ELSEVIER

Catalysis Today 29 (1996) 37–42

CATALYSIS TODAY

Selective reduction of NO_x by hydrocarbons in excess oxygen by alumina- and silica-supported catalysts.

R. Burch *, P.J. Millington

Catalysis Research Group, Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK

Abstract

A range of alumina- and silica-supported metal catalysts have been investigated for the selective reduction of NO_x by propene in excess oxygen. Platinum, in particular, has been found to have a high activity and selectivity. There is a close correlation between the activity for NO_x reduction and propene combustion. For platinum group metals, it is found that silica-supported catalysts are more active than alumina-based materials. For Pt/SiO_2 catalysts, it is found that the specific activity for NO_x reduction decreases with decreasing metal dispersion. NO is found to inhibit the oxidation of propene on Pt-based catalysts

Keywords: NO_x reduction; Pt-catalyst

---

1. Introduction

The emission of nitrogen oxides (NO_x), both from stationary and automotive sources is environmentally damaging, contributing to the formation of acid rain and tropospheric ozone. The 3-way automotive catalyst has been highly successful in controlling exhaust emissions from conventional petrol engines which operate under stoichiometric conditions. However, the exhaust from lean burn and from diesel engines contains over 5% oxygen. Under these net-oxidising conditions, the 3-way catalyst is no longer effective for NO_x control. Therefore, for automotive uses, alternative catalyst systems must be developed.

Copper-exchanged zeolite ZSM-5 has generated a great deal of interest as a potential catalysts for NO_x control and has been widely studied [1]. However, it has become clear that due to its instability under thermal and hydrothermal conditions [2,3], Cu-ZSM-5 is unlikely to be suitable as an automotive catalyst and a non-zeolitic alternative is of interest.

Metal oxide-supported metal catalysts show considerable promise [4], especially Pt and other noble metals [5–7]. In this paper we present a study of the selective reduction of NO_x by propene in the presence of excess oxygen over alumina- and silica-supported catalysts.

2. Experimental

Catalytic activities were measured using a microreactor system. 0.1 g of catalyst sample was used. The reactant gas mix contained 500 ppm NO, 1000 ppm C_3H_6 and 5% O_2 with a gas flow rate of 200 cm^3 min^{-1} (GHSV =

---

[*] Corresponding author.

SSDI 0920-5861(95)00257-X

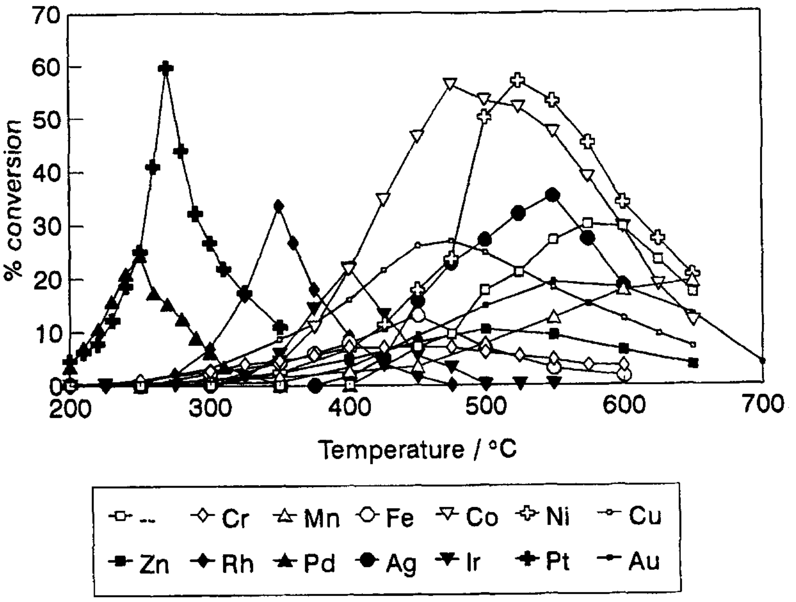

Fig. 1. NO_x reduction on 1% metal/-Al_2O_3 catalysts.

60000 h^{-1}). The effluent gas was analysed by gas chromatography (for N_2O, CO_2 and C_3H_6) or using a chemiluminescence detector (for NO and total NO_x). All the catalysts were prepared by incipient wetness impregnation using aqueous solutions of the appropriate metal salt. Pt catalysts were prepared using $Pt(NO_3)_2(NH_3)_2$, Ir using $(NH_4)_2(IrCl_6)$ and Au from the chloride. The nitrate was used for the other metals. The support materials were γ-alumina or silica

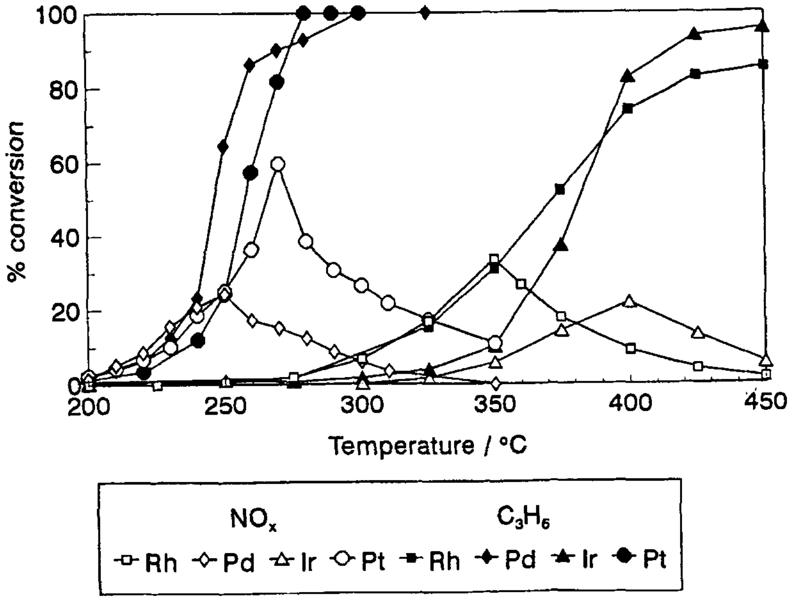

Fig. 2. Coincidence of NO_x reduction and C_3H_6 combustion on PGM catalysts.

which was crushed and sieved prior to impregnation to give a particle size of between 250 and 800 μm. The catalyst metal loading was 1 wt.-%. The standard calcination treatment was heating overnight in air at 500°C. Catalysts with varying metal dispersion were prepared by calcining the catalyst at higher temperatures for differing periods of time. Platinum metal dispersions were determined by H_2 chemisorption using a volumetric technique.

3. Results

The NO_x conversion obtained with a range of 1% metal/Al_2O_3 catalysts are shown in Fig. 1. It can be seen that. while many of the metals have moderate activity, the most active are Pt, Co and Ni, but these are effective over very different temperature ranges. For each of the catalysts there is a close correlation between propene combustion and NO_x conversion, both in terms of the temperature at which the reaction commences and of the width of the activity window. These results for the platinum group metals (PGMs: Pt, Pd, Rh, Ir) are shown in Fig. 2. The PGMs (Pd, Pt, Rh and Ir) have relatively narrow activity temperature windows (full width at half maximum (FWHM) of about 50°C). This is matched by the very rapid light-off of propene combustion which rises from effectively zero to 100% over a 50°C interval. The other, base metal catalysts, generally have much wider activity windows (FWHM of about 200°C), but activity is seen at higher temperatures than with the PGM catalysts. Of these base metal catalysts, by far the most active are Co/Al_2O_3 and Ni/Al_2O_3 (approximately 55% NO_x conversion at 475 and 525°C, respectively). These activities are comparable with those produced by the platinum catalyst.

With Pt and Pd, significant quantities of N_2O were formed — the selectivity was approximately 50% to N_2O — which is in accord with other work [6,7]. No N_2O was detected with the other catalysts which are active at higher temperatures than Pd and Pt.

The activities of Pt, Pd and Rh supported on Al_2O_3 or SiO_2 are shown in Fig. 3. Pt is the most active metal, although Rh shows consider-

