The reduction of NO with H_2 over Ru/MgO

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Ruthenium supported on magnesia was found to be a highly active and selective catalyst for the reduction of NO to N_2 with H_2. The adsorption of NO on Ru/MgO was studied at room temperature by applying frontal chromatography with a mixture of 2610 ppm NO in He. Subsequently, temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR) experiments in H_2 were performed. The adsorption of NO was observed to occur partly dissociatively as indicated by the formation of molecular nitrogen. The TPD spectrum exhibited a minor NO peak at 340 K indicating additional molecular adsorption of NO during the exposure to NO at room temperature, and two N_2 peaks at 480 K and 625 K, respectively. The latter data are in good agreement with previous results with Ru(0001) single-crystal samples, where the interaction with NH_3 was found to lead to two N_2 thermal desorption states with a maximum coverage of atomic nitrogen of about 0.38. Heating up the catalyst after saturation with NO at room temperature in a H_2 atmosphere revealed the self-accelerated formation of NH_3 after partial desorption of N_2, whereby sites for reaction with H_2 become available. As a consequence, the observed high selectivity towards N_2 under steady-state reduction conditions is ascribed to the presence of a saturated $N + O$ coadsorbate layer resulting in an enhanced rate of N_2 desorption from this layer and a very low steady-state coverage of atomic hydrogen. The formation of H_2O by reduction of adsorbed atomic oxygen is the slow step of the overall reaction which determines the minimum temperature required for full conversion of NO.

Keywords: SCR of NO, Ru, MgO, frontal chromatography, TPD, TPSR

1. Introduction

The application of ruthenium-based catalysts, in particular of Ru/γ-Al_2O_3, for the selective catalytic reduction (SCR) of nitrogen oxides (NO_x) with hydrogen or ammonia has been studied thoroughly because of their high activity and outstanding selectivity to nitrogen and water [1,2]. The intensive research and development effort in this field was initiated by the Clean Air Act of 1970, which defined permissible concentration levels for CO, hydrocarbons and NO_x from automotive emissions. The first catalytic solution for the combined abatement of these pollutants in automotive emissions was the dual-bed system, in which a first catalyst was used to reduce NO_x in a fuel-rich exhaust stream to N_2 under net reducing conditions and a second one, after the injection of air downstream of the reduction catalyst, to oxidize CO and hydrocarbons in a net fuel-lean stream [3]. The main problem of this system was the formation of ammonia in the first converter, which was then oxidized to NO_x in the second one. Because of its high selectivity to N_2 and its stability against sulfur poisoning, ruthenium appeared to be the ideal catalyst for this application. A serious hindrance to the use of ruthenium in this system was the metal loss under the oxidising conditions at warm-up because of the formation of volatile and noxious RuO_4. Although successful examples of stabilisation of the metal under these conditions were reported [4], the dual-bed concept was later on abandoned in favour of the three-way conversion catalyst, which operates in a single bed at nearly-stoichiometric air/fuel ratio [5].

$RuCl_3 \cdot 3H_2O$ was generally employed as metal precursor for the preparation of supported Ru catalysts. However, several investigations demonstrated the existence of tightly bound atomic chlorine both on the metal surface and on the support of catalysts prepared by wet impregnation with solutions of $RuCl_3$ [6,7]. Adsorbed chlorine was shown to act as efficient poison for hydrogen chemisorption, which can only be removed by severe high-temperature reduction [6,7]. Aika et al. [8–10] proposed the use of $Ru_3(CO)_{12}$ as metal precursor for the synthesis of chlorine-free supported Ru catalysts. Following this preparation route and using high-purity reagents, we obtained catalysts with a negligible amount of impurities as confirmed by X-ray photoelectron spectroscopy (XPS), a high metal dispersion and a narrow particle size distribution as determined by static hydrogen chemisorption and transmission electron microscopy (TEM) [11].

The chlorine-free Ru/MgO catalyst turned out to exhibit a high activity for NH_3 synthesis, which was further improved by adding cesium compounds [11]. The high rate of hydrogenation of adsorbed atomic nitrogen (N–$*$) to NH_3 under NH_3 synthesis conditions seems to contradict the high selectivity to N_2 under SCR conditions. It is the aim of the present study to elucidate this apparent contradiction by investigating the kinetics of the reduction of NO with H_2 by steady-state and transient techniques. The Ru/MgO catalyst was indeed found to have a high steady-state SCR

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activity with a selectivity of 93% to N_2 and a small NH_3 slip at full NO conversion at 473 K. The interaction of NO with Ru/MgO was studied by frontal chromatography at room temperature. Subsequently, temperature-programmed desorption (TPD) and temperature-programmed surface reaction (TPSR) experiments were performed. For the TPSR experiments, the catalyst was heated in either pure or strongly diluted H_2 in order to monitor the effect of the partial pressure of H_2 on the rate of reduction.

2. Experimental

The catalyst was prepared by wet impregnation of high-purity magnesium oxide (Johnson–Matthey, 99.9955%) with a solution of $Ru_3(CO)_{12}$ (Johnson–Matthey, 99%) in THF_{abs} (Merck, p.a.). Details about the preparation and the characterization of the catalyst were reported in [11]. The BET area determined after reduction was 25.0 $m^2\,g^{-1}$. The Ru metal surface area of 12.9 $m^2\,g^{-1}$ was derived from static H_2 chemisorption assuming a H : Ru ratio of 1 : 1 [11].

The transient experiments were carried out in an all stainless-steel microreactor set-up equipped with four gas lines: He (99.9999%), 2610 ppm NO in He (99.9999%), H_2 (99.9999%) and a mixture of 25% N_2 in H_2 used as ammonia synthesis feed gas (99.9996%). The set-up was described in detail in [12]. Due to the minimized dead volume between the flow-switching valves and the reactor, the period of time required by a concentration front of NO, generated by switching from pure He to the mixture of NO in He, to reach the catalyst bed is estimated to amount to about 6 s using a flow of 40 $Nml\,min^{-1}$. All experiments were carried out using 200 mg of the 250–450 μm sieve fraction of the catalyst, resulting in a bed height of roughly 15 mm. The reduction was carried out in ammonia synthesis gas (flow = 80 $Nml\,min^{-1}$) with a heating rate of 0.5 $K\,min^{-1}$ up to 773 K. The temperature was then repeatedly cycled between 773 and 673 K until the production of ammonia reached a constant value. This procedure was chosen in order to achieve a well-defined, reduced surface as a starting point for the transient experiments. Prior to each experimental run, the steady-state ammonia synthesis activity was measured in order to check the condition of the catalyst. After ammonia synthesis the catalyst was treated for at least two hours at 773 K in a He flow of 50 $Nml\,min^{-1}$ and subsequently cooled in He to room temperature in order to get an adsorbate-free state.

The steady-state SCR activity of the catalyst was studied at atmospheric pressure in a set-up similar to the one described above, the only differences being the presence of an on-line combined IR-UV detector for NO and NO_2, respectively (Fisher–Rosemount, BINOS), in addition to a quadrupole mass spectrometer (Balzers, QMS 125) calibrated with binary reference gas mixtures, and the possibility of mixing the gases. The following feed gases were used: Ar (purity 99.9996%), 2675 ppm of NO in Ar (purity 99.9996%) and H_2 (5.4 vol%) in Ar (purity 99.9996%) supplied by Linde. The gases were used without further purification. The steady-state investigations were carried out using a gas mixture containing 900 ppm of NO and 3% H_2 in Ar at a constant total flow of 120 $Nml\,min^{-1}$, corresponding to a GHSV of about 40000 h^{-1}.

3. Results

The steady-state measurements were carried out in order to compare the activity and selectivity of the Ru/MgO catalyst with the values reported in previous studies with similar catalysts ([13–17] and references therein). The catalyst showed the expected high activity and selectivity at low temperature, although the ammonia slip at full NO conversion measured in the present study was slightly higher than the values reported for mainly γ-Al_2O_3-supported Ru catalysts [13–17]. Table 1 summarizes typical values observed for the conversion of NO and the selectivities to N_2, N_2O and NH_3 at three different temperatures after several days on stream with the properties of the feed gas as indicated above.

Prior to each temperature-programmed experiment, NO was dosed at room temperature up to saturation onto the adsorbate-free catalyst, by switching from pure He to a mixture of 2610 ppm NO in He with equal flow rates of 40 $Nml\,min^{-1}$. Simultaneously, the composition of the gas phase at reactor outlet was analysed by mass spectrometry. Figure 1 shows a typical result of such a frontal chromatography experiment at room temperature as a function of time. NO was completely adsorbed by the catalyst up to saturation, which is indicated by the breakthrough of the NO front. Additionally, after 2 min, the simultaneous desorption of N_2 at room temperature was detected, which was never observed for the coadsorbate-free nitrogen-covered state of the same catalyst [12]. The enhanced rate of N_2 desorption points to a strong destabilisation of N–$*$ by the presence of larger amounts of atomic adsorbates (N–$*$ and O–$*$) than may be achieved by exposure to N_2. This aspect will be discussed in detail below.

A quantitative comparison of the amount of NO adsorbed (251 $\mu mol\,g^{-1}$) with the number of surface Ru atoms determined by H_2 TPD (243 $\mu mol\,g^{-1}$) yields a ratio of NO : Ru_{surf} roughly equal to 1 : 1. The integration of the N_2 trace results in 27 $\mu molN_2\,g^{-1}$. Thus, at least 20% of the adsorbed NO molecules dissociated during the exposure at room temperature, presumably before saturation with adsorbed NO was reached.

Table 1
Steady-state activity of Ru/MgO in the catalytic reduction of NO with H_2.

Temperature (K)		393	433	473
NO conversion (%)		7.7	64.4	100.0
Selectivity (%)	N_2O	100.0	67.7	0.0
	N_2	0.0	32.1	92.8
	NH_3	0.0	0.2	7.2

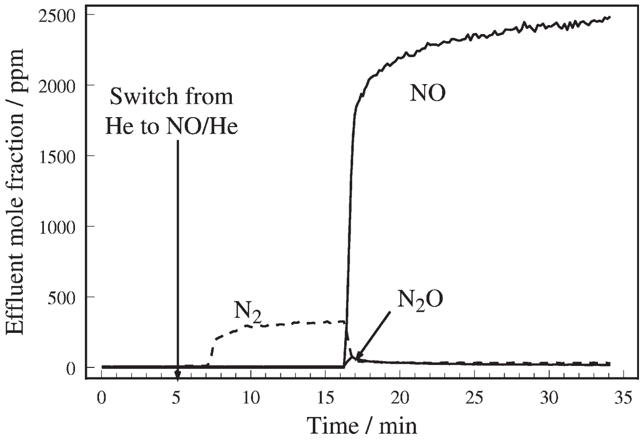

Figure 1. Exposure of the reduced Ru/MgO catalyst to NO at room temperature by switching from pure He to a gas mixture containing 2610 ppm of NO in He. The flow rates were 40 Nml min^{-1}.

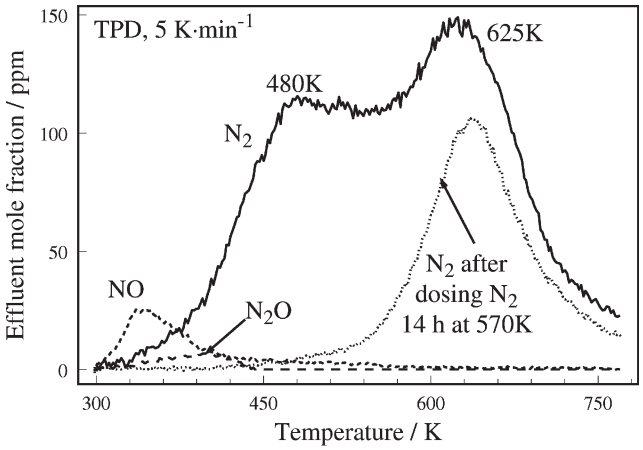

Figure 2. Temperature-programmed desorption data for Ru/MgO obtained with 50 Nml min^{-1} He and a heating rate of 5 K min^{-1} after saturating with NO at room temperature. The dotted line shows the TPD spectrum obtained under the same experimental conditions after exposing Ru/MgO to N_2 at 570 K for 14 h followed by cooling in flowing N_2.

