Oxidation state of platinum clusters during the reduction of NO_x with propene and propane

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The oxidation state of platinum supported on mesoporous SiO_2 and Al_2O_3 with MCM-41 type structure during the reduction of NO_x with propene or propane was investigated using *in situ* X-ray absorption spectroscopy. Platinum supported on MCM-41 (SiO_2) was reduced at low and oxidized at high reaction temperatures when propene was used as reducing agent, while it was found to be always oxidized in Pt/MCM-41 (Al_2O_3). When propane was used as reducing agent significant NO conversion was not observed over Pt/MCM-41 (SiO_2) and on both supports platinum was in an oxidized state. At the successive adsorption of the reactants, the prereduced catalysts were oxidized after NO adsorption and reduced after addition of the hydrocarbons. Addition of oxygen re-oxidized the catalysts, while the presence of water vapor did not influence the oxidation state.

KEY WORDS: *in situ* XANES; deNO_x; Pt/MCM-41; oxidation state

1. Introduction

Stationary and mobile sources account for the main part of the NO_x emissions today [1]. Therefore, future legislation will further strengthen the limits for the emission of nitrogen oxide as well as carbon monoxide, hydrocarbon, sulfur dioxide and particulates in the exhaust gases from vehicles [2–5]. For diesel and lean-burn engines the traditionally used three-way catalysts cannot be applied for the reduction of NO_x into nitrogen, because the exhaust gases contain an over-stoichiometric concentration of oxygen. Therefore, the reduction of NO_x under oxidizing reaction conditions requires the addition of a reducing agent such as hydrocarbons or ammonia. For reactions using hydrocarbons as reducing agents catalysts based on transition-metal-containing zeolites, e.g., Cu/ZSM-5 and Fe/ZSM-5 [6–10] and noble metals, e.g., Pt supported on SiO_2 and Al_2O_3 [11–13] were successfully used. Additionally, noble-metal-containing MCM-41 catalysts were found to be an attractive alternative to transition-metal-containing zeolites [14].

One of the key questions for the understanding of the reaction is the oxidation state of the metal under reaction conditions. In the literature contradictory statements were published. It was reported by Burch et al. [13] that Pt supported on SiO_2 and Al_2O_3 was reduced when propene was used as reducing agent and in an oxidized state in reactions with propane. In contrast, Pitchon et al. reported [15] that platinum on alumina was in an oxidized state using propene as reducing agent.

In order to relate the catalytic activity to the chemical properties of Pt the oxidation state during the NO reduction with saturated and unsaturated hydrocarbons was studied in this paper using X-ray absorption spectroscopy.

2. Experimental

2.1. Materials

The synthesis of siliceous mesoporous molecular sieves with MCM-41 type structure was carried out according to [16] using fumed silica (SiO_2, Sigma), hexadecyl-trimethylammonium bromide (CTABr, Aldrich) and tetramethylammonium hydroxide pentahydrate (TMAOH, Fluka). The gel composition for the synthesis was $SiO_2 : TMAOH : CTABr : H_2O = 1 : 0.19 : 0.27 : 40$. The reaction gel was prepared by solving TMAOH and CTABr in distilled water under stirring and mild heating. Subsequently, the silica was added to the clear solution under continuous stirring for additional 2 h. The gel was aged for 24 h at room temperature and the condensation of the mesoporous molecular sieve was carried out at 423 K for 48 h in a teflon autoclave. After the synthesis the product was filtered, washed extensively with distilled water and dried in air at 323 K.

Mesoporous Al_2O_3 with MCM-41 type structure was synthesized according to [17] using aluminum *sec*-butoxide, lauric acid and 1-propanol (all obtained from Fluka). The gel composition was $Al(OCH(CH_3(C_2H_5)_3 : C_{11}H_{23}CO_2H : H_2O : C_3H_7OH = 1 : 0.3 : 3.2 : 26$. An aluminum hydroxide suspension was prepared from hydrolysis of aluminum *sec*-butoxide with distilled water in 1-propanol during continuously stirring at 298 K. After 1 h lauric acid was added, the synthesis gel was transferred into a teflon autoclave, aged for 24 h at room temperature and heated under static conditions

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Table 1
Composition and structural properties of the catalysts.

Sample	Metal concentration (wt%)	Dispersion H/Me ratio	Metallic surface sites (μmol g^{-1})
Pt/MCM-41 (SiO_2)	1.61	0.63	52
Pt/MCM-41 (Al_2O_3)	1.62	0.39	32

at 383 K for 48 h. The solid product was filtered, washed with ethanol and dried at room temperature.

The organic template was removed from the mesoporous molecular sieves by calcination in synthetic air at 813 K for 10 h using a heating rate of 1 K/min from room temperature to 813 K.

The structure of the mesoporous supports after the calcination was verified by XRD and by N_2 sorption. Four Bragg reflexes for the siliceous and one for the mesoporous Al_2O_3 with MCM-41 type structure and a sharp step in the N_2-isotherms at $p/p_0 \approx 0.4$ [18,19] were observed. The BET surface areas were 1006 and 411 m^2/g for MCM-41 (SiO_2) and MCM-41 (Al_2O_3), respectively.

The supports were loaded with 1.6 wt% Pt applying incipient wetness impregnation in aqueous solution using $PtCl_4$ as precursor. After incorporation of Pt the catalysts were calcined in air at 823 K for 3 h, crushed and sieved. The grain size smaller than 180 μm was used for the experiments. The composition and structural properties of the catalysts, indicated as Pt/MCM-41 (SiO_2) and Pt/MCM-41 (Al_2O_3), are summarized in table 1.

2.2. X-ray absorption spectroscopy

The X-ray absorption spectra were measured at the HASYLAB (Hamburger Synchrotronstrahlungslabor, Hamburg, Germany) at the beamline X1.1 in transmission mode using ionization chambers filled with argon (100 mm path length). The energy resolution of the monochromator equipped with Si(311) crystals was approximately 1 eV at the energy of the Pt-L_{III} edge. To calibrate the energy of the monochromator a Pt foil was inserted between the second and the third ionization chamber.

The catalysts were pressed into self-supporting wafers and placed inside a stainless-steel cell (volume 55 ml, operated as a CSTR), which allows X-ray absorption spectra to be collected *in situ* during the reaction. The weight of the samples was selected to achieve an absorption of $\mu x = 2.5$ for the reduced catalysts to optimize the signal to noise ratio. The temperature of the sample was measured with a thermocouple placed in direct contact to the sample holder. To determine qualitative changes in the oxidation state of Pt we assumed that Pt is present as reduced Pt^0 or oxidized Pt^{4+}, because other oxidation states of Pt are unlikely. Consequently, the spectra obtained should result from a superposition of the XANES of Pt^0 and Pt^{4+} and, therefore, the average oxidation state was calculated using the XANES of Pt foil (Pt^0) and PtO_2 (Pt^{4+}) as reference by a direct correlation of the area of the peak above the L_{III} edge (determined by numerical integration after the simulation of the continuum step using an *acttan* function [20] and the oxidation state.

2.2.1. Adsorption of reactants and catalytic activity

Four electronic mass flow controllers (Brooks 5850E) were used to prepare a reactant gas mixture with the following composition: 1010 ppm NO, 1012 ppm C_3H_6 or C_3H_8, respectively, and 4.9 vol% O_2 (balance He). 2.5 vol% water vapor could be added into the gas stream with a syringe pump. The total flow rate of the reactant gases was 100 cm^3/min, which resulted in a space velocity of $W/F = 9 \times 10^{-2}$ g s cm^{-3}. The NO and NO_2 concentrations in reactant and after the reactor were analyzed with a chemiluminescence NO/NO_2 analyzer (Horiba APNA-350E).

Before the subsequent adsorption of the reactants, the catalysts were reduced with 5% H_2 in He at 773 K for 30 min. After the catalysts were cooled to 573 K in He, the gases in the order NO, C_3H_6 or C_3H_8, O_2 and H_2O were adsorbed. The catalytic activity and the oxidation state of Pt during the NO reduction were determined after the catalysts were activated in He at 773 K for 1 h in a temperature range between 793 and 403 K.

3. Results and discussion

3.1. Adsorption experiments of NO, C_3H_6/C_3H_8, O_2 and H_2O

The XANES of the prereduced Pt/MCM-41 (SiO_2) catalyst (5% H_2 in He at 773 K for 30 min) after subsequent adsorption of 1010 ppm NO, 1012 ppm C_3H_6, 5 vol% O_2 and 2.5 vol% water vapor are compared in figure 1. Adsorption of 1010 ppm NO at 573 K on the catalyst led to a partial oxidation of platinum. In the presence of NO and C_3H_6 (the reducing agent) Pt was reduced to a level comparable to that observed after the reduction in H_2. This clearly indicates that the oxidized surface species of Pt can be reduced to metallic Pt with the hydrocarbon in absence of O_2. After adding oxygen into the reactant gas mixture all catalysts were oxidized. Since changes in the oxidation state of Pt during the adsorption of water could not be observed, we would like to speculate that the decrease in the activity is mainly caused by a competitive adsorption of water and the reactant molecules on the metallic sites [21–23]. Note that our results support the model of Burch et al. [24], who reported that on the SiO_2-based catalyst the reaction can proceed only on a reduced Pt surface.

3.2. Influence of temperature on the oxidation state of Pt during the NO reduction

The NO conversion and the oxidation state of Pt in Pt/MCM-41 (SiO_2) (after activation in He) during the C_3H_6–NO–O_2 reaction are shown in figure 2. As already reported in [15], the conversion of NO and C_3H_6 started simultaneously and increased with increasing temperature until the

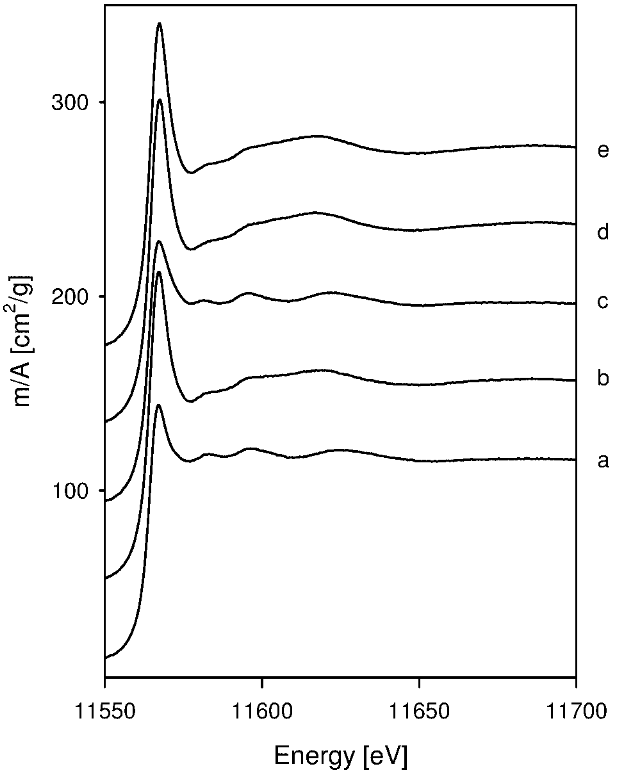

Figure 1. XANES of the prereduced Pt/MCM-41 (SiO_2) (a) and after adsorption of NO (b), NO + C_3H_6 (c), NO + C_3H_6 + O_2 (d) and NO + C_3H_6 + O_2 + H_2O (e) at 573 K.

