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Reduction of NO by H_2 and CO on $Pt/TiO_2/SiO_2$

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Different catalysts based on platinum and a silica, titania or mixed titania/silica support were studied in NO reduction reactions by CO and H_2 in the temperature range of 25–400°C. The mixed oxide catalysts showed considerably lower onset temperatures in NO/CO reactions but this coincided with a maximum in N_2O formation. In NO/H_2 reactions all titania containing catalysts produced more N_2O than silica supported platinum at low temperatures but were more selective to N_2 at high temperatures.

Keywords: automotive catalysis; platinum; promoter; NO reduction

1. Introduction

The removal of NO_x from exhaust gas is one of the main features of the automotive catalytic converter [1]. NO_x is reduced by CO, hydrocarbons and H_2, which is primarily a product of the water–gas shift and hydrocarbon decomposition reactions. Present three-way catalysts contain the noble metals Pt or Pd and Rh that selectively reduces NO to N_2 with a small formation of NH_3. Because of the high price and scarcity of rhodium on the world market there is strong incentive to find rhodium-free alternatives. One possibility to improve the performance of a noble metal three-way catalyst is by promoting the noble metal with a suitable metal oxide. Recently, a rhodium-free promoted Pd three-way catalyst has been introduced [2]. In a series of studies we investigate the effects of transition metal oxides on the performance of Pt-only three-way catalysts.

Several studies have been published on the use of metal oxides as promoters to Pt or Pd catalysts, such as WO_3 [3], La_2O_3 [4], MoO_3 [5] and CoO_x [6]. Nakamura et al. [7,8] observed superior catalytic activity of TiO_2 and TiO_2/SiO_2 supported Pt in CO/NO reactions. In earlier papers of our group the effects of the addition of CoO_x and MnO_x to Pt catalysts have been described [6,9].

In this paper we report on the performance of $Pt/TiO_2/SiO_2$ with high TiO_2 loading since earlier results indicated this to be necessary to achieve a promoting effect [7]. A preparation technique earlier described by Vogt [10] was used to bring about a complete coverage of the silica surface by TiO_2. Here we report on the activities and selectivities of $Pt/TiO_2/SiO_2$ (25 and 80 wt% TiO_2 loading) and as references Pt/SiO_2 and Pt/TiO_2 in NO/H_2, CO/O_2 and NO/CO reactions. TiO_2 itself was under our reaction conditions not active for any of these reactions.

2. Experimental

2.1. PREPARATION OF CATALYSTS

A 5 wt% Pt/SiO_2 catalyst, denoted as Pt/SiO_2, was made by urea decomposition [11]. As precursor $H_2Pt(OH)_6$ was used. After drying, the catalyst was reduced for 3 h at 400°C under a H_2 flow. A 5 wt% Pt/TiO_2 catalyst, denoted as Pt/TiO_2, was made by impregnating TiO_2 (P-25 Degussa) with the same $H_2Pt(OH)_6$ precursor, followed by calcination at 400°C for 3 h in air. The catalysts with mixed TiO_2/SiO_2 support were made by first depositing the proper amount of TiO_2 (25 or 80%) onto the silica (precursors $TiCl_3$ and Aerosil-200) using the technique of homogeneous deposition precipitation [10]. The catalysts were then filtered, dried overnight and calcined in air for 3 h at 400°C. Pt was then impregnated onto these supports, resulting in Pt 5 wt%/TiO_2 25 wt%/SiO_2 and Pt 5 wt%/TiO_2 80 wt%/SiO_2 denoted as Pt/TiO_2 25%/SiO_2 and Pt/TiO_2 80%/SiO_2 respectively.

2.2. ACTIVITY MEASUREMENTS AND ANALYSIS

The catalysts were pretreated in either a reductive hydrogen flow or oxidative air flow for 3 h at 400°C. The measurements were performed in an atmospheric flow apparatus. The gases used were 4 vol% NO/He, 4 vol% CO/He and 4 vol% H_2/He (Hoekloos). The flow rate could be adjusted with mass flow controllers to a maximum of 40 ml/min. For each experiment 0.2 g of catalyst was used. The CO/O_2 reactions were studied at a 2 : 1 ratio, NO/CO reactions at a 1 : 1 ratio, the NO/H_2 reactions at either a 1 : 1 or 1 : 3 ratio. Product distribution was continuously measured by a mass spectrometer (VG Masstorr DX) while increasing the temperature from ambient values to 400°C at a heating rate of 3°C/min. Every activity measurement was carried out in duplo to verify the reproducibility of the experiments.

Because of the equality in the masses of CO/N_2 and CO_2/N_2O and the limited sensitivity of our mass spectrometer only the differences in overall activity in CO/NO reactions could be measured. For the NO reduction by H_2 product distribution of NH_3, N_2 and N_2O was followed by monitoring the intensities of masses 17, 28 and 44.

X-ray diffraction (XRD) was used to determine crystal structure and to calculate the average Pt particle size. CO chemisorption measured the extent of dispersion of the platinum metal. All the freshly prepared catalysts were reductively pretreated in a hydrogen atmosphere at 400°C prior to the XRD and CO chemisorption experiments.

3. Results and discussion

3.1. CHARACTERIZATION

The results are summarized in table 1. Platinum dispersion of Pt/SiO_2 and Pt/TiO_2 was greater than those of the mixed oxide catalysts. The mixed oxide catalysts produced rather unclear X-ray patterns which could only be partially related to the common crystal structures of TiO_2.

3.2. CO OXIDATION BY O_2

Although our prime interest is in the NO reduction properties of titania supported platinum the catalysts were also studied in the $CO + O_2$ reaction since CO oxidation by adsorbed oxygen is one of the steps in the NO + CO reaction. Fig. 1 shows that the platinum catalysts of high titania loading have a lower onset temperature. However, this promotional effect of TiO_2 is much smaller than reported for some other transition metal oxides like CoO_x [9].

3.3. NO REDUCTION BY CO

The following overall reactions occur:

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

$$2NO + CO \rightarrow N_2O + CO_2$$

For reasons mentioned earlier only the overall conversion of NO will be considered. On metals like Pt and Rh the main mechanism of NO reduction by CO is well established: dissociative adsorption of NO followed by reaction of O_{ads} with CO_{ads} to CO_2, combination of 2 N_{ads} to N_2 and at lower temperature reaction of N_{ads} with NO_{ads} to either N_2O or N_2 and O_{ads}.

Table 1
Characterization results

Catalyst	Dispersion (%)	Av. Pt particle size (Å)	X-ray powder data
Pt/SiO_2	10	90	Pt
Pt/TiO_2	6.5	145	Pt, Ana, Rut
Pt/TiO_2 25%/SiO_2	2.1	–	Pt, undefined
Pt/TiO_2 80%/SiO_2	2.4	187	Pt, undefined, Rut

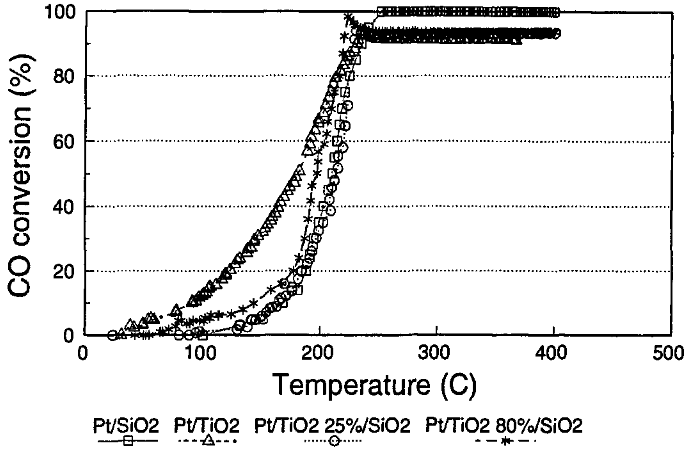

Fig. 1. Activity of the catalysts in CO conversion at a CO/O_2 gas mixture after a reductive pretreatment.

Figs. 2 and 3 show the NO conversion at a NO/CO ratio of 1 : 1 after a reductive and oxidative pretreatment at 400°C respectively. On a pure Pt catalyst the selectivity towards N_2 and N_2O is determined by the relative coverages of NO and O on the surface. At low temperatures the NO coverage is high and N coverage low [12,13] and N_2O is the major product. With an increase in temperature NO coverage decreases resulting in a decreased N_2O formation [14]. Based on the results obtained for the NO reduction by H_2 (see section 3.4) we assume that initially most of the NO will be reduced to N_2O on all catalysts below 250°C.

