

On the effects of residual chloride and of barium promotion on Pt/ γ -Al₂O₃ catalysts in the reduction of NO by propene

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Partial retention of chloride by Pt/ γ -alumina catalysts prepared from chlorine-containing precursors markedly poisons both activity and nitrogen selectivity in the reduction of NO by propene. In the complete absence of chloride, Ba acts as a very strong promoter, dramatically improving activity, nitrogen selectivity and NO conversion. Very strikingly, when Ba is used to promote a catalyst prepared from chloride-containing precursors, *all* the original chloride is retained, yet the catalyst exhibits very strong promotion, and in every aspect its behavior is identical to that of the chloride-free Ba-promoted catalyst. This behavior is rationalized in terms of BaCl₂ formation and the relative effects of Cl and Ba in inhibiting and promoting, respectively, the dissociation of chemisorbed NO—the reaction-initiating step.

KEY WORDS: Pt/ γ -Al₂O₃ catalysts; chlorine poisoning; barium promotion; NO reduction; propene.

1. Introduction

Supported platinum group metal catalysts, in particular those comprising Pt itself, are commonly prepared by impregnation of a support (*e.g.* Al₂O₃) with chlorine-containing salts, followed by calcination in air. In such cases it has been reported that residual chlorine cannot be totally removed from the support by conventional oxidative treatments [1,2], which can lead to catalyst poisoning. The catalytic combustion of methane provides an important example of this effect [1–7]. Thus Simone *et al.* [1] and more recently Roth *et al.* [2] and Marceau *et al.* [3] showed that chlorine-containing precursors produced inferior catalysts compared with others made from chlorine-free precursors when the residual chloride was not fully removed. Simone *et al.* [1] showed that when chlorine-containing precursors are used, a combination of reduction and washing treatments gave catalysts with activity comparable with those prepared from nitrate precursors. In this connection, Roth *et al.* [2] and Marceau *et al.* [3] demonstrated that residual chlorine could be slowly removed as HCl under reaction conditions, resulting in performance similar to that of corresponding catalysts prepared from a nitrate precursor.

Legislative pressures to improve performance, especially in applications aimed at environmental protection [8], have stimulated the search for means of enhancing the catalytic properties of platinum metal formulations used for emissions control from mobile and stationary sources. Most such studies focus on the use of surface promoters that enhance activity and/or selectivity by direct interaction

with the catalytically active phase. In this regard, alkalis and alkaline earths are very effective in improving the efficiency of NO_x reduction by platinum metal catalysts [9–13].

Therefore it is of interest to inquire whether these promoters are still effective when the catalysts in question are produced from chlorine-containing precursors, and whether their performance is comparable with the corresponding materials synthesized by a chlorine-free route. Here we address these issues in the case of Ba-promoted Pt/ γ -Al₂O₃ catalysts produced by both methods and tested for the reduction of NO by C₃H₆.

2. Experimental methods

The basic catalyst consisted of Pt dispersed on γ -Al₂O₃, four samples of which were produced as follows. Two batches of powdered γ -Al₂O₃ carrier (Alfa products, surface area ~ 90 m²/g) were first impregnated in two different solutions of H₂PtCl₆ (Alfa products) and Pt(NH₃)₂(NO₂)₂ (Alfa products) with appropriate concentrations so as to yield 0.5 wt% Pt metal loading in both cases. The slurries were heated while vigorously stirred and subsequently dried in air for 12 h at 110 °C. Before thermal decomposition of the active metal precursor, each of these two samples was again divided into two parts, one of which was then impregnated with a solution containing Ba(NO₃)₂ at the appropriate concentration so as to yield catalysts with 15.2 wt% of Ba. This Ba loading was chosen because it is known to optimize both activity and selectivity of Pt/ γ -Al₂O₃ for the NO + C₃H₆ reaction over a wide range of conditions [13]. The two resulting samples were dried at 110 °C for

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Table 1
Properties of unpromoted and Ba-promoted 0.5 wt% Pt/ γ -Al₂O₃ catalysts prepared from different precursors

Code	Catalyst	Precondition	Ba-loading (wt%)	H ₂ uptake (cm ³ STP/g)	Dispersion (%)	Cl (wt%)
Catalysts prepared by H ₂ PtCl ₆ precursor						
C	Pt/ γ -Al ₂ O ₃	Fresh ^a	0	0.290	~100	0.25
		Stage 1 ^b		0.110	38	— ^d
		Stage 2 ^c		0.086	30	0.20
CBa	Pt(Ba)/ γ -Al ₂ O ₃	Stage 2 ^c	15.2	0.108	38	0.45
Catalysts prepared by Pt(NH ₃) ₂ (NO ₂) ₂ precursor						
N	Pt/ γ -Al ₂ O ₃	Stage 2 ^c	0	0.172	60	0
NBa	Pt(Ba)/ γ -Al ₂ O ₃	Stage 2 ^c	15.2	0.08	28	0

^a Fresh: preconditioned in air at 600 °C for 8 h followed by H₂ flow at 500 °C for 2 h.

^b Stage 1: as fresh plus 1 day aging at reaction conditions (550 °C, 1000 ppm NO + 1000 ppm C₃H₆).

^c Stage 2: as fresh plus 5 day aging at reaction conditions (550 °C, 1000 ppm NO + 1000 ppm C₃H₆).

^d Not measured.

12 h. Then, all four samples were heated for 8 h in flowing air (100 cm³/min) at 600 °C and reduced in H₂ (100 cm³/min) for 2 h at 500 °C. Thus we produced four Pt/ γ -Al₂O₃ catalysts: the two catalysts prepared by means of the chlorine-containing precursor are designated C and CBa (unpromoted and Ba-promoted respectively). The corresponding catalysts prepared by the Cl-free route are designated N and NBa. Metal dispersion was determined by H₂ chemisorption at 25 °C following the method of Benson and Boudart [14] by extrapolation of the “plateau” region (~10–40 Torr) of the adsorption isotherms. These measurements were performed after reducing the catalysts in H₂ at 300 °C for 1 h and degassing in vacuum at 400 °C for 1 h. Hydrogen-to-metal (H/M) ratios were calculated by assuming 1:1 hydrogen metal stoichiometry and the resulting data are summarized in table 1.

Catalyst testing was performed in a 4 mm i.d. quartz tube, fixed-bed reactor, operating at atmospheric pressure. The catalyst sample was held between plugs of quartz wool and a K-thermocouple was located at the centre of the bed. Catalyst loadings were typically ~8 mg (grain size 180–250 μ m), the sample being diluted further by admixture with ~80 mg γ -Al₂O₃ (100 to 325 mesh, Alpha products). Reactant and product analysis was by means of on-line gas chromatography (Shimadzu-14B). Separation of N₂, NO and CO was achieved with a molecular sieve 5 Å column at 80 °C while CO₂, N₂O and C₃H₆ were separated using a Porapak-N column at the same temperature. NO and C₃H₆ in He certified standard gases (Air Liquide), and ultrapure 99.999% He were used in order to produce the required gas mixtures in a mixing and feed unit, which then supplied the reactor at 1 bar total pressure.

During acquisition of kinetic (turnover frequency) data, the reactor was operated under differential conditions, with reactant conversion $\leq$ 15%. Care was taken to ensure the absence of intra-particle and inter-particle diffusional limitations by varying catalyst particle size

and gas flow rate. Carbon and nitrogen mass balances were found to close within 2%, and control experiments showed that the quartz wool was catalytically inert at temperatures up to 550 °C. Studies of temperature dependence were carried out in steps between 200 and 500 °C. At each step the temperature, total flow and inlet composition were kept constant for 30 min before taking measurements. The inlet composition was 1000 ppm(v) NO + 1000 ppm(v) C₃H₆ diluted in He. For each catalyst sample, the total flow rate was chosen so as to produce the same reactant *contact time* [9] of 1 s.

In order to examine the effect of time on stream on the catalyst dispersion and on the influence of residual chloride, catalyst C was tested at several stages of its pretreatment. Thus after initial activation (calcination in air at 600 °C for 8 h, reduction in H₂ at 500 °C for 2 h) the dispersion of this fresh catalyst (designated as Fresh, table 1) was ~100%. Its performance was not studied since it would be expected to be unstable due to thermal sintering and partial elimination of residual chlorine. This fresh catalyst was then run under reaction conditions for 1 day (1000 ppm NO + 1000 ppm C₃H₆, f = 80 cm³ STP/min at 550 °C) to produce an aged sample designated Stage 1. Its dispersion was then measured again and found to be very much lower, namely 38%. A portion of sample Stage 1 was further treated under reaction conditions for 3 days to produce catalyst Stage 2, which exhibited an additional decrease in dispersion to 30%: the performance of this sample was then evaluated. The remainder of the sample was further treated under reaction conditions for 5 days, after which the measured dispersion and catalytic properties were found to be identical to those of catalyst Stage 2. We therefore employed the 5 days' pretreatment protocol for all the other catalysts before measuring their dispersions (table 1) and catalytic properties. The chlorine content of catalysts C and CBa was measured by X-ray fluorescence (XRF). Quantification of the

XRF results was performed by comparison with NaCl/ γ -Al₂O₃ standards and relevant data are summarized in table 1.

3. Results and discussion

In order to examine the effect of residual chloride on Pt activity and selectivity in the NO + propene reaction, with and without Ba-promotion, the following experiments were performed. The turnover frequency, selectivity and conversion delivered by catalyst samples C, CBa, N and NBa, were measured under comparable conditions.

The chlorine analyses shown in table 1 indicate that the theoretical initial chlorine content (0.46 wt%) of the unpromoted catalyst was halved (~ 0.25 wt%) during pretreatment with H₂. However this residual chlorine was almost unaffected by reaction conditions, decreasing only very slightly (~ 0.2 wt%) after 5 days on stream. We conclude that the 1:1 NO + C₃H₆ feed gas is much less effective for chlorine removal than CH₄ + O₂ [2]. Note that the Ba-promoted catalyst (CBa) retained almost all the original initial chlorine (~ 0.45 wt%), even after reduction by H₂ followed by 5 days on stream. A possible explanation is that formation of BaCl₂ prevented chlorine depletion.

Figures 1(a)–(c) show the N₂, CO₂ and N₂O turnover frequencies (molecules of products per surface Pt atom per second) for the catalyst pairs C–N and CBa–NBa at constant [C₃H₆] and [NO] as a function of temperature. The corresponding selectivity towards N₂ is depicted in figure 2. It is apparent that the chlorine-free unpromoted catalyst (N) is substantially better than its chlorine-containing analogue (C). The N₂ TOF of the former is higher by a factor of about two (figure 1(a)) and its N₂ selectivity is superior (figure 2).

In striking contrast to the above observations, the two Ba-promoted catalysts NBa and CBa show essentially identical behavior, despite, respectively, the absence and presence of chloride. Both catalysts exhibit very pronounced activity promotion by Ba (figures 1(a)–(c)). Their nitrogen selectivities are almost identical over the entire temperature range, approaching 100% at $T > 400$ °C, and always substantially higher than those of the unpromoted catalysts (figure 2). That is, Ba induces strong promotion of Pt activity and selectivity, regardless of the presence or absence of residual chloride.

Figure 3 shows a comparison between the two pairs of catalysts in terms of NO conversion as a function of temperature. In every case the feed composition was 1000 ppm NO + 1000 ppm C₃H₆, the total flowrate being adjusted so as to maintain the effective contact time at 1 s. Since the various catalysts did not have identical dispersions (table 1), the effective contact time is the key parameter that should be kept constant in order to obtain a rational comparison of their relative merits. It is defined as surface Pt atoms/(reactant

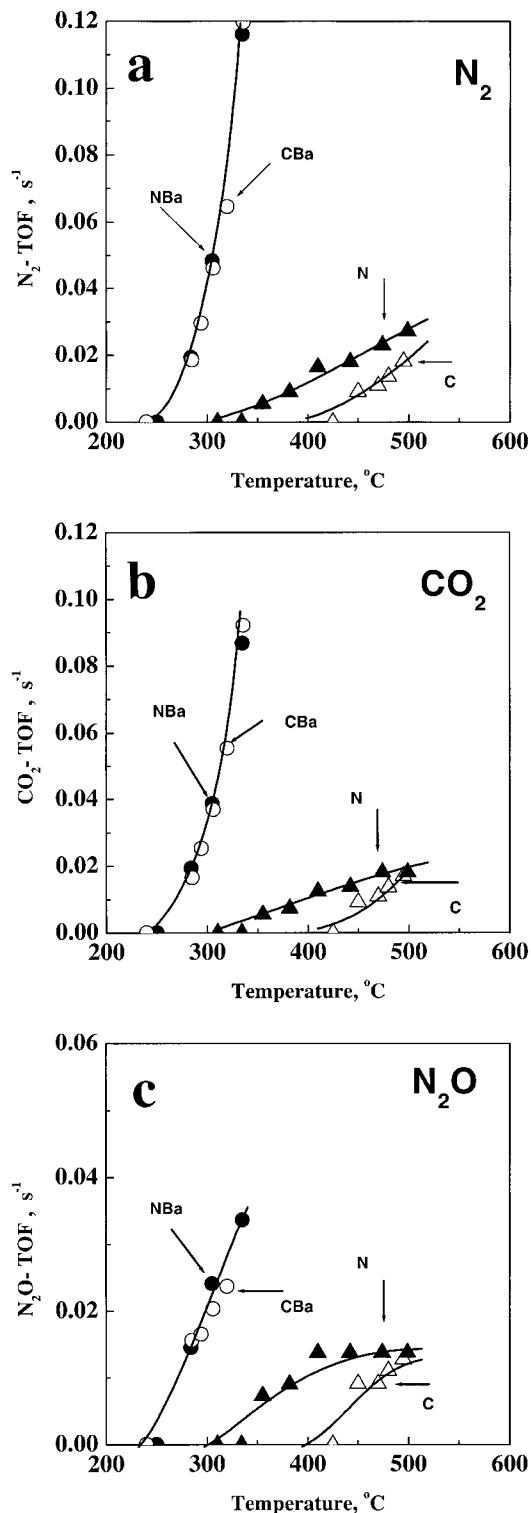


Figure 1. Comparison of N₂ (a), CO₂ (b) and N₂O (c) TOFs of Ba-free unpromoted catalysts (N, C) and Ba-promoted catalysts (NBa, CBa) as a function of temperature.

molecules/s) [9,18]. In the present case, a 1 s effective contact time required total flowrates of 81, 163, 104 and 76 cm³ STP/min for catalysts C, N, CBa and NBa respectively. It is again clear that both Ba-promoted catalysts hugely outperform the unpromoted catalysts

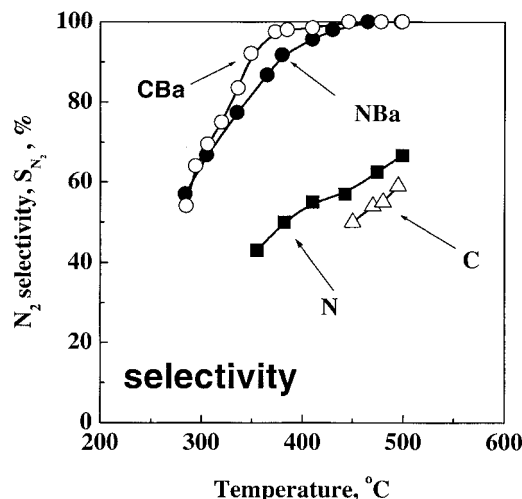


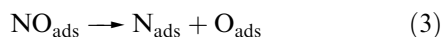
Figure 2. Temperature dependence of nitrogen selectivity for catalysts C, N, CBa and NBa.

and that their light-off curves are essentially identical. In contrast, the chloride-containing unpromoted catalyst is significantly worse than its chloride-free counterpart.

Although the performances of the Ba-promoted catalysts (NBa and CBa) are essentially identical in every respect, the same is not true for the unpromoted catalysts (N and C). In this case it is clear that the presence of residual chlorine does result in impaired performance, an effect that has often been reported [1–7]. Therefore we need to consider the origin of Cl poisoning and Ba promotion, and why the presence of the latter overwhelms the effect of the former.