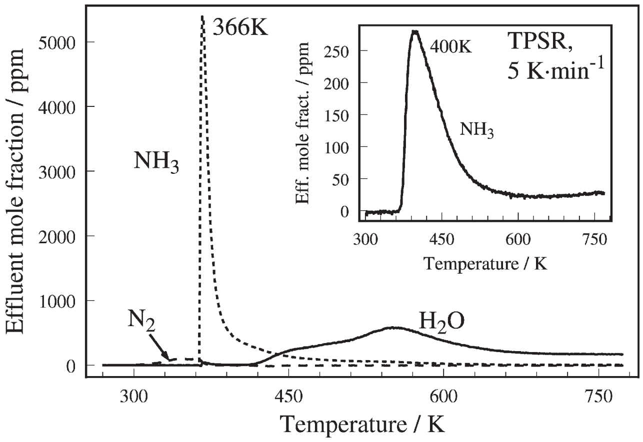

Figure 3. Temperature-programmed surface reaction data for Ru/MgO obtained with 50 Nml min^{-1} H_2 and a heating rate of 5 K min^{-1} after saturating with NO at room temperature. The inset shows the TPSR spectrum for Ru/MgO measured under the same experimental conditions after exposing the catalyst to N_2 at 570 K for 14 h followed by cooling in N_2.

Figure 2 shows TPD data obtained by heating the NO saturated catalyst in a He flow of 50 Nml min^{-1} with a linear heating rate of 5 K min^{-1}. For comparison, the TPD data obtained under the same experimental conditions and from the same sample after dosing N_2 at 570 K for 14 h followed by cooling in N_2 are shown, too, taken from [12]. The exposure to NO is found to lead to a much higher maximum coverage of N–∗ than the exposure to N_2.

The NO TPD peak at 340 K indicates the presence of a small amount of adsorbed molecular NO in addition to N–∗ and O–∗. Obviously, the complete dissociation of NO–∗ becomes inhibited by the high coverages of N–∗ and O–∗, as also achieved during the frontal chromatography experiment. The observed desorption of N_2O is attributed to the reaction of NO–∗ with N–∗.

Heating up the saturated N–∗, O–∗ and NO–∗ coadsorbate layer in a flow of 50 Nml min^{-1} H_2 with a rate of 5 K min^{-1} (figure 3) gave rise to the sudden onset of NH_3 formation at 363 K. The sharp onset of the TPSR peak and its full width at half maximum (FWHM) of only 10 K suggest an autocatalytic mechanism. A similar phenomenon, termed “surface explosion”, was observed on Pt(100) when performing TPSR experiments with NO and CO [18]. The desorption of NH_3 following the reaction of N–∗ with H–∗ leaves free surface sites for the dissociative adsorption of H_2, resulting in a self-accelerating reaction mechanism. TPSR data obtained under identical experimental conditions after the adsorption of N_2 for 14 h at 570 K followed by cooling in N_2 are shown in the inset of figure 3 for comparison. The FWHM of the TPSR NH_3 peak obtained by dosing NO is significantly smaller than the FWHM of the one obtained after dosing N_2, which is attributed to the different coverage conditions. The desorption of H_2O was observed only at higher temperatures, resulting in a rather broad peak shape due to additional strong interactions of H_2O with MgO.

The presented data indicate that there exists a competition between the recombination of 2 N–∗ to N_2 and the reaction between N–∗ and H–∗, leading to the formation of NH_3, whereby the branching ratio is governed by the adsorption of hydrogen. A similar mechanism had previously been proposed by Uchida and Bell [19].

