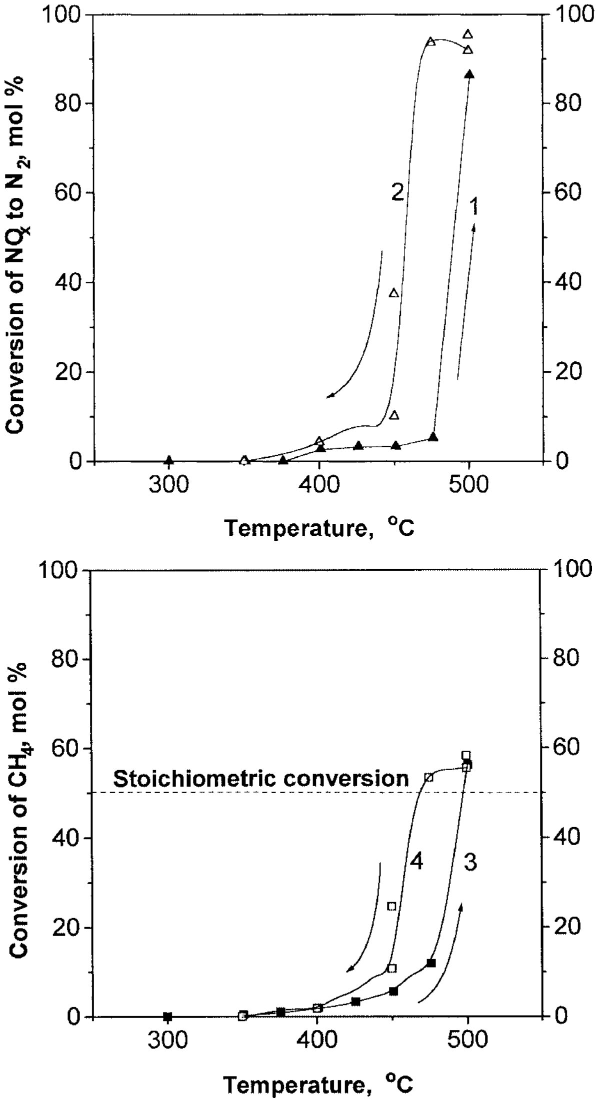

Figure 4. Methane oxidation with NO_2 catalyzed by Pt-ZSM-5. Curves (1) and (3) represent NO_2 conversion to N_2 and CH_4 conversion in the experiment shown in figure 1. Curves (2) and (4) represent conversion of NO_2 to N_2 and CH_4 conversion as the temperature of the catalyst was decreased in the flow of 2000 ppm CH_4 and 2000 ppm NO_2 in He after the experiment shown in table 1. The dotted line represents the upper limit of CH_4 conversion to CO_2 for the CH_4/NO_2 ratio of 1 according to the stoichiometry of reaction (1).

shown by the decrease in conversions of CH_4 and NO_x (from 37 to 10% and from 25 to 10%, respectively, in ~20 min on stream). The hysteresis ceased at 400 °C. The carbon balance was within 10% of the value obtained during the entire hysteresis.

To identify the state of Pt in the catalyst samples, X-ray diffraction (XRD) patterns were obtained for as-received, calcined samples and for a sample after $CH_4 + NO_2$ reaction. All samples had indistinguishable XRD patterns with lines belonging only to ZSM-5 and metallic Pt. The average size of Pt particles calculated from line broadening was 5 nm for all samples studied. Thus, Pt sintering did not take place during catalytic experiments and, hence, did not contribute to the catalytic performance.

4. Discussion

4.1. Nature of catalyst

Platinum does not form oxides stable at elevated temperatures [32]. Even though PtO can be obtained by direct oxidation of metallic Pt with pure O_2 at 1 atm and 510 °C [33], at lower O_2 partial pressures the Pt oxidation is limited essentially to the surface layer of Pt atoms [34]. Our results are consistent with these previous observations – neither the catalyst sample pretreated in O_2/He flow at 500 °C nor the sample used in $NO_x + CH_4$ reaction contains bulk Pt oxides.

4.2. Comparative activity of NO and NO_2

According to the generally accepted mechanism of lean NO SCR with hydrocarbons catalyzed by Pt, the reaction consists of two main pathways. The NO decomposes to form adsorbed nitrogen and oxygen atoms. Two N atoms combine to form a N_2 molecule that desorbs from the surface, and the surface oxygen reacts with a hydrocarbon intermediate to form CO_2 and regenerate active sites [9,35,36]. Hence, the comparison of reactions of CH_4 with NO or NO_2 and with O_2 should be informative.

The typical temperature dependence of CH_4 oxidation by O_2 catalyzed by supported Pt is a very slow increase in conversion followed by a rapid increase when the ignition temperature is reached [11]. This macroscopic behavior has been explained in terms of the most active surface being partially oxidized Pt surface [12]. The completely reduced Pt surface lacks oxygen; the surface excessively covered with adsorbed oxygen has few $Pt^{\delta+}$–$O^{\delta-}$ sites where the C–H bond activation occurs. Thus, at relatively low temperatures the Pt surface is almost completely covered with oxygen due to the much higher sticking coefficient of O_2 than of CH_4 [37,38] and higher temperatures are required to release surface sites for CH_4 adsorption. This interpretation provides a key for understanding the relative reactivity of NO and NO_2 toward CH_4 on the Pt surface.

Nitric oxide rapidly dissociates on the reduced Pt surface to form gas phase N_2 and O adatoms even at temperatures below 100 °C [39]. However, at temperatures above 300 °C the Pt surface is at least partially reduced, because it shows catalytic activity for NO decomposition [18]. Notably, the conversions of NO and CH_4 are detectable for the Pt-ZSM-5 catalyst reaction temperature greater than 300 °C (figure 3). A similar result was obtained for CH_4 combustion; both 1% Pt/SiO_2 and 1% Pt/Al_2O_3 exhibited no activity at temperatures below 380 °C [11].

The N–O bond energy of NO_2 is significantly lower than that of NO (305 and 627 kJ/mol, respectively [40]) and one can expect NO_2 to dissociate rapidly on the Pt surface. Thus, the steady state oxygen coverage of Pt surface at the same partial pressures of NO and NO_2 will be higher for the latter. This is a reason of lower rate of the $CH_4 + NO_2$ reaction than of the CH_4 + NO reaction (figures 1 and 2).

4.3. Chemistry of the $NO_x + CH_4$ reaction

Increasing steady state oxygen coverage of the Pt surface resulting from increasing NO_2 partial pressure in the reaction mixture (table 1) dramatically suppresses the selectivity toward N_2 according to the stoichiometry of reaction (1). Because CO_2 forms, one can conclude that the NO_2 reduction occurred but only to form NO instead of N_2:

$$CH_4 + 4NO_2 \rightarrow CO_2 + 4NO + 2H_2O \qquad (3)$$

Apparently, NO cannot compete with NO_2 for adsorption sites and desorbs into gas phase rather than dissociate on the surface. Decreasing the concentration of oxygen atoms in the gas phase and, as a consequence, on the catalyst surface by switching the reaction mixture from 2000 ppm CH_4 + 4000 ppm NO_2 to 2000 ppm CH_4 + 4000 ppm NO increases the selectivity toward N_2 from few percents for the former mixture to more than 80% for the latter (table 1).

Elucidating the crucial role of steady state oxygen surface coverage on the selectivity of NO_x reduction toward N_2 allows one to speculate on the reasons for the dramatically different behavior of Pt-based catalysts when CH_4 [9] or C_{2+} hydrocarbons [35,41–47] are used as reductant in the presence of excess of O_2. The sticking coefficient for oxygen on Pt is high and normally with the excess of O_2 in the reaction mixture the Pt surface is completely covered with oxygen. This inhibits the adsorption and dissociation of NO. The interaction of a hydrocarbon molecule with the oxidized Pt surface results in the oxidation of the hydrocarbon and formation of an island of the reduced metal surface. The size of the island of reduced metal surface depends on the number of C and H atoms in the initial hydrocarbon molecule. Apparently, in the case of CH_4 the size of the island is not large enough to allow NO to compete with O_2 for adsorption sites on the Pt surface, making the Pt surface unselective for SCR NO_x. For comparison, the oxidation of a C_3H_8 molecule on the catalyst surface to form CO_2 and H_2O consumes ten surface O adatoms, while the oxidation of a CH_4 molecule consumes only three.

Figures 1–3 and table 1 show that under some conditions the methane conversion may be higher than the stoichiometric requirements of $NO_x + CH_4$ reactions. It leads to the deposition of carbonaceous species on the Pt surface. In general, it is not surprising because reduced Pt surfaces are highly active toward CH_4 decomposition [48]. When the rate of CH_4 decomposition is significantly high, the catalyst deactivates with TOS (table 1).

An increasing of the rate of CH_4 + NO reaction by surface carbon was found for Pd-ZSM-5 [49]. The same effect of carbonaceous deposits was observed for NO decomposition catalyzed by carbon- and alumina-supported Pt [50]. Thus, the positive hysteresis of the $CH_4 + NO_2$ reaction when the temperature was cycled from 350 to 500 °C and back to 350 °C (figure 4) can be explained in terms of influence of carbonaceous deposits on the reaction rate. As shown in table 1, the conversion of the 1000 ppm CH_4 + 2000 ppm NO_2 occurs with a CH_4 conversion higher than the requirement of the stoichiometry. Hence, before switching this mixture to the 2000 ppm CH_4 + 2000 ppm NO_2 mixture the surface of the catalyst is partially covered by carbonaceous species. The consumption of these species eliminates the hysteresis. This consumption most likely causes the conversion drop with TOS at 450 °C (figure 4).

5. Conclusions

Metallic Pt in Pt-ZSM-5 catalyzes the $CH_4 + NO_2$ and CH_4 + NO reaction to form CO_2 and N_2. The former reaction has significantly higher ignition temperature than the latter one (∼475 and ∼300 °C, respectively). The kinetics results are consistent with the reaction mechanism including NO_x decomposition on the Pt surface and subsequent CH_4 interaction with O-containing moieties to form the reaction products. Increasing the steady state surface coverage of oxygen atoms results in a dramatic decrease in the selectivity of NO_x reduction toward N_2. Methane decomposition on the Pt surface was found to occur under certain experimental conditions to form carbonaceous deposits. These deposits enhance the NO_2 reduction to N_2.

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