

Reaction of NO and O₂ to NO₂ on supported and model Pt catalysts: Catalyst deactivation and kinetics as a function of particle size

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Introduction

The oxidation of NO to NO₂ (NO+O₂ ⇌ NO₂) over a supported noble metal component is an important intermediate step involved in NO_x abatement using the NO_x storage/reduction (NSR) process that is being developed for diesel engines. In fact, NO oxidation to NO₂ is the first step that occurs in the cyclic NSR process. It is also a key step for soot removal. In the work reported here, we have measured the kinetics (apparent activation energy and power rate law reaction orders) for NO oxidation on a series of Pt catalysts with varying Pt particle sizes. Deactivation of the catalyst was observed during reaction. Flow experiments and XPS measurements suggest that the deactivation is particle size dependent and is due to over-oxidation of Pt by the reaction mixture. The larger particles, being composed of the more stable (111) faces, do not deactivate and are proposed as the active sites.

Materials and Methods

The Pt/Al₂O₃ catalysts used in this study were supplied by EmeraChem, LLC in the form of monolith and had a Pt loading of ca. 50 g/ft³. Two different Pt/Al₂O₃ monoliths having Pt dispersions of 42% and 15% were studied. Additionally, three Pt catalysts (1 wt%) supported on mesoporous SBA-15 silica material, prepared by the method described by Rioux *et al.* [1], were also studied. Table 1 lists all the catalysts that were used, along with the average Pt particle size (measured by both H₂-O₂ titration and TEM). The NO oxidation reaction kinetics on Pt/Al₂O₃ monoliths were studied in a stainless steel (SS) plug flow reactor described elsewhere [2]. The SS reactor was replaced by a vertical PyrexTM reactor for the powder catalysts. The reactor was operated in a differential manner by using an excess of NO₂ in the feed and restricting the NO conversions to below 10%. The reaction conversion was continuously monitored using a FT-IR gas analyzer (Thermo Electron Corporation, Nicolet Antaris IGS). The experiments were conducted with a total flow of 6.6 L min⁻¹ for the monoliths, and 3.5 L min⁻¹ for the powders.

Results and Discussion

Table 1 summarizes the results of the NO oxidation kinetics measurements on the Pt catalysts. Over the concentration range studied, the rate of NO oxidation was found to be close to first order with respect to both reactants NO and O₂, while it was close to negative first order with respect to the product NO₂, indicating that the product NO₂ is an inhibitor of this reaction. A reaction mechanism that is consistent with the observed reaction orders has been proposed [2]. The reaction was found to be sensitive to the structure of the catalyst with higher turnover rates (TOR) seen for larger Pt clusters. Based on the particle size distribution obtained by transmission electron microscopy (TEM) measurements, it appears that only large

Pt particles are responsible for the observed activity, with the smaller Pt particles deactivating under the oxidizing reaction conditions. The catalyst deactivation observed was found to be completely reversible; a brief exposure (< 3 min) to a reductant (H₂ or CO) would increase the TOR to the original level. Based on the XPS measurements, the Pt on both an active and deactivated catalyst was found to be oxidized, with higher Pt oxidation (towards PtO) seen upon deactivation. The catalyst deactivation was, therefore, attributed to an increase in the bulk oxidation of the Pt particles towards PtO [3]. High resolution TEM imaging (Fig. 1) revealed the presence of single crystalline large Pt particles with <111> faces exposed on 9 nm (average) Pt/SBA-15 catalyst, which was not the case with the other two SBA-15 supported samples having smaller Pt cluster sizes. This result, combined with the high TOR seen on the 9 nm Pt/SBA-15 sample, suggests that (111) surfaces may be the active sites for NO oxidation reaction, capable of resisting oxidation and hence, deactivation, when compared to the more open surfaces. NO oxidation rate measurements on a Pt(111) single crystal, under similar conditions noted in Table 1, indeed gave a TOR of 0.3 s⁻¹, about two orders of magnitude higher than the rate seen on the 2 nm Pt/SBA-15 catalyst, and may represent the limiting rate on Pt for NO oxidation reaction.

Table 1. Summary of NO Oxidation reaction kinetics on Pt catalysts

Catalyst	Pt size/nm		Ea/ kJ mol ⁻¹	NO order	O ₂ order	NO ₂ order	TOR*/ 10 ⁻³ s ⁻¹
	Titration	TEM					
Pt/Al ