Catalytic reduction of NO_x over transition-metal-containing MCM-41

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The catalytic properties of Pt, Rh and Co supported on mesoporous molecular sieves with MCM-41-type structure consisting of SiO_2 and Al_2O_3 were studied for the reduction of NO with propene. Pt supported on siliceous MCM-41 was the most active catalyst, however, significant quantities of undesirable N_2O were formed during the reaction. Pt supported on mesoporous Al_2O_3 and Rh supported on both mesoporous oxides showed a lower activity, but an improved selectivity towards N_2 formation. Co supported on MCM-41-type materials had only a low level of activity for the reduction of NO with propene. For Pt supported on MCM-41-type materials only a minor decrease in the activity was observed when water vapor was added into the reactant gas mixture, while on Rh- and Co-containing catalysts the activity strongly decreased.

Keywords: NO_x reduction with C_3H_6, Co/MCM-41, Pt/MCM-41, Rh/MCM-41

1. Introduction

The catalytic reduction of air pollutants is one of the most rapidly growing applications in the field of environmental catalysis [1], an area, which today accounts for more than one third of the world catalyst market with respect to the value of catalysts applied [2]. Within this field the reduction of NO_x emissions is an important contribution to make combustion processes in power plants and waste incinerators, but also in diesel and lean-burn automotive engines environmentally more friendly. While for stationary sources of NO_x emission the SCR process using V_2O_5/TiO_2 catalysts and NH_3 as the reducing agent is regularly applied [3], extensive research is necessary to discover alternative catalytic systems for mobile NO_x sources, where environmentally more acceptable molecules such as hydrocarbons can be used for the reduction [4–6].

Initially, most of the research was focussed on transition-metal-containing zeolites such as Cu/ZSM5 [7] and Co/ZSM5 [8], but their drastic drop in activity when H_2O and/or SO_2 are present in the gas stream [9] as well as their low thermal stability [10] led to the development of catalysts such as Fe/ZSM5 [11–14], a material that has very promising activity in the presence of H_2O and SO_2. However, special synthesis methods must be applied to prevent the precipitation of iron hydroxide during the catalyst preparation [11–15].

An alternative route to develop highly active catalysts is based on the application of Pt-group metals supported on oxides such as SiO_2 and Al_2O_3 [16]. These materials showed a high activity and only a low deactivation in the presence of H_2O vapor, especially when unsaturated hydrocarbons and alcohols are used as reducing agents [17]. Additionally, it was reported that the support has only little effect on the activity when olefins were used for the reduction, while Pt/SiO_2 catalysts were the most active when paraffins were used as reductants [18,19]. The activity depends, however, not only on the kind of metal, support and reducing agent, but also on the particle size of the metal clusters, as it was described that the TOF strongly increased with increasing particle size [19,20]. The main restriction of Pt-group metals supported on metal oxides, however, is the formation of high quantities of N_2O [21,22], which acts as a greenhouse gas.

In order to combine the advantages of zeolites with oxide-based systems, we studied the catalytic properties of transition metals supported on mesoporous molecular sieves with MCM-41-type structure. Similar to metal-oxide-based systems these materials contain metal clusters, which can be reduced under reaction conditions [23]. In these catalysts the mesoporous molecular sieve mainly acts as a support for the metal and due to the special characteristics of MCM-41-type materials, metal clusters that are highly stabilized against thermal sintering, can be generated [24]. On the other hand, the pore openings of MCM-41-type materials are significantly larger compared to those of zeolites and, therefore, these catalysts should additionally allow the simultaneous conversion of larger gaseous molecules, which might be present in the exhaust gas during the NO_x reduction.

Recently, the catalytic properties of Pt supported on siliceous MCM-41 for the reduction of NO_x with methane, ethylene, propane and propylene were reported in the presence of water vapor and traces sulfur dioxide [25]. Our contribution mostly agrees with the data published, addi-

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tionally we compare the catalytic activity of Pt, Rh and Co supported on two types of mesoporous support, i.e., silica and alumina with MCM-41-type structure and discuss the influence of the support, of a hydrothermal treatment and of the hydrocarbon concentration.

2. Experimental

2.1. Materials

The synthesis of siliceous MCM-41 was carried out according to [26] using fumed silica (SiO_2, Sigma), hexadecyltrimethylammoniumbromide (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 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 [27] using aluminum sec-butoxide, lauric acid and 1-propanol (all obtained from Fluka). The gel composition was $Al(OCH(CH_3(C_2H_5)_3 : C_{11}H_{23}CO_2H : H_2O : C_2H_5CH_2OH = 1 : 0.3 : 3.2 : 26$. 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 at 383 K for 48 h. The solid product was filtered, washed with ethanol and dried at room temperature.

The organic templates were 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 supports were loaded with the metals applying the incipient wetness impregnation method in aqueous solution using $Rh(NO_3)_3$, $Co(NO_3)_2$ and $PtCl_4$ as precursors. After the incorporation of the metals the catalysts were calcined in air at 823 K for 3 h, crushed and sieved. A grain size smaller than 180 μm was used for the catalytic experiments. For comparison, Pt supported on dense SiO_2 (Degussa Aerosil 200) and on γ-Al_2O_3 (170 m^2/g), both catalysts with a metal loading of 1.6 wt% Pt, were used.

In this paper the catalysts are denoted with the type of metal and with the material the mesoporous support consists of, e.g., Pt/MCM-41(SiO_2) and Pt/MCM-41(Al_2O_3).

Table 1
Composition and structural properties of the catalysts.

Sample	Metal concentration (wt%)	Dispersion H/Me ratio	Metallic surface sites (mmol g^{-1})
Pt/MCM-41(SiO_2)	3.17	0.32	0.052
Pt/MCM-41(SiO_2)	1.61	0.63	0.052
Pt/MCM-41(SiO_2)	0.81	0.46	0.019
Pt/MCM-41(SiO_2)	0.40	0.58	0.012
Pt/SiO_2 (Aerosil)	1.61	0.49	0.040
Pt/MCM-41(Al_2O_3)	1.62	0.39	0.032
Pt/Al_2O_3	1.62	0.42	0.035
Co/MCM-41(SiO_2)	0.98	0.7[a]	0.116
Co/MCM-41(Al_2O_3)	0.98	n.d.	n.d.
Rh/MCM-41(SiO_2)	1.76	0.88	0.150
Rh/MCM-41(Al_2O_3)	1.76	0.89	0.152

[a] Determined from EXAFS results after reduction in H_2 at 873 K.

2.2. Characterization of the structural properties

The chemical compositions and the structural properties of all catalysts investigated are summarized in table 1. The structure of the mesoporous supports after calcination was verified by XRD and by N_2 sorption, where the usual features of MCM-41-type materials, e.g., four Bragg reflexes for the siliceous and one for the mesoporous Al_2O_3 with MCM-41 structure and a sharp step in the N_2-isotherm at $p/p_0 \approx 0.4$ [28,29] were observed. The d-spacing of the hexagonal unit cell, determined from the (100) reflex in the XRD, was 39 Å for MCM-41(SiO_2) and 28 Å for MCM-41(Al_2O_3). The BET surface areas were 1006 and 411 m^2/g for MCM-41(SiO_2) and MCM-41(Al_2O_3), respectively. H_2 chemisorption, carried out in a volumetric adsorption system, was used to determine the metal dispersion. Before these experiments the catalysts were reduced at 773 K for 2 h in flowing H_2 and, after sealing the system, evacuated at 773 K for 2 h at a pressure below 10^{-6} mbar. Note, that under these conditions both Co/MCM-41 samples could not be completely reduced, therefore, the number of accessible surface atoms was estimated from the results of the EXAFS analysis after reduction in H_2 at 873 K [23]. The H_2-sorption isotherm was measured at 295 K by exposing the samples to decreasing amounts of H_2. The H/Me ratio was calculated from the hydrogen uptake obtained from the extrapolation of the horizontal part of the isotherm to zero pressure. In a recent publication we have shown that for Pt supported on dense oxides and on zeolites an excellent correlation for each of the materials between the number of surface atoms, determined by EXAFS and by H_2 chemisorption, exists [30]. Therefore, a significant extent of H_2 spillover onto the mesoporous oxide, resulting in an increased H_2-chemisorption capacity, can be excluded.

2.3. Catalytic activity

The catalytic activity was determined in a quartz downflow reactor (i.d. 8 mm) using 100 mg of the catalysts. The reactant gas mixture was blended with four mass-flow controllers (Brooks 5850E) to give a total flow of 100 cm^3/min. The reaction gas consisted of 1010 ppm NO (about 91 ppm NO were directly oxidized in the reaction system to NO_2), 1012 ppm propene and 4.9 vol% O_2, the balance gas used was He. Up to 8 vol% water vapor could be added into the carrier gas stream using a syringe pump. The space velocities of the reactants over the catalysts were 11000 and 51000 $h^{-1}$for MCM-41(SiO_2) and MCM-41(Al_2O_3), respectively, resulting in a W/F of 6×10^{-2} g s cm^{-3} for all catalysts. Reactants and products were analyzed with a chemiluminescence NO_x analyzer and a gas chromatograph using TCD and FID detectors. A PoraPLOT-Q column for the separation of CO_2, N_2O, C_3H_6 and H_2O, and a Molsieve 5 Å column for the separation of O_2, N_2 and CO were used. Before each reaction the catalysts were activated in He at 773 K for 1 h. The conversion was measured as a function of the temperature between 453 and 773 K.

3. Results

The activity and selectivity of the transition-metal-containing mesoporous molecular sieves are compiled in table 2. The NO_x and propene conversion as a function of the temperature for MCM-41(SiO_2)-based catalysts is shown in figure 1, a comparison of the activity between MCM-41(SiO_2)- and MCM-41(Al_2O_3)-supported catalysts is given in figure 2.

For all catalysts investigated, the NO_x and C_3H_6 conversion started simultaneously and increased with the temperature until a hydrocarbon conversion of almost 100% was reached. A further temperature increase led to a decrease of the NO_x conversion, while the C_3H_6 conversion level remained at 100%. The highest NO_x conversion was observed for Pt/MCM-41(SiO_2) and it decreased for the Rh- and Co-containing MCM-41 catalysts. In parallel to the lower activity of these catalysts, the temperature at the maximum conversion increased from 483 K for

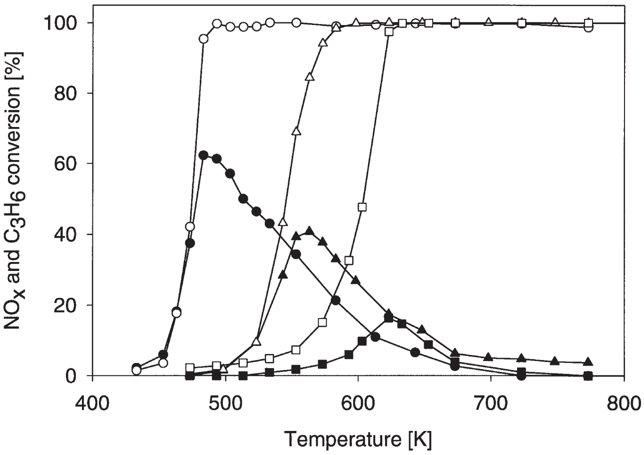

Figure 1. Conversion of NO_x (full symbols) and C_3H_6 (open symbols) as a function of temperature for (●, ○) Pt/MCM-41(SiO_2), (▲, △) Rh/MCM-41(SiO_2) and (■, □) Co/MCM-41(SiO_2) (all catalysts with 1 mol% metal loading).