At the most fundamental level, alkali promotion of NO reduction is best understood in terms of the analysis given long ago by Lang *et al.* [15] using the methods of condensed matter physics. In essence this provides a formal justification of the chemisorption model due to Blyholder, which is an extension of the classical Dewar–Chatt model of ligand bonding. Lang *et al.* showed that when a diatomic molecule such as NO is adsorbed in the vicinity of an alkali ion, the local electric field due to the latter depresses the π^* molecular orbital below the metal Fermi level. In effect, this is a manifestation of the well-known Stark effect. The resulting charge transfer from metal to molecule weakens the N–O bond, thus promoting dissociation. By the same argument, co-adsorption of an electronegative species such as chloride should inhibit the dissociation of adsorbed NO.

The catalytic reduction of NO is thought to occur by the following pathway [16,17], where the surface chemistry is triggered by the dissociation of NO:



where $\text{C}_x\text{H}_y\text{,ads}$ refers to chemisorbed propene and propene fragments [19].

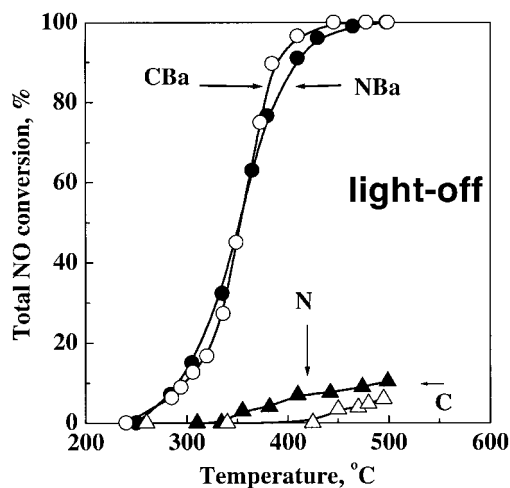
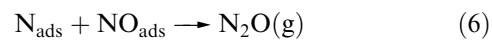
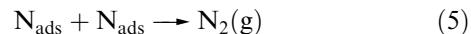


Figure 3. Temperature dependence of NO conversion for catalysts C, N, CBa and NBa all measured at the same effective reactant contact time of 1 s.

These steps are then followed by the reaction O_{ads} with adsorbed propene and propene fragments to produce CO_2 and H_2O . Recombination of N_{ads} or reaction with NO_{ads} yields N_2 and N_2O respectively:



Thus Ba ions should favour equations (3) and (5), enhancing both overall activity and selectivity, as observed. Conversely, chloride should have the opposite effect, again in accord with observation. However, the strength of the effect is much smaller. On a simple basis, we may rationalize this in terms of the very different electric field [12]. Indeed we have already demonstrated that Ba is a very powerful promoter [13], especially when compared with the relatively weak poisoning effect of Cl found here and elsewhere. Thus in a general sense we can understand the present results in the following way. Chloride alone on Pt poisons NO dissociation and hence overall activity; this is a significant effect because Pt, unlike Rh, is not very effective for NO dissociation [16]. Ba alone induces very strong promotion (relatively small, highly-charged cation). When present together on the metal surface as a two-dimensional BaCl_2 phase, the positive effect of Ba overwhelms the negative effect of Cl and a large net promotion is observed. However, the stability of BaCl_2 leads to retention of most of the original Cl by the catalyst, as indeed we find. Note that while the Cl content of the Ba-promoted catalyst is enough to cover the entire Pt surface, the Ba content is much higher still. This undoubtedly makes an important contribution to the effect whereby Ba overcomes Cl poisoning. A further implication is that the Ba- and Cl-containing species are principally located on the alumina support and in

equilibrium with a dispersed “BaCl₂” phase present on the Pt particle surfaces in sub-monolayer amounts.

4. Conclusions

1. Pt/alumina catalysts prepared from chlorine-containing precursors retain a significant amount of Cl even after calcination, reduction, and exposure to reaction conditions. This residual Cl significantly poisons both activity and nitrogen selectivity in the NO + C₃H₆ reaction.
2. Ba is a very strong promoter of both activity and selectivity. When a Cl-containing precursor is used, most of the Cl is retained by the catalyst but the promotional effect of Ba overwhelms any negative effects of Cl. Performance is identical to that of Ba-promoted catalysts prepared *via* a chlorine-free route.
3. This behavior may be understood in terms of the relative effects of Cl and Ba in inhibiting and promoting, respectively, the dissociation of chemisorbed NO—the reaction-initiating step.

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