In order to check this hypothesis, the dependence of the product composition on the partial pressure of H_2 in a TPSR experiment was investigated. In this way, a variation of the rate of hydrogen adsorption (and, hence, presumably of NH_3 formation) was achieved, while an identical heating rate ascertained an unaltered rate of N_2 evolution. The results of a TPSR experiment with a 0.6 vol% H_2/He mixture (instead of 100% H_2, leading to the data of figure 3) are reproduced in figure 4. Obviously, the fraction of N–∗ being converted into N_2 increased now substantially. The integration of the TPSR traces yields that, with 100% H_2 (figure 3), 97% of the adsorbed N–∗ was released in the form of NH_3, while with 0.6 % H_2 (figure 4), only 53%

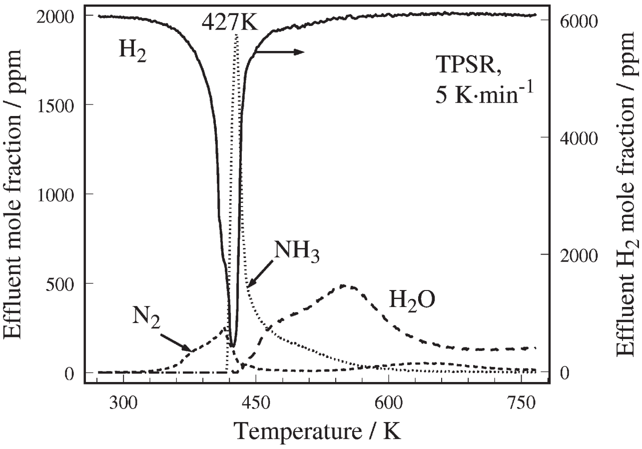

Figure 4. Temperature-programmed surface reaction data for Ru/MgO obtained with 0.6% H_2 in He using 50 Nml min^{-1} and a heating rate of 5 K min^{-1} after saturating with NO at room temperature.

were converted into NH_3 and 47% desorbed as N_2. Moreover, the adsorption profile for H_2 in figure 4 shows that hydrogen uptake (subsequently leading to NH_3 formation) takes place only after partial recombination of 2 N–$*$ and desorption of N_2.

4. Discussion

The N_2 thermal desorption data from the Ru/MgO catalyst reproduced in figure 2 exhibit remarkable similarities to corresponding results obtained with Ru(0001) single-crystal surfaces under ultrahigh vacuum conditions, so that the latter may well serve as adequate model systems without invoking any problems due to "pressure" or "material" gaps. Thereafter, the high-temperature TPD peak (Nα) arises from the recombination of N atoms adsorbed in three-fold hcp-sites forming a 2 × 2-phase, which saturates at a coverage $\Theta_N = 0.25$ [20,21]. Beyond this coverage, closer packing into domains of a $\sqrt{3} \times \sqrt{3} R\,30°$-phase causes a considerable decrease of the adsorption energy leading to a low-temperature (Nβ) peak in thermal desorption. By decomposition of NH_3, a saturation coverage by N–$*$ up to 0.38 is reached, while N_2 exposure leads only to completion of the 2 × 2-phase with $\Theta_N = 0.25$.

The data of figure 2 indicate that the population of the Nβ-state can equally be reached by dissociative chemisorption of NO. The simultaneously formed adsorbed O-atoms occupy again hcp-sites, whereby the coverage can reach up to $\Theta_O = 1$, accompanied by the formation of a 1 × 1-phase [22], or even beyond, leading to the build-up of "subsurface" oxygen [23]. Recent investigations by scanning tunnelling microscopy (STM) revealed that at higher coverages chemisorbed N and O atoms at room temperature tend to the formation of mixed phases with (to a good approximation) random occupation of the adsorption sites [24], and hence the presence of adsorbed O atoms has a similar effect on the energetics of N chemisorption as higher nitrogen coverages. Dissociation of NO on Ru(0001) at 300 K occurs predominantly at monoatomic steps to which the adsorbed NO molecules migrate and from where the created N and O atoms diffuse away. (However, with half of the steps the O atoms remain attached and, thus, cause inhibition of the "active" sites [25].)