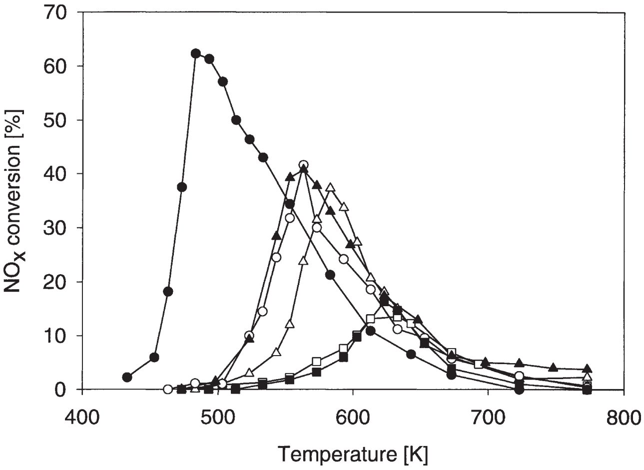

Figure 2. Activity comparison of (●) Pt/MCM-41(SiO_2), (▲) Rh/MCM-41(SiO_2), (■) Co/MCM-41(SiO_2), (○) Pt/MCM-41(Al_2O_3), (△) Rh/MCM-41(Al_2O_3) and (□) Co/MCM-41(Al_2O_3) (all catalysts with 1 mol% metal loading).

Table 2
Catalytic activity of transition-metal-containing MCM-41.

Sample	Metal concentration (wt%)	Max. NO_x conversion (%)	Temperature at maximum NO conversion (K)	N_2 selectivity[a] (%)
Pt/MCM-41(SiO_2)	3.17	63	483	36
Pt/MCM-41(SiO_2)	1.61	62	493	35
Pt/MCM-41(SiO_2)	0.81	59	503	40
Pt/MCM-41(SiO_2)	0.40	50	513	37
Pt/SiO_2 (Aerosil)	1.61	51	513	29
Pt/MCM-41(Al_2O_3)	1.62	41	563	58
Pt/Al_2O_3	1.62	46	543	34
Co/MCM-41(SiO_2)	0.98	16	623	53
Co/MCM-41(Al_2O_3)	0.98	15	623	60
Rh/MCM-41(SiO_2)	1.76	41	563	67
Rh/MCM-41(Al_2O_3)	1.76	37	583	67

[a] Versus formation of N_2O.

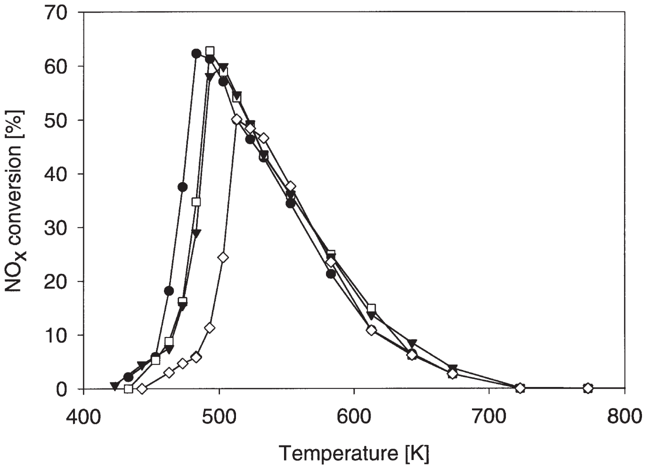

Figure 3. NO_x conversion as a function of the metal loading for Pt/MCM-41(SiO_2): (●) 3.17 wt% Pt, (□) 1.61 wt% Pt, (▼) 0.81 wt% Pt and (◇) 0.40 wt% Pt.

Pt/MCM-41(SiO_2) to 563 K for Rh/MCM-41(SiO_2) and up to 623 K for Co/MCM-41(SiO_2). Pt supported on dense SiO_2 (Aerosil) with a similar metal loading showed a lower activity compared to Pt/MCM-41(SiO_2). In general, for catalysts supported on MCM-41(Al_2O_3), a lower conversion and a higher temperature necessary for reaching the maximum conversion were observed compared to the catalysts supported on MCM-41(SiO_2) (see figure 2). The largest difference in activity between the MCM-41(SiO_2) and MCM-41(Al_2O_3) support was found for Pt. For Rh this difference was smaller and Co, the metal with the lowest activity in the series of catalysts studied, showed almost identical activity for the two types of mesoporous supports. In contrast, the selectivity for the reduction of NO_x to N_2 was the lowest for Pt/MCM-41(SiO_2) (between 35 and 40%, the main reaction product being N_2O) among all catalysts investigated, while on Rh- and Co-based catalysts and on Pt/MCM-41(Al_2O_3), a significantly higher selectivity to N_2 formation was observed (60–67%).

The activity of Pt/MCM-41(SiO_2) as a function of the metal loading is compared in figure 3. With decreasing Pt content the activity decreased, while temperature necessary for reaching the maximum conversion increased. However, when comparing the activity at temperatures above the maximum NO_x conversion all Pt/MCM-41(SiO_2) catalysts showed an identical activity. It is interesting to note that not only the activity, but also the temperature needed to reach the maximum activity for the NO_x reduction, depends on the metal loading and the particle size.

The activity and selectivity for Pt/MCM-41(SiO_2) as a function of the C_3H_6 concentration at 523 K are shown in figure 4. While at a $C_3H_6 : NO_x$ ratio of 1 : 1 the conversion was 50%, it increased up to 90% when a $C_3H_6 : NO_x$ ratio of 4 : 1 was used. Also the selectivity of Pt/MCM-41(SiO_2) towards N_2 formation increased from 30 to almost 50% at this $C_3H_6 : NO_x$ ratio.

The activity before and after a hydrothermal treatment for 31 h at 873 K with 5 vol% water vapor for Pt/MCM-41(SiO_2) and for Pt/SiO_2, both catalysts with a metal loading of 1.6 wt%, is compared in figure 5. The changes in the selectivity to N_2 formation, after interrupting the hydrothermal treatment and cooling the catalysts to 508 K, are compared in figure 6. Initially, Pt/MCM-41(SiO_2) showed a higher activity compared to Pt/SiO_2, while selectivity to N_2 formation was similar on both catalysts. During the first 2 h reaction time the selectivity to N_2 formation on Pt/MCM-41(SiO_2) increased from 31 to 45% and in the following 30 h it finally approached 50%. On Pt/SiO_2 the selectivity towards N_2 formation remained constant during the first 5 h of the hydrothermal treatment and increased only slightly from 29 to 35% during the subsequent time. After the reaction under hydrothermal conditions the H/Me ratio of the Pt/MCM-41(SiO_2) catalyst decreased from 0.63 to 0.57 and of the Rh/MCM-41(SiO_2) catalyst from 0.88 to 0.78.

The activity in the presence of water vapor (0–8.5 vol%), normalized to the activity in water-free atmosphere, at the temperature of the maximum NO_x conversion of each cat-

