INVESTIGATION OF THE OXIDATION OF NO OVER PLATINUM CATALYSTS

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The oxidation of NO to NO_2 over Pt/SiO_2 was investigated in the temperature range 150-450°C. Powdered catalysts were prepared by incipient wetness impregnation, followed by calcination and reduction. The feed gas typically contained oxygen, nitrogen monoxide, water and nitrogen. The concentration of NO in the feed was varied at constant concentration of O_2 in order to study its influence on the reaction. A decrease of the conversion with increasing concentration of NO was observed. A similar study was performed with various oxygen concentrations at constant concentration of NO. Oxygen involved in the surface reaction originates from the dissociative chemisorption of O_2 on the platinum surface.

1 INTRODUCTION

The removal of nitrogen oxides, soot, carbon monoxide and hydrocarbons from exhaust gases is a major topic of environmental catalysis. NO_2 plays an increasing role in advanced exhaust gas aftertreatment techniques. Therefore, we are investigating the catalytic oxidation of NO to NO_2 over platinum catalysts in lean conditions:

$$NO + ½\, O_2 \rightarrow NO_2 \quad (1)$$

2 NO_2: A KEY MOLECULE IN EXHAUST GAS AFTERTREATMENT TECHNIQUES

The major part of NO_x emitted by diesel engines consists of NO (95%). Selective catalytic reduction (SCR) using ammonia as a reducing agent is the most promising process for removing NO_x from lean exhaust gases. A possible way to achieve a high DeNOx at low temperatures is to oxidize a part of NO to NO_2 over a platinum catalyst positioned upstream of the SCR catalyst. An ideal NO_x mixture contains 50% NO and 50% NO_2 and reacts according to reaction 2, with a faster rate than the standard SCR reaction 3 [1]:

$$4\, NH_3 + 2\, NO + 2\, NO_2 \rightarrow N_2 + 6\, H_2O \quad (2)$$

$$4\, NH_3 + 4\, NO + O_2 \rightarrow N_2 + 6\, H_2O \quad (3)$$

Another exhaust-gas cleaning process utilizes the better oxidizing properties of NO_2 compared to O_2. For example, the continuously regenerating trap (CRT) for soot removal from diesel exhaust gases utilizes an oxidation catalyst (Pt on alumina) positioned upstream of a soot trap [2]. NO_2 generated by the oxidation catalyst oxidizes soot according to reaction 4, thus regenerating continuously the filter. The presence of NO_2 reduces the temperature of soot oxidation from ≈550°C to values below ≈350°C:

$$C + 2\, NO_2 \rightarrow 2\, NO + CO_2 \quad (4)$$

NO_2 also plays a key role in the adsorption of NO over NO_x storage catalysts, e.g. $Pt/BaO/Al_2O_3$. The reaction mechanism involves the oxidation of NO to NO_2 over platinum as a first step [3] and the reaction of NO_2 with the barium oxide to form $Ba(NO_3)_2$ according to reaction 5:

$$BaO + 3\, NO_2 \rightarrow NO + Ba(NO_3)_2 \quad (5)$$

3 GAS-PHASE EQUILIBRIUM

Figure 1 shows the thermodynamic stability of NO_2 as a function of temperature for various partial pressures of O_2. NO_2 is stable at low temperatures. At temperatures above 200°C, NO_2 dissociates into NO and O_2. High $P(O_2)$ increases the stability of NO_2.

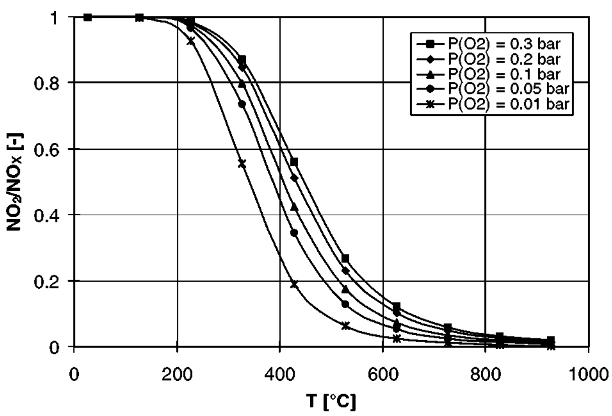

Fig. 1: Thermodynamic gas-phase stability of NO_2 for various partial pressures of oxygen.

4 EXPERIMENTAL

A catalyst sample containing 2.5 % Pt on SiO_2 was prepared by incipient wetness impregnation using $Pt(NH_3)_4Cl_2$ as precursor. The powder was calcined at 300°C for 2 hours, and finally reduced at 450°C in 5% H_2/N_2 for 1 hour. Figure 2 shows a TEM micrograph of the fresh sample. The platinum particle size was about 15 nm, corresponding to a low dispersion of Pt. The oxidation of NO was investigated in a microreactor with 0.8 g Pt/SiO_2 at a gas flow rate of 150 $l \cdot h^{-1}$. Analysis of the gases was achieved by infrared spectroscopy. More details are given in [1]. Between successive oxidation tests, we observed a deactivation of the catalyst. However, the initial activity could be recovered by treating the sample for 1 hour at 650°C.

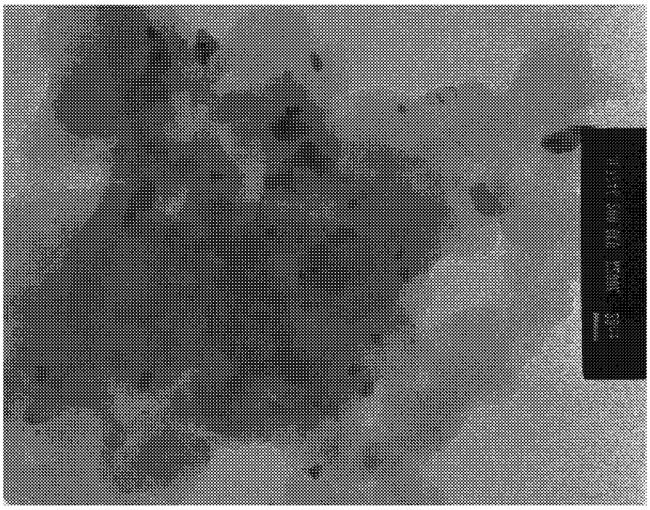

Fig. 2: TEM micrograph of a fresh Pt/SiO_2 catalyst.

5 RESULTS

Influence of NO (Figure 3)

Figure 3 shows the influence of the NO feed concentration on the conversion with a feed containing 10% O_2 and 5% H_2O. The conversion depends strongly on the concentration of NO in the feed. At 200°C, the conversion of 100 ppm NO is 55%, whereas it falls to 12% with 1000 ppm NO. At higher NO concentration, the conversion remains constant.

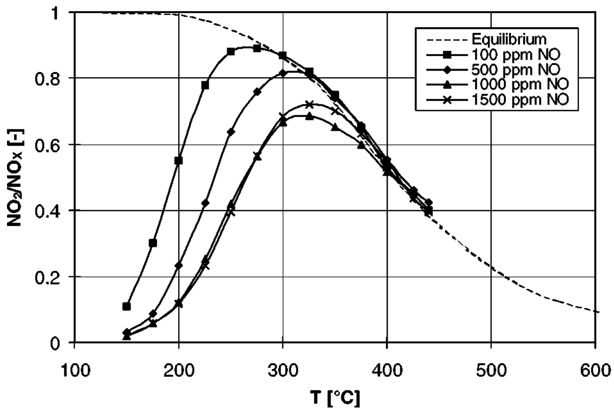

Fig. 3: Influence of NO on the conversion. 0.8 g Pt/SiO_2, 150 l_N/h, 10% O_2, 5% H_2O, balance N_2.

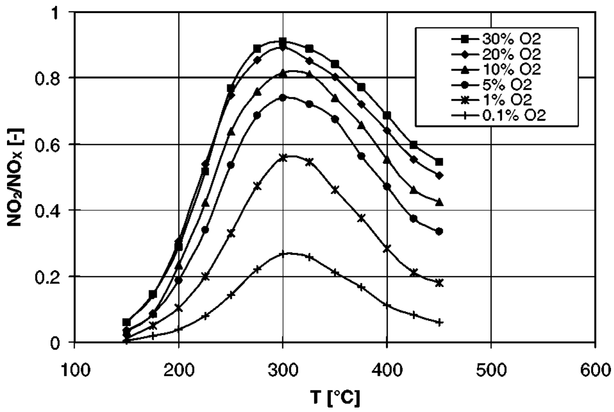

Fig. 4: Influence of O_2 on the conversion. 0.8 g Pt/SiO_2, 150 l_N/h, 500 ppm NO, 5% H_2O, balance N_2.

Influence of O_2 (Figure 4)

Between 150°C and 300°C, we observed an increase of the conversion of 500 ppm NO with increasing concentrations of O_2. However, above 10% O_2 in the feed, the conversion remains almost constant. Above 300°C, the conversion is limited by the thermodynamic equilibrium (Figure 1). Results obtained at low temperatures, i.e. in the kinetically controlled region, reflect a saturation effect with increasing oxygen feed concentration. Platinum is able to chemisorb oxygen dissociatively, even at room temperature, according to the following reaction:

$$O_{2\,(gas)} \rightarrow 2\ O_{ads} \quad (6)$$

The capability of platinum to split small molecules like H_2 or O_2 has also been claimed for the dissociation of NO_2 on model Pt(111) surfaces [4]. Although platinum supported on SiO_2 is expected to remain in the elementary (metallic) state even in a feed containing oxygen, we could expect the change of its oxidation state during the experimental test. The strong oxidizing properties of NO_2 might even lead to the formation of a platinum oxide layer around a Pt core.

6 CONCLUSION

Experimental tests have shown a decrease of the conversion with increasing feed concentrations of NO. Further studies (XPS, DRIFTS) will be performed in order to obtain a better understanding of the reaction mechanism and of the deactivation process.

7 ACKNOWLEDGEMENTS

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8 REFERENCES

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