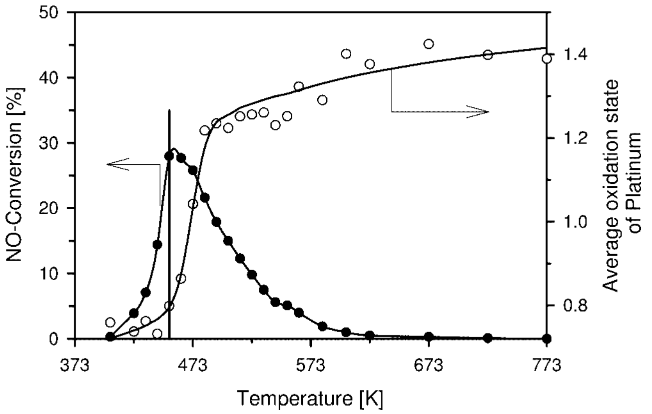

Figure 2. Conversion of NO_x (●) and oxidation state of Pt in Pt/MCM-41 (SiO_2) (○) during the C_3H_6–NO_x–O_2 reaction.

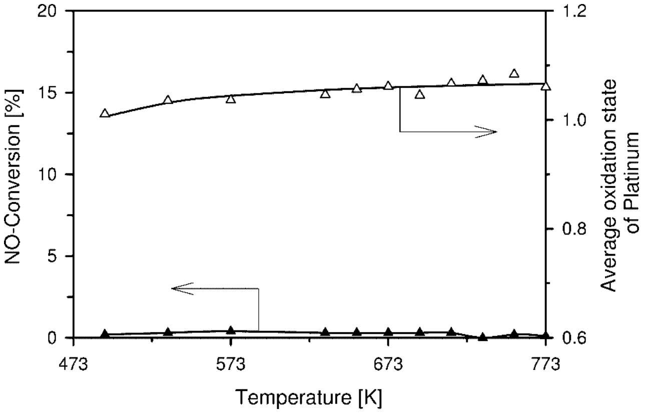

Figure 3. Conversion of NO_x (▲) and oxidation state of Pt in Pt/MCM-41 (SiO_2) (△) during the C_3H_8–NO_x–O_2 reaction.

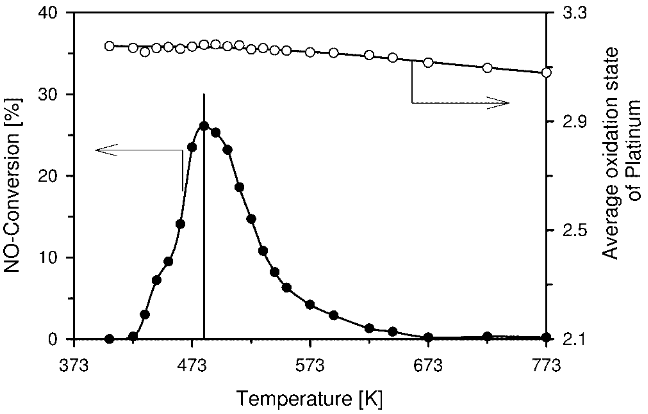

Figure 4. Conversion of NO_x (●) and oxidation state of Pt in Pt/MCM-41 (Al_2O_3) (○) during the C_3H_6–NO_x–O_2 reaction.

hydrocarbon conversion reached ~100%. The XANES observed during this reaction indicated that Pt was only slightly oxidized up to the temperature of the maximum NO conversion (453 K). Simultaneously to the decrease in the NO conversion at higher temperatures platinum became oxidized. This clearly indicates that on MCM-41 (SiO_2) reduced platinum is significantly more active for C_3H_6–NO–O_2 reaction compared to platinum oxide. At propene conversion levels below 100% propene was available over the whole catalyst bed. Therefore, an oxidation of Pt was not observed in the XANES. At higher temperatures propene was completely consumed via the direct oxidation and the NO reduction and thus a fraction of residual oxygen remained on the surface. Due to the lack of reducing agent the formation of Pt–O species could be observed at this temperature. With increasing temperature the rate of propene oxidation by O_2 increased, which led to a further formation of Pt–O species and to a decrease of the NO conversion. At temperatures above 623 K the rate for the direct oxidation of C_3H_6 was so high that a further NO reduction was not observed.

The influence of the temperature on the oxidation state of Pt and the NO conversion during the C_3H_8–NO–O_2 reaction over Pt/MCM-41 (SiO_2) is shown in figure 3. Pt was always in an oxidized state in the presence of propane, which increased slightly over the temperature range studied, while the catalyst did not show any activity for the NO reduction. Although it was found that propane could reduce Pt–O species in the absence of oxygen (figure not shown here), it was found that the metal could not be reduced in the presence of oxygen.

The temperature dependence of the NO conversion and the oxidation state of Pt/MCM-41 (Al_2O_3) for the reaction with C_3H_6 and C_3H_8 are compared in figures 4 and 5. The catalyst was found to be active in the NO reduction for both reducing agents. In agreement with [14] the maximum in the NO conversion was observed at higher temperatures com-

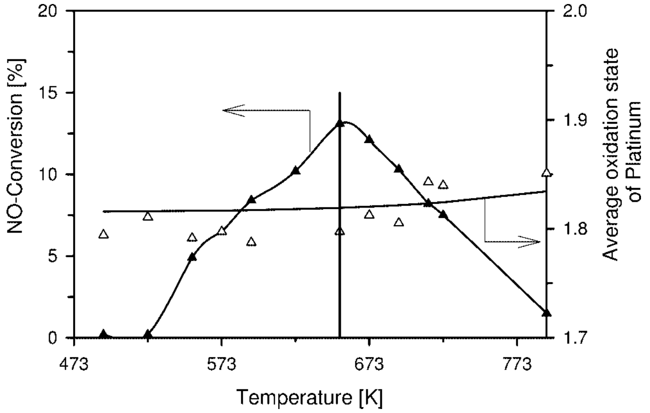

Figure 5. Conversion of NO$_x$ (▲) and oxidation state of Pt in Pt/MCM-41 (Al_2O_3) (△) during the C_3H_8–NO$_x$–O_2 reaction.

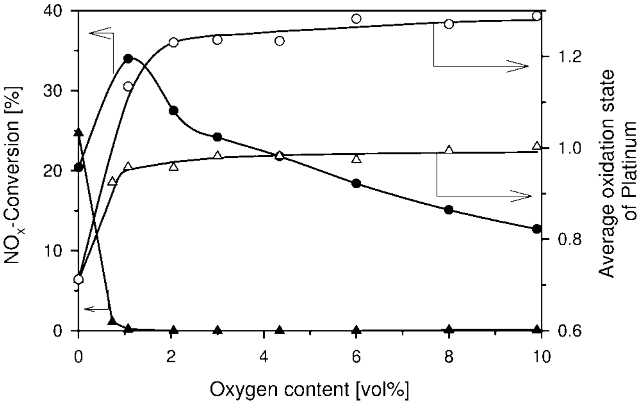

Figure 6. Conversion of NO$_x$ (solid symbols) and oxidation state of Pt (open symbols) in Pt/MCM-41 (SiO_2) for the HC–NO$_x$–O_2 reaction with C_3H_6 (●,○) and C_3H_8 (▲,△) at 493 K as a function of the O_2 concentration.

pared to Pt/MCM-41 (SiO_2). For the reaction with C_3H_6 the maximum conversion was 26% at 483 K, while for the reaction with C_3H_8 a lower activity, i.e., 13% NO conversion at 653 K was found. At higher reaction temperatures the activity decreased. Under all reaction conditions studied Pt was in an oxidized state, which did not significantly change as a function of the reaction temperature. The high formal oxidation state for Pt (>3) for the complete temperature range indicated that during the NO reduction the metal [15] is most probably structurally incorporated into the MCM-41 (Al_2O_3) lattice, e.g., by the formation of an Pt-aluminate phase [25–27]. During the reaction with propane the formal oxidation state of in Pt/MCM-41 (Al_2O_3) was found to be lower compared to the reaction with propene. This resulted from the lower reactivity of propane compared to propene, which is also reflected in a significant increase in the light off temperature of the hydrocarbon only [14]. According to the lower reactivity and consequently higher residence time of the alkane on the adsorption sites compared to the alkene, the concentration of available hydrocarbon species on the catalyst surface is significantly higher. Therefore, the enhanced availability of hydrocarbon species, also at higher reaction temperatures, led to a partial reduction of the metal. The stability of the oxidation state of platinum within the complete temperature region indicated the presence of platinum species, which were still incorporated into the walls of MCM-41 (Al_2O_3). Furthermore, the oxidation state of platinum is independent of the oxygen content in the reaction feed (see figure 7, discussed in section 3.3). Even under oxygen-free conditions platinum was oxidized, which indicated that platinum incorporated into the walls of MCM-41 (Al_2O_3) cannot be reduced by propene or propane such as on MCM-41 (SiO_2).

3.3. *Influence of oxygen concentration on the oxidation state of Pt*

The oxidation state of Pt in Pt/MCM-41 (SiO_2) and the NO conversion for the reaction with C_3H_6 and C_3H_8 at 493 K as a function of the O_2 concentration are shown in figure 6. The reduction of NO with C_3H_6 and C_3H_8 was measured isothermally at 493 K, thus the combustion rate of the hydrocarbon was not influenced by the temperature. For both reducing agents Pt was found to be in an oxidized state at oxygen concentrations between 1 and 10 vol%, while at lower oxygen concentrations the metal was partially reduced. For the NO reduction with C_3H_6 a NO conversion of 13% was observed at an oxygen concentration of 10 vol% O_2. The NO conversion strongly increased with decreasing oxygen concentration and reached a maximum of 34% at 1.1 vol% O_2 [28], while the oxidation state of the metal decreased only slightly. In the absence of oxygen the metal was reduced and the NO conversion decreased. Note that reduced platinum was significantly more active for C_3H_6–NO–O_2 reaction compared to platinum oxide (see figure 2). Due to the reducing reaction conditions a direct oxidation of the hydrocarbon was not possible on the metal surface. Therefore, a high coverage with propene should be achieved, which limited nitric oxide to adsorb and further react. The presence of oxygen may prevent the deposition of carbonaceous deposits, which could cover the active sites [29].

When propane was used as reducing agent Pt/MCM-41 (SiO_2) did not show any activity for the NO$_x$ conversion in the presence of O_2. Platinum was in an oxidized state for oxygen concentrations above 0.7 vol%, while in the absence of oxygen the conversion of NO was 25% and Pt was in a reduced state.

Over catalysts with inert supports (e.g., SiO_2) the reaction cannot occur via a bifunctional mechanism such as over Al_2O_3 [30,31], which seems to be necessary for platinum oxide to be active for the reduction of NO.

The oxidation state of Pt in Pt/MCM-41 (Al_2O_3) and the conversion of NO as a function of the O_2 concentration for the reaction with propane and propene are compared in figure 7. In contrast to Pt/MCM-41 (SiO_2) the highest NO$_x$ conversion was observed at an oxygen concentration of 10 vol% [32,33] and it decreased with decreasing O_2 concentration [34]. In the absence of oxygen no NO conversion was observed. At the use of propene as reducing agent the oxidation state of the metal decreased slightly with decreasing oxygen concentration in the feed, which indicates, that

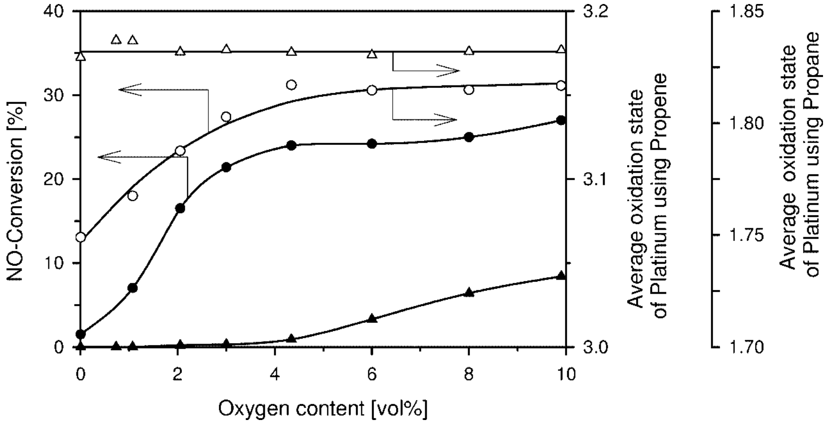

Figure 7. Conversion of NO_x (solid symbols) and oxidation state of Pt (open symbols) in Pt/MCM-41 (Al_2O_3) for the HC–NO_x–O_2 reaction with C_3H_6 (●,○) and C_3H_8 (▲,△) at 493 K as a function of the O_2 concentration.

the hydrocarbon is adsorbed on the catalyst. In the literature the contribution of propene in the generation of carbonaceous deposits was reported [35–37]. An *in situ* FT-IR study indicated that the concentration of carbonaceous and olefinic surface species increased with decreasing oxygen concentration [38]. The continuous decrease of the NO conversion with decreasing oxygen concentration can tentatively be explained by an enrichment of carbon deposits [34,39], which led to a poisoning of the active sites. Theoretical studies concerning benzene adsorbed on transition metal surfaces showed that benzene molecular orbitals can couple with the d-orbitals of the metal [40–44]. Calculations for benzene adsorbed on Pt(111) suggest a donation of electrons from π-orbitals into orbitals on the metal surface [45]. Carbonaceous deposits might also donate electrons from their π-orbitals to the metal, which might lead to a formal decrease of the oxidation state of Pt.

4. Conclusion

Adsorption of NO, C_3H_6/C_3H_8 and O_2 on platinum-containing MCM-41 catalysts induced strong changes in the oxidation state of the metal. The presence of NO oxidized Pt, while subsequent adsorption of C_3H_6 led to a reduction. The metal was re-oxidized with oxygen in the feed. The adsorption of water vapor did not further influence the oxidation state of platinum, while the activity of the catalyst decreased due to the competitive adsorption of the reactants and water.

During the reaction of C_3H_6–NO–O_2 on Pt/MCM-41 (SiO_2) the metal was reduced at temperatures below 453 K and oxidized at higher temperatures. On the MCM-41 (SiO_2) support metallic platinum was significantly more active for the reduction of NO than partially oxidized Pt species. Pt/MCM-41(SiO_2) catalysts were not active with propane as reducing agent, because the metal was always in an oxidized state in the presence of oxygen. Pt/MCM-41 (Al_2O_3) was active for both reducing agents. The maximum in the NO conversion was observed at higher temperatures compared to Pt/MCM-41 (SiO_2). The metal was always in an oxidized state indicating that the active sites on Pt/MCM-41 (Al_2O_3) for the NO reduction were partially oxidized Pt species.

The highest activity of Pt/MCM-41 (SiO_2) in the reduction of NO with propene was found in the presence of low oxygen concentrations, while in the absence of oxygen the activity decreased. We assume that oxygen prevents carbonaceous deposits leading to a decrease of activity. When propane was used for the NO reduction, Pt/MCM-41 (SiO_2) was only active in the reduced state.

The influence of the oxygen concentration on the oxidation state of Pt on MCM-41 (Al_2O_3) is not so strong as on MCM-41 (SiO_2), but the activity decreased continuously with decreasing oxygen content in the feed for both reducing agents. This might be due to an enrichment of carbonaceous deposits leading to a poisoning effect.

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