The TiO_2 clearly has a promoting effect in the mixed oxide catalysts as is evident from the high activity starting at 200°C. Pt/TiO_2 25%/SiO_2 reached a maximum in activity, after which it fell to levels comparable to Pt/SiO_2. A similar maximum in NO conversion was also found for this catalyst in NO/H_2 reactions related to

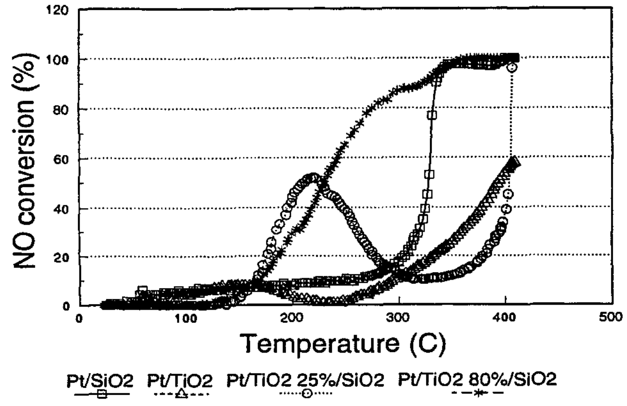

Fig. 2. Activity of the catalysts in NO conversion at a NO/CO 1 : 1 gas mixture after a reductive pretreatment.

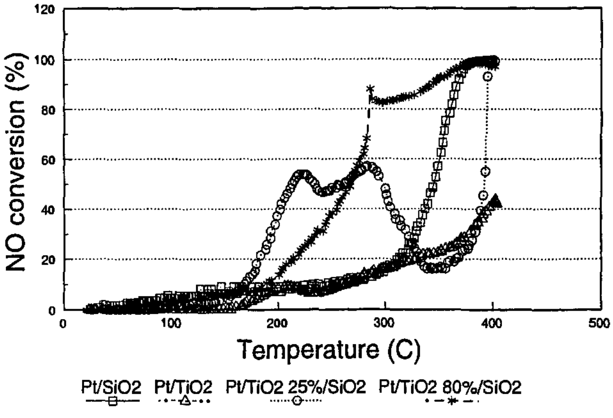

Fig. 3.Activity of the catalysts in NO conversion at a NO/CO 1 : 1 gas mixture after an oxidative pretreatment.

N_2O formation. At higher temperatures the N_2O may react further [6] competing for the same active sites as NO and this causes the local maximum in the NO conversion curve. At about 400°C the unpromoted Pt species in the catalyst also becomes active leading to 100% NO conversion at 400°C. This local maximum in NO conversion is absent from the higher loaded Pt/TiO_2 80%/SiO_2 catalyst and the catalyst shows superior catalytic activity over Pt/SiO_2 up to 350°C.

The poor performance of Pt/TiO_2 in relation to the other titania catalysts may be partially caused by the differences in crystalline structure. Anatase supported platinum is about 1.3 times more active in the initial stage of the NO–CO reaction than rutile supported platinum [7]. Using the same TiO_2 precursor (80% anatase, 20% rutile) Ravindranathan Thampi [15] prepared a Ru/TiO_2 catalyst and found the Ru to be selectively dispersed over the rutile phase. This would also explain why this Pt/TiO_2 was the most active catalyst in CO oxidation (see section 3.2) since in this reaction rutile supported platinum is known to be the better catalyst [16].

3.4. NO REDUCTION BY H_2

The main overall reactions are:

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

$$2NO + H_2 \rightarrow N_2O + H_2O$$

$$2NO + 5H_2 \rightarrow NH_3 + 2H_2O$$

The differences in product distribution can be understood on the basis of our earlier results. Dissociation of NO is essential for the formation of N_2 [12,13]. At low temperatures the platinum is mainly covered by molecularly adsorbed NO leaving few vacant sites for the dissociation of NO. N_2O formation is now predominant and especially favorable at high NO/H_2 ratios [12,13]. At higher temperatures more NO desorbs, thus creating more vacancies for NO dissociation, resulting in an increased N_2 production. NH_3 formation is favored at high temperatures and with excess hydrogen when coverage of N_{ads} and H_{ads} is high [12,13,17].

3.4.1. *Activity of the catalysts*

Table 2 shows the temperatures at which 50% of NO was converted into products after different pretreatments and at two gas ratios.

Compared with Pt/SiO_2, Pt/TiO_2 is more active after a reductive pretreatment but after an oxidative pretreatment its activities are comparable. Both mixed oxide catalysts clearly have higher onset temperatures. These differences may be partly attributed to the lower dispersion of the platinum metal on these catalysts. To take into account the differences in the number of Pt atoms at the surface the turnover frequency (TOF) was calculated (see table 3). The calculation was based on the assumption that on every surface Pt atom one CO molecule adsorbs. Table 3 shows that the activity in NO conversion on a per Pt atom basis is increased an order of magnitude by the addition of TiO_2.

The Pt/TiO_2 80%/SiO_2 catalyst showed considerably higher onset temperatures when it was reductively pretreated, especially at the NO/H_2 1 : 3 ratio. Also when this catalyst was cooled after an experiment at the 1 : 3 NO/H_2 ratio which was preceded by an *oxidative* pretreatment and the experiment was carried out for a second time a high onset temperature of 135°C was found. During the first experiment the catalyst is exposed to excess hydrogen at high temperatures, very much in a way similar to a reductive pretreatment. Pt/TiO_2 25%/SiO_2 did not show any increase in onset temperatures in such repeated measurements. This effect might be related to the occurrence of so-called strong metal–support interaction when overlayers of TiO_x $(1 < x < 2)$ partly decorate the platinum surface [18].

Table 2
Temperature of 50% NO conversion (°C) after a reductive or oxidative pretreatment at different NO/H_2 ratios

Catalyst	Pretreatment	Gas ratio NO : H_2	
		1 : 1	1 : 3
Pt/SiO_2	reduction	64	46
	oxidation	68	50
Pt/TiO_2	reduction	55	30
	oxidation	61	62
Pt/TiO_2 25%/SiO_2	reduction	115	95
	oxidation	114	111
Pt/TiO_2 80%/SiO_2	reduction	115	157
	oxidation	101	90

Table 3
TOF values of the catalysts in NO reduction by H_2 at a ratio of 1 : 1 after a reductive pretreatment

Catalyst	TOF (s^{-1}) (NO/H_2 1 : 1)	
	50°C	100°C
Pt/SiO_2	3.1×10^{-4}	–
Pt/TiO_2	2.6×10^{-3}	–
Pt/TiO_2 25%/SiO_2	–	4.4×10^{-3}
Pt/TiO_2 80%/SiO_2	–	5.7×10^{-3}

3.4.2. Selectivity of the catalysts

Our results with Pt/SiO_2 (fig. 4) support earlier results and the above mentioned view of the product distribution. At a NO/H_2 ratio of 1 : 1 N_2O is produced at low temperatures and only N_2 was detected above 200°C. With excess hydrogen though mainly NH_3 is produced at higher temperatures.

Pt/TiO_2 (fig. 5), in comparison, produced much more N_2O at lower temperatures, even with excess hydrogen. At higher temperatures, though, it is significantly more N_2 selective in feeds rich in H_2 than Pt/SiO_2.

Pt/TiO_2 25%/SiO_2 (fig. 6) produced N_2O over the whole temperature region examined at the 1 : 1 ratio. With excess hydrogen there was a remarkable difference in the performance depending on the pretreatment. After an oxidative pretreatment NH_3 formation was substantially less and strikingly lower than Pt/SiO_2. The difference between pre-oxidized an pre-reduced Pt/TiO_2 25%/SiO_2 vanished at 350°C when both the product distributions resembled Pt/TiO_2.

Pt/TiO_2 80%/SiO_2 (fig. 7) also primarily produced N_2O at lower temperatures but at higher temperatures NH_3 was found even at a 1 : 1 NO/H_2 ratio in contrast to the other three catalysts. This would indicate that on this catalyst even at this ratio a sufficient hydrogen coverage exists.

In general, all titania supported catalysts produced significantly more N_2O than Pt/SiO_2. This may suggest that the NO–surface bond remains intact up to much higher temperatures on the titania supported catalysts than on Pt/SiO_2. Furthermore, all the titania supported catalysts showed about the same product distribution with excess hydrogen at 350–400°C, producing considerably less NH_3 than Pt/SiO_2. The nature of the interaction between Pt and TiO_x which accounts for this shift in selectivity remains unknown. It is also not clear why Pt/TiO_2 performed as good as the other two titania supported catalysts in NO/H_2 reactions but showed about the same activity as Pt/SiO_2 in NO/CO reactions. It is planned to study Pt/TiO_2(/SiO_2) catalysts in more detail to understand their interesting catalytic properties in NO reduction reactions.

4. Conclusions

In CO/O_2 reactions the onset temperatures of the titania supported catalysts

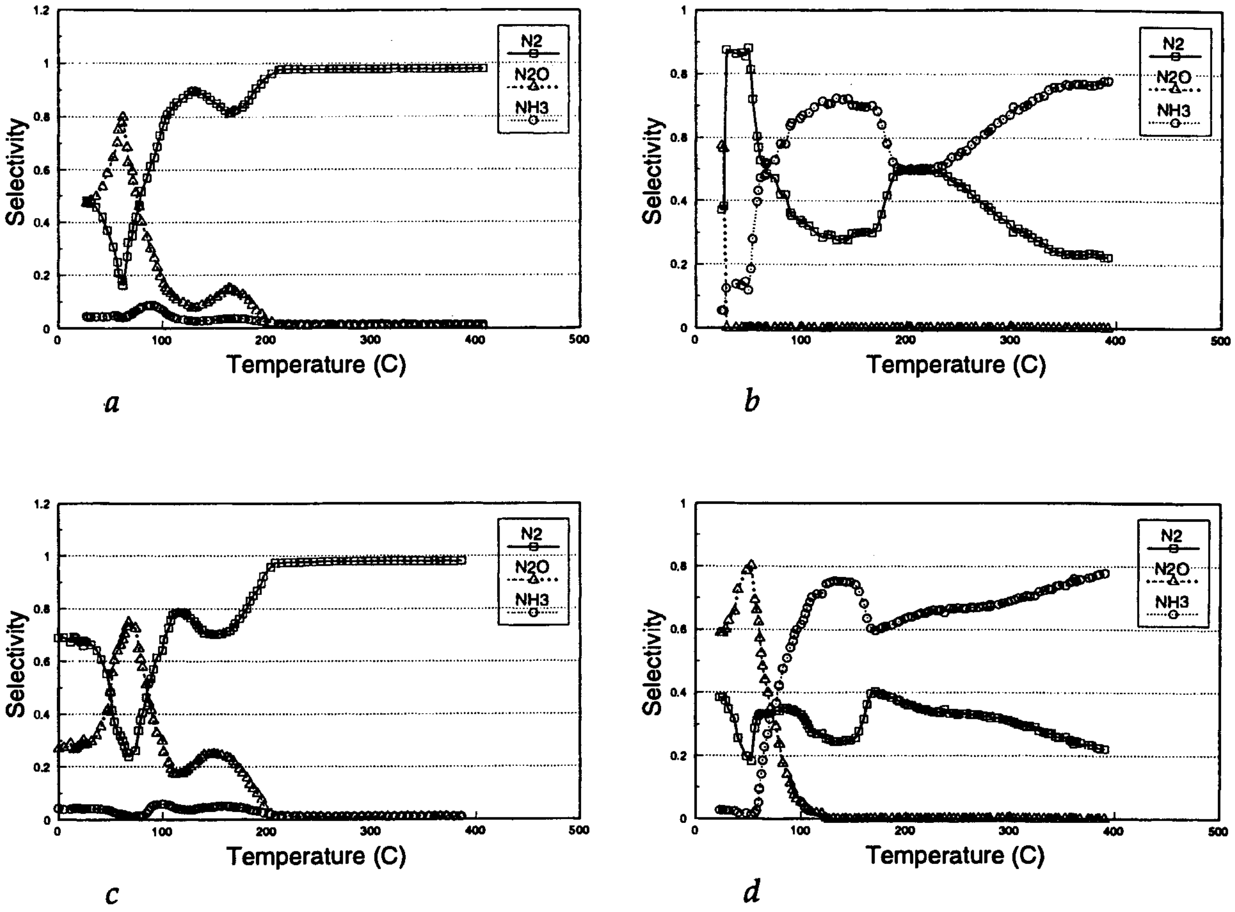

Fig. 4. Selectivity of Pt/SiO_2 after a reductive or oxidative pretreatment. (a) Red. NO/H_2 1 : 1, (b) red. NO/H_2 1 : 3, (c) ox. NO/H_2 1 : 1, (d) ox. NO/H_2 1 : 3.

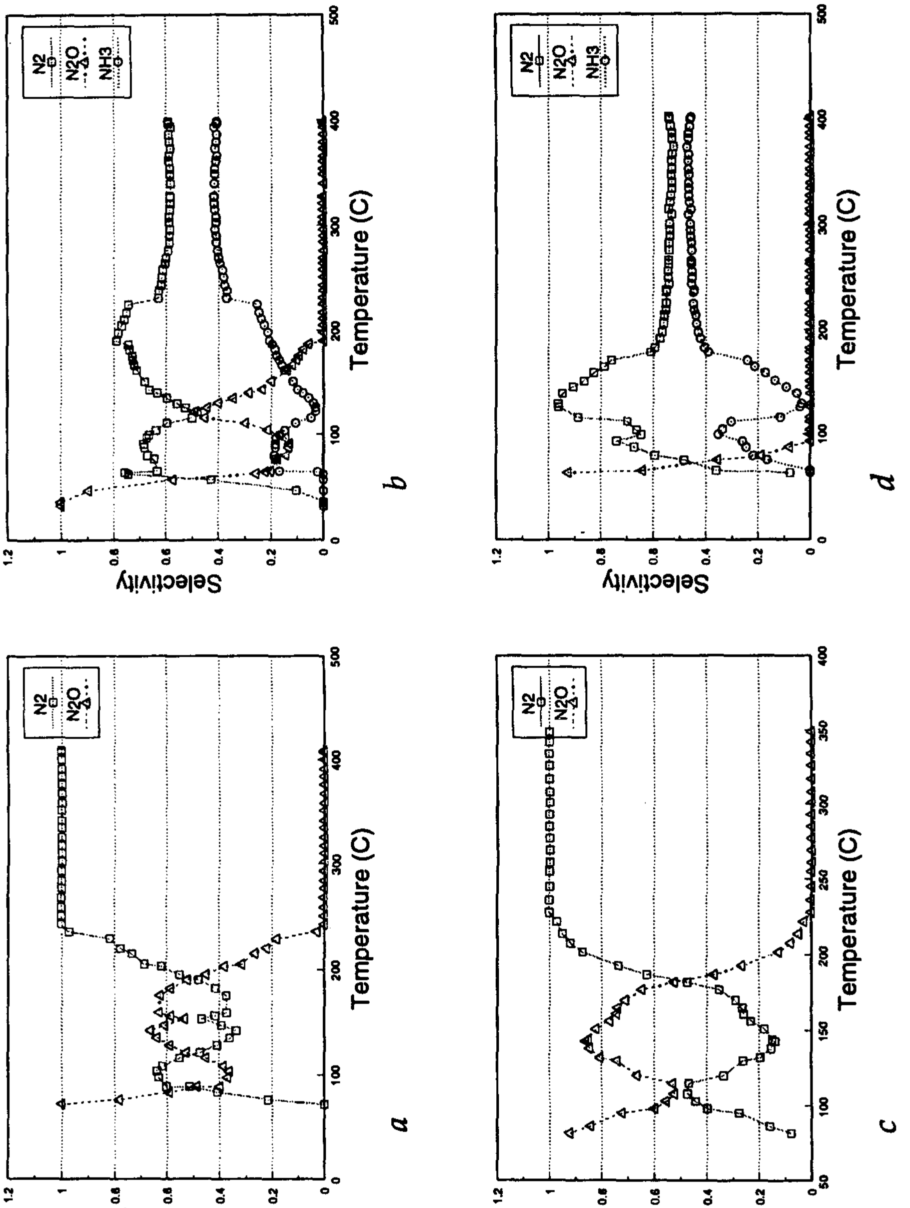

Fig. 5. Selectivity of Pt/TiO_2 after a reductive or oxidative pretreatment. (a) Red. NO/H_2 1 : 1, (b) red. NO/H_2 1 : 3, (c) ox. NO/H_2 1 : 1, (d) ox. NO/H_2 1 : 3.

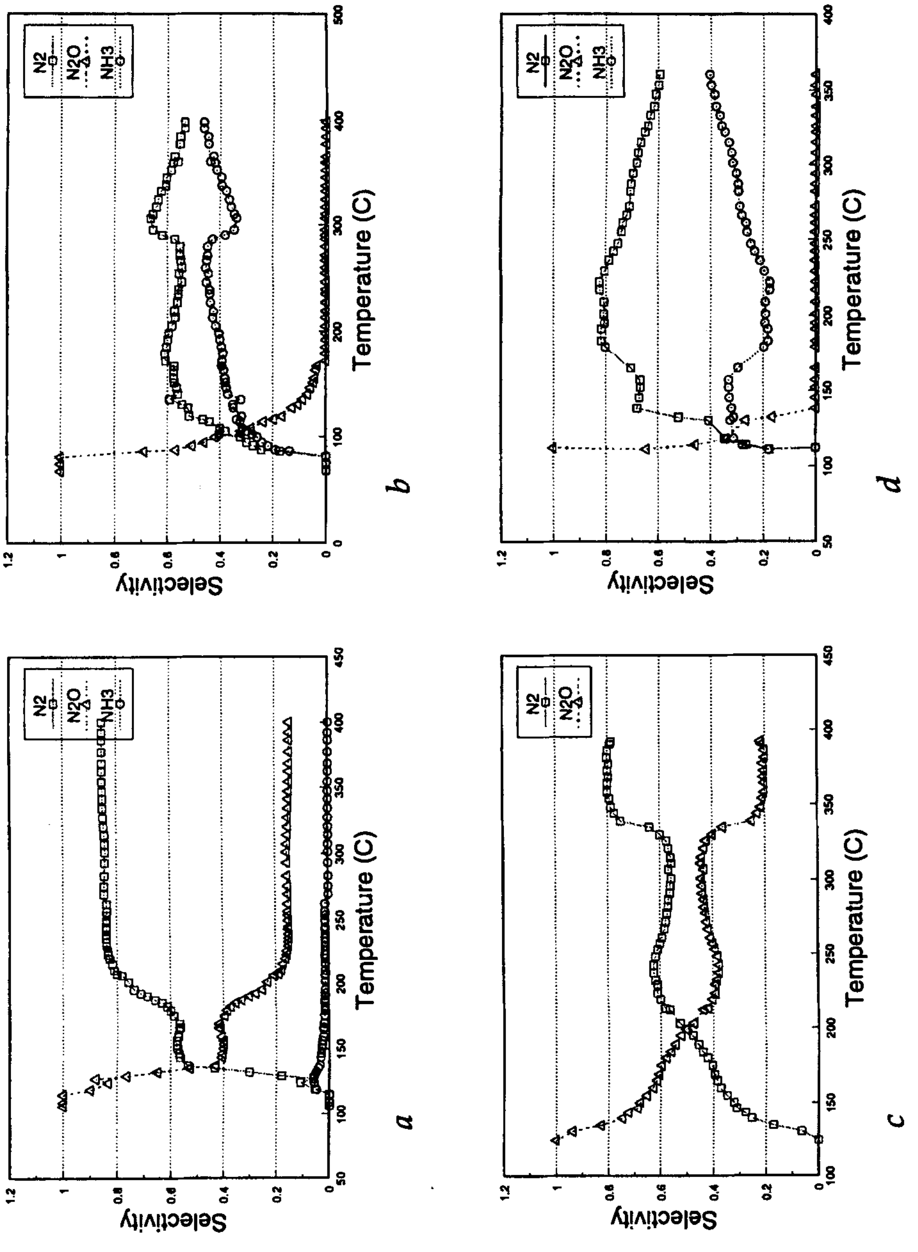

Fig. 6. Selectivity of Pt/TiO_2 25%/SiO_2 after a reductive or oxidative pretreatment. (a) Red. NO/H_2 1 : 1, (b) red. NO/H_2 1 : 3, (c) ox. NO/H_2 1 : 1, (d) ox. NO/H_2 1 : 3.

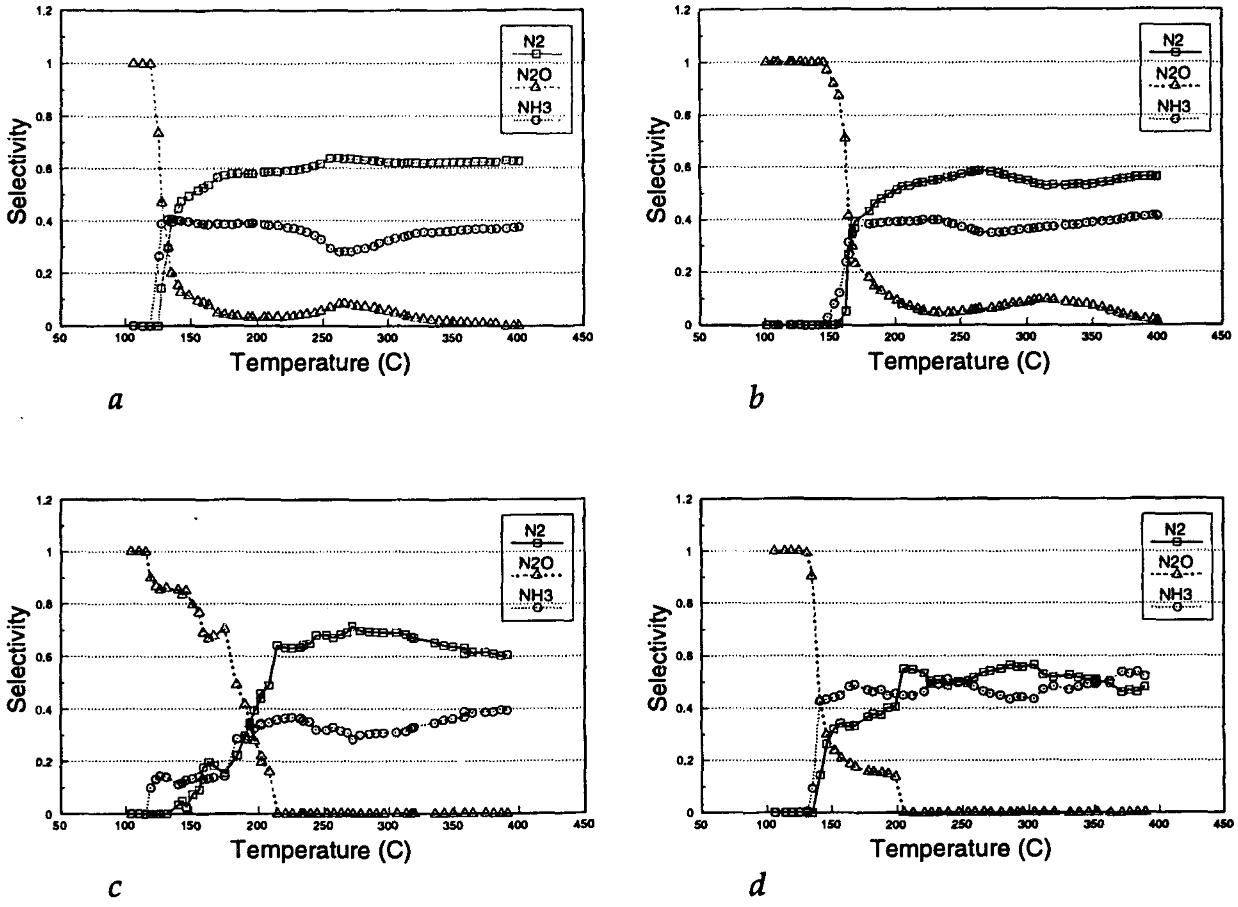

Fig. 7. Selectivity of Pt/TiO_2 80%/SiO_2 after a reductive or oxidative pretreatment. (a) Red. NO/H_2 1 : 1, (b) red. NO/H_2 1 : 3, (c) ox. NO/H_2 1 : 1, (d) ox. NO/H_2 1 : 3.

were decreased relative to Pt / SiO_2 but this effect was small compared to other transitional metal promoters like CoO_x.

In NO/CO reactions the catalysts of mixed oxide support were considerably more active from 200 to 300°C but produced mostly N_2O. A high TiO_2 loading of 80% was necessary to achieve superior activity over Pt / SiO_2 up to 350°C.

In NO / H_2 reactions all titania supported catalysts produced significant quantities of N_2O. In excess hydrogen these catalysts were much more selective to the formation of N_2 than Pt / SiO_2.

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