In view of these results, the present findings can be rationalized as follows: exposure of the Ru/MgO catalyst to NO at room temperature leads to dissociation at defect sites and the build-up of an adsorbed N + O layer. At a sufficiently high coverage the binding energy of N–$*$ becomes low enough to enable partial recombination and desorption of N_2 even at 300 K (figure 1). Thermal desorption spectroscopy (figure 2) reveals the formation of both the Nα- and Nβ-states, where appreciably higher total coverages are reached than with exposure to N_2. Desorption of a small amount of NO suggests that part of the NO molecules which were adsorbed at terrace sites far away from steps and other defects are hindered from reaching these "active" sites by the presence of high concentrations of atomic adsorbates. If the latter exceed a critical value beyond which the Nβ-TPD state evolves, chemisorption of H_2 is inhibited until N–$*$ leaves the surface as N_2 (cf. figures 3 and 4). However, as soon as empty sites are created in this way, the formation of NH_3 becomes self-accelerated, leading to the narrow TPSR peak in figure 3. As already outlined above, the reduction of H_2 partial pressure in a TPSR experiment will favour N_2 desorption on the expense of the competing formation of NH_3, as confirmed by comparison of the data of figures 3 and 4. The removal of O–$*$ by hydrogen, on the other hand, takes place only above 420 K, and hence higher temperatures will be needed under steady-state conditions.

The TPD data after dosing NO at room temperature, presented by Uchida and Bell [19], were quite similar to the present data, and their conclusion that high coverages of N–$*$ and O–$*$ favour the non-dissociative adsorption of NO is supported by the present results. Their TPSR measurements with a 20 vol% H_2/He gas mixture, on the other hand, revealed a higher selectivity towards N_2 formation. This effect might in part be due to the higher NO exposure employed, which presumably causes the onset of oxidation of the Ru particles, but is also likely to be caused by the use of $RuCl_3$ as precursor: chlorine is a strong poison for hydrogen adsorption [6,7], and spurious amounts of this element might thus suppress the activity for NH_3 formation. Furthermore, the TPSR measurements presented in [19] were carried out using a rather high heating rate of 60 K min^{-1}, which may have resulted in lower coverages of H–$*$.

The data for the steady-state activity, listed in table 1, become plausible in view of the proposed mechanism: at 393 K the surface will be largely covered by oxygen, and the few N atoms created by NO dissociation preferably react with NO to N_2O. With increasing temperature this reaction path will be progressively suppressed in favour of N_2 and NH_3 formation, due to the increasing reduction of O–$*$ enabling enhanced NO dissociation. The recombination of 2 N–$*$ to N_2 dominates under these conditions over NH_3

formation: H_2 and NO compete for free adsorption sites, whereby N–$*$ and O–$*$ are considerably stronger held on the surface than H–$*$. As long as sufficient NO supply from the gas phase is available, the H–$*$ concentration and hence the NH_3 yield will be low. The variation of the $H_2 : NO$ partial pressure ratio under steady-state reaction conditions is expected to directly affect the selectivity.

5. Conclusions

Ru/MgO was found to be a highly active catalyst for the reduction of NO with H_2 to N_2. Under steady-state reaction conditions, high enough surface concentrations of chemisorbed nitrogen and oxygen atoms on a Ru catalyst surface resulting from NO dissociation suppress the adsorption of H_2 and, thus, the formation of NH_3. Furthermore, the high coverages of N–$*$ and O–$*$ lead to a strongly enhanced rate of N_2 desorption. As a consequence, high selectivities with respect to N_2 formation by recombination of N–$*$ are achieved under steady-state reaction conditions, for which the reduction of O–$*$ by H_2 to H_2O is the slowest step determining the minimum temperature required for full conversion of NO.

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