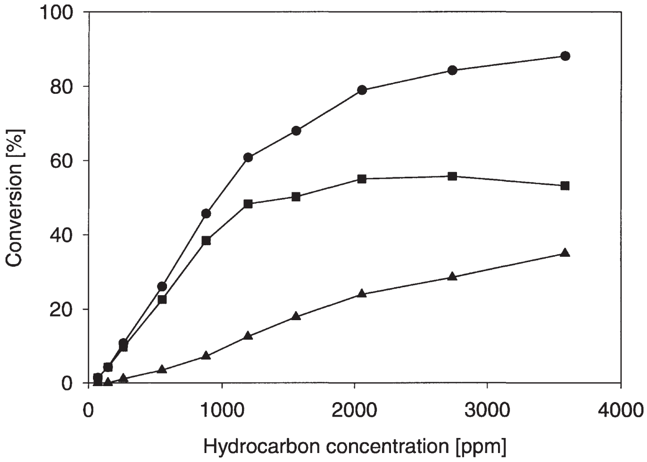

Figure 4. Activity of Pt/MCM-41(SiO_2) at 523 K as a function of the C_3H_6 concentration (NO concentration: 1010 ppm): (●) NO conversion, (▲) formation of N_2, (■) formation of N_2O.

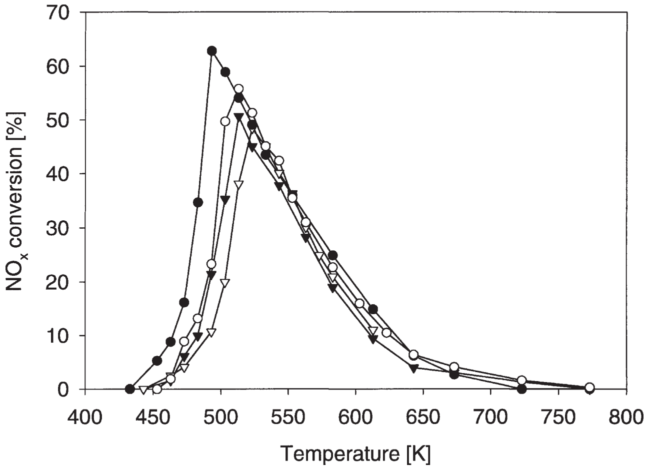

Figure 5. Comparison of the activity before (full symbols) and after (open symbols) hydrothermal treatment at 873 K with 5 vol% water vapor for 31 h: (●, ○) Pt/MCM-41(SiO_2) and (▼, ▽) Pt/SiO_2.

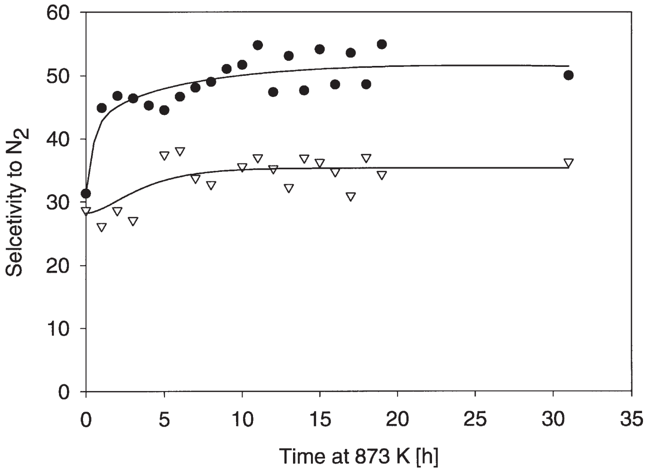

Figure 6. Selectivity to N_2 formation during the hydrothermal treatment with 5 vol% water vapor at 873 K as a function of time: (●) Pt/MCM-41(SiO_2) and (▽) Pt/SiO_2.

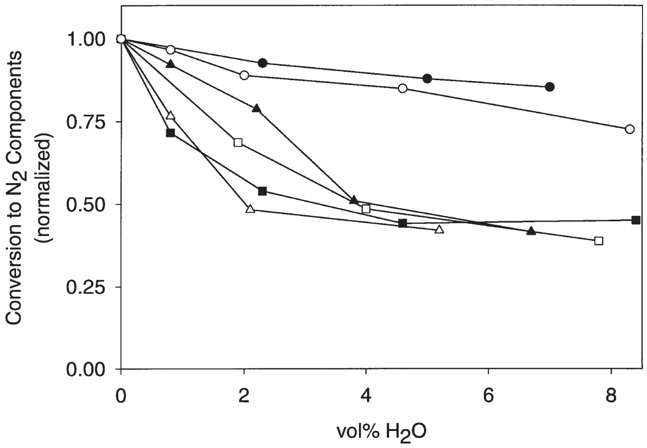

Figure 7. Activity in presence of water vapor normalized to the initial activity: (●) Pt/MCM-41(SiO_2), (▲) Rh/MCM-41(SiO_2), (■) Co/MCM-41(SiO_2), (○) Pt/MCM-41(Al_2O_3), (△) Rh/MCM-41(Al_2O_3) and (□) Co/MCM-41(Al_2O_3).

alyst is shown in figure 7. For Pt/MCM-41(SiO_2) and Pt/MCM-41(Al_2O_3) only a minor decrease in the activity of about 15% was observed up to 8 vol% H_2O, while for the Rh- and Co-based catalysts the activity decreased about 50%.

4. Discussion

Pt supported on siliceous mesoporous molecular sieves of MCM-41-type structure showed a high activity for the reduction of NO_x with propene at a low reaction temperature (483 K). Rh/MCM-41 was not so active, however, significantly less N_2O was formed compared to Pt/MCM-41(SiO_2). Co/MCM-41 catalysts had the lowest activity in the series of MCM-41-based catalysts studied. Compared to the noble metals Pt and Rh, metallic Co is thermodynamically not stable in the presence of water vapor [23,31]. Therefore, we assume that the Co/MCM-41 catalysts must be partially oxidized, as traces of water vapor are formed during the reaction. Additionally, the oxygen present in the reactant easily oxidizes metallic Co. Accordingly, we would like to speculate that the main reason for the low activity of Co/MCM-41 is the (partial) oxidation of the Co clusters.

In general, catalysts with a high activity showed a low selectivity towards N_2 formation and vice versa. Compared with Pt supported on dense SiO_2 the Pt/MCM-41(SiO_2), catalysts were more active and showed a better selectivity for the N_2 formation [22].

In the series of Pt/MCM-41(SiO_2) catalysts investigated, the catalyst with 3.17 wt% Pt was the most active, while the catalysts with 1.61 and 0.81 wt% Pt showed almost the same activity. Note that the number of metallic surface sites, determined by H_2 chemisorption, of the catalysts with 3.17 and with 1.61 wt% Pt was identical, while it was almost three times smaller on the catalyst with 0.81 wt% Pt. Therefore, based on the number of accessible metal sites, the catalysts with 3.17 and with 1.61 wt% Pt should have the same activity, while the catalyst with 0.81 wt% Pt should be less active. The dispersion, however, was the highest on the catalyst with 1.61 wt% Pt, indicating that the smallest metal particles were present in this sample. The comparison between the three catalysts (3.17, 1.61 and 0.81 wt% Pt) clearly reflects how strongly the size of the metal clusters determines the catalytic activity in the reduction of NO_x [20]. Larger metal clusters have a higher activity per accessible metal atom, which compensates, in the case of the catalysts containing 1.61 and 0.81 wt% Pt, the lower number of metal surface atoms present on the catalyst with the lower metal loading. On the catalysts with 3.17 and 1.61 wt% Pt loading the same number of accessible metal sites was present, but the larger particle size of the catalyst with the higher metal loading resulted in an increased catalytic activity. The catalyst with the lowest Pt loading (0.40 wt% Pt) was the less active in the series of Pt/MCM-41(SiO_2) catalysts due to the lowest number of metal surface sites and the small particle size (H/Pt = 0.58).

It is interesting to note that at temperatures above the maximum NO_x conversion the decay in the activity was the same over all catalysts investigated. This decay mainly depends on the reaction conditions such as the ratio between NO_x and propene, the space velocity and the O_2 concentration chosen and results from the complete conversion of the reducing agent [32]. This is clearly reflected in the dependence of the activity on the $C_3H_6:NO_x$ ratio, as shown in figure 4, where with increasing hydrocarbon concentration the activity strongly increased. While all other experiments reported in this contribution were carried out at a $C_3H_6:NO_x$ ratio of 1 : 1, at higher hydrocarbon concentrations (i.e., $C_3H_6:NO_x = 3:1$) almost 100% NO_x conversion could be reached. Also the N_2/N_2O selectivity was improved at higher $C_3H_6:NO_x$ ratios. For each $C_3H_6:NO_x$ ratio and space velocity applied a temperature is reached at which the hydrocarbon is completely converted and, therefore, not all active sites are supplied with a sufficient concentration of the reducing agent. With increasing reaction temperature the rate of the hydrocarbon oxidation increases, a larger fraction of sites in the catalyst bed gets inactive due to the lack of reducing agent and, consequently, the overall activity for the NO_x reduction vanishes.

Both Pt/MCM-41 catalysts showed a high stability in the presence of water vapor [12,13,33]. Even at water vapor concentration of 8 vol% the activity of these catalysts decreased only 15% compared with their activity in water-free atmosphere, while for the Co- and Rh-containing MCM-41 catalysts the activity decreased to 50% (see figure 7). Note that the type of support, i.e., MCM-41(SiO_2) or MCM-41(Al_2O_3), was only of minor influence on the activity in presence of water vapor. After heating the catalyst under hydrothermal conditions for 31 h the activity of Pt/MCM-41(SiO_2) and of Pt/SiO_2 decreased slightly on both catalysts, however, significantly less N_2O was formed over the Pt/MCM-41(SiO_2) catalyst already after the first 2 h of the hydrothermal treatment. During the time period studied (31 h) the selectivity finally reached 50%, which was significantly better compared to the Pt/SiO_2 catalyst where only a small increase in the selectivity from 29 to 35% was observed (see figure 6).

5. Conclusions

Transition-metal-containing MCM-41 catalysts are an attractive alternative to transition-metal-containing microporous molecular sieves and noble metals supported on dense metal oxides to prepare highly active and hydrothermally stable catalysts for the reduction of NO_x with hydrocarbons.

Pt supported on siliceous MCM-41 was the most active catalyst. Pt supported on mesoporous Al_2O_3 was less active, but compared with Pt/MCM-41(SiO_2), the selectivity to the N_2 formation was much higher. Both Pt/MCM-41 catalysts showed only a minor decrease in the activity in presence of water vapor. Compared with the corresponding dense metal oxide supports, MCM-41-supported catalysts were more active and less N_2O was formed during the reaction. Moreover, after a hydrothermal treatment the selectivity towards N_2 formation strongly improved on the Pt/MCM-41 catalysts.

The Rh/MCM-41 catalysts were less active compared to Pt/MCM-41(SiO_2), their selectivity to N_2 formation was significantly better, but the decrease in activity in the presence of water vapor was more pronounced than on Pt/MCM-41. However, Rh/MCM-41 seems to be an interesting option as the selectivity to N_2 formation is significantly higher when MCM-41 is used as the support compared to γ-Al_2O_3 [22].

Co/MCM-41 catalysts showed a lower activity compared with both noble-metal-containing MCM-41 catalysts, which might result from an oxidation of Co during the reaction. Additionally, the activity strongly decreased when water was added into the reaction gas mixture. This clearly reflects that noble metals supported on MCM-41-type materials have a higher potential to be applied as catalysts for the reduction of NO_x than non-noble metals.

The activity and selectivity of the catalysts can be further improved by increasing the $C_3H_6 : NO_x$ ratio. The higher concentration of the hydrocarbon compensates the decrease of the concentration of the reducing agent over the active sites resulting from the direct oxidation reaction, which occurs in parallel with the NO_x reduction.

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