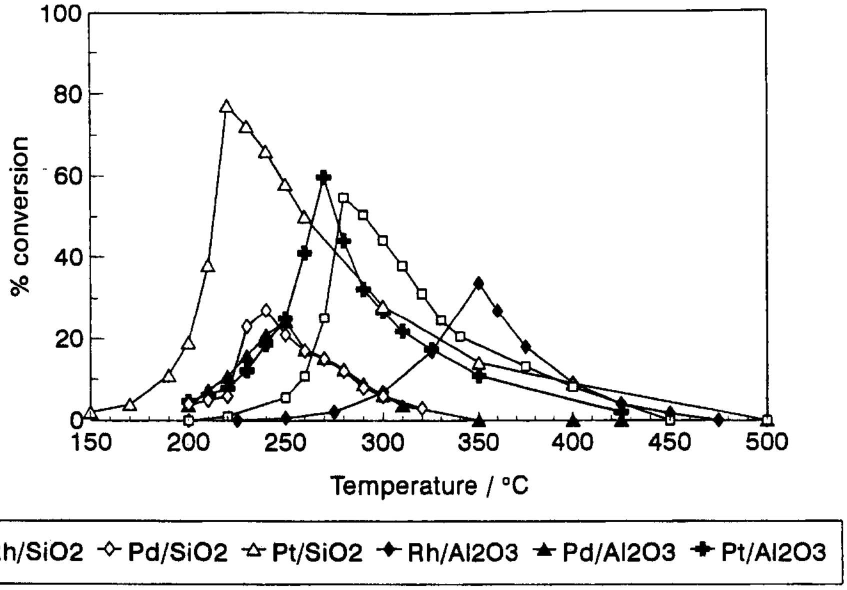

Fig. 3. Activity of 1% Rh, Pd or Pt supported on SiO_2 or Al_2O_3.

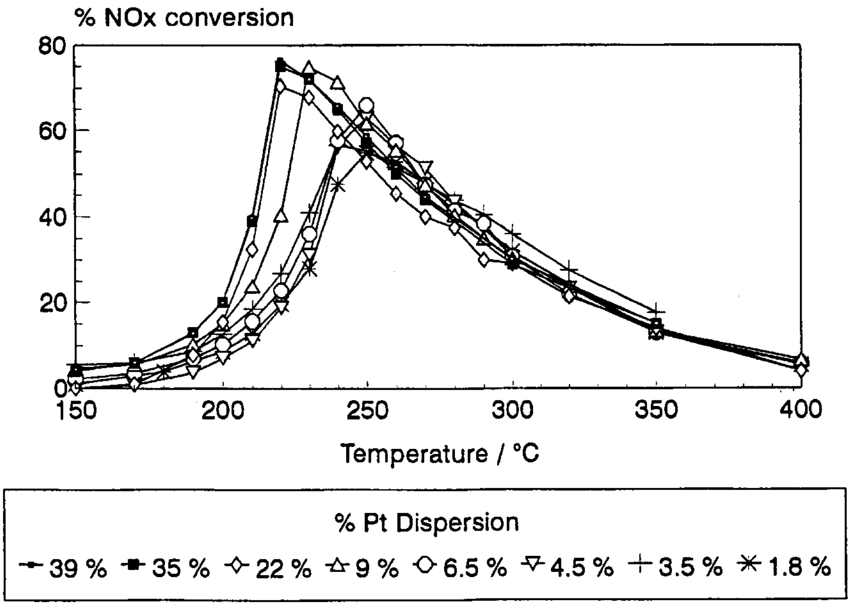

Fig. 4. Activity of 1% Pt/SiO_2 with different Pt metal dispersions.

able activity at higher temperatures. For each metal, the SiO_2 supported catalysts appear more active than those on Al_2O_3.

The activity of Pt/SiO_2 catalysts with differing metal dispersions are shown in Fig. 4. It can be seen that activity decreases with decreasing dispersion and also moves to a higher temperature. In terms of turnover frequencies (TOF), expressed as molecules of NO_x reacting (to form N_2 or N_2O) per s per surface platinum atom, there is a small effect of particle size between 3 (40% dispersion) and 25 nm (5%),

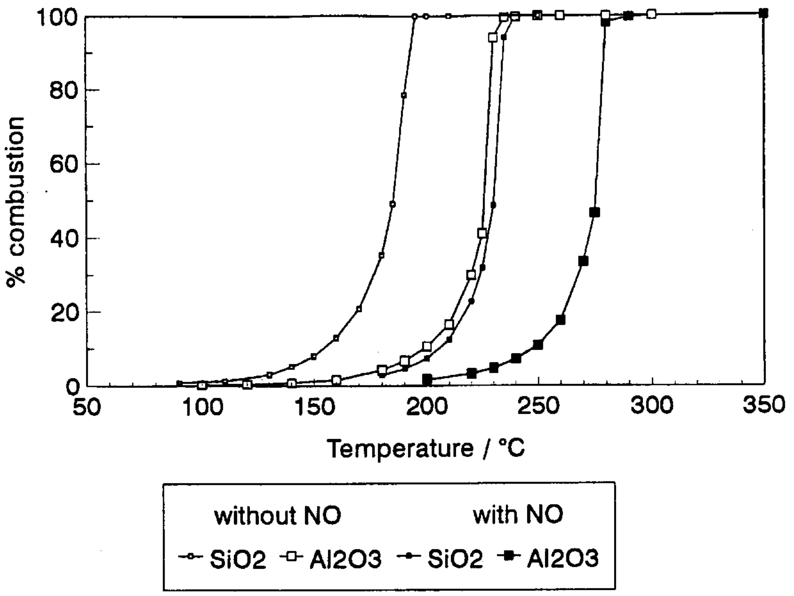

Fig. 5. Propene combustion on Pt/SiO_2 and Pt/Al_2O_3 catalysts.

with the turnover frequency (TOF) of the large particles being about twice that of the smaller ones.

Shown in Fig. 5 is a comparison of the C_3H_6 combustion profiles in the presence (during deNO$_x$ experiments) and absence of NO. In either case, Pt/SiO$_2$ is active at a temperature 40°C below Pt/Al$_2$O$_3$. NO inhibits the oxidation of C_3H_6 and its presence increases the C_3H_6 combustion temperature by 50°C. It should be noted that the curves for both supports shift together. Furthermore, NO$_x$ reduction (results not shown in Fig. 5) shifts in parallel with the shift in the C_3H_6 combustion curve, (i.e., from the Pt/SiO$_2$ to the Pt/Al$_2$O$_3$ catalyst) suggesting that the reduction of NO$_x$ is secondary to, and dependent upon, the prereduction of the active sites by propene.

4. Discussion

Alumina- and silica-supported catalysts can be effective for the selective reduction of NO$_x$ by propene in the presence of a large excess of oxygen, at temperatures varying from ca. 230 for Pt to ca. 500°C for Ni. Clearly it is not essential to have a zeolitic structure in order to observe good deNO$_x$ activity and selectivity with a wide range of active metals. However, it is also clear that for the base metal catalysts they are not selective when present as free oxide phases. Such phases are too reactive for propene oxidation and selective reduction of NO$_x$ is not observed. Instead, these base metal oxides are selective under conditions where they have strongly interacted with the alumina-support, for example to form surface mixed oxide phases. On the other hand, the platinum group metals, especially Pt and Pd are selective and active at low temperatures.

Based on this, and previous work [7], we believe that the predominant mechanism for this reaction over these oxide-supported catalysts proceeds via a redox process. We propose that the propene reduces the active sites, which may be essentially isolated ions in the case of the base metal oxides, or metal particles in the case of the platinum group metals. On these reduced sites NO decomposition is facile but, although N_2 is released into the gas phase, the surface becomes oxidized and deactivated for NO decomposition. Re-reduction of the active sites by propene completes the catalytic cycle.

The results obtained in the present work are consistent with this redox model. Thus, the fact that the reduction of the NO$_x$ only occurs at temperatures at which the reduction of the catalyst by propene commences (see Fig. 2) is evidence for a linking between the two parts of the redox cycle. In earlier work with these Pt catalysts [7], we have shown in transient kinetic studies that these two parts of the redox cycle can be decoupled but still the same high activity for NO removal is observed. Therefore, the lower temperature activity of silica-supported catalysts compared with alumina-based samples (Fig. 3) is explained in terms of the reduced temperature required to activate propene on these catalysts.

The results shown in Fig. 5 are again consistent with a simple redox model. In this case by changing the support from alumina to silica, we have observed a significant difference in the temperature required to activate the propene for combustion in the absence of NO. When NO is added to the propene/O$_2$ mixture there is a significant shift in the positions of the curves. Therefore, NO inhibits the oxidation of propene and indicates that NO can effectively compete for the surface. The difference between the two supports remains. In both cases, the temperature at which NO reduction is observed corresponds to the new temperature at which propene activation occurs. Thus, although NO reduction can occur on a Pt catalyst (Pt/SiO$_2$) at below 200°C, no reaction is observed on a different Pt catalyst (Pt/Al$_2$O$_3$) until ca. 250°C. We interpret this in terms of a redox model, i.e., NO decomposition is limited by the pre-reduction of the active sites on Pt particles.

References

[1] M. Iwamoto and H. Yahiro, Catal. Today, 22 (1994) 5 and references therein.

[2] R.A. Grinsted, H-W. Jen, C.N. Montreuil, M.J. Rokosz and M. Shelef, Zeolites, 13 (1993) 602.

[3] J.O. Petunchi and W.K. Hall, Appl. Catal. B, 3 (1994) 239.

[4] H. Hamada, Catal. Today, 22 (1994) 21 and references therein.

[5] G. Zhang, T. Yamaguchi, H. Kawakami and T. Suzuki, Appl. Catal. B, 1 (1992) L15.

[6] A. Obuchi, A. Ohi, M. Nakamura, A. Ogata, K. Mizuno and H. Ohuchi, Appl. Catal. B, 2 (1993) 71.

[7] R. Burch, P.J. Millington and A.P. Walker, Appl. Catal. B, 4 (1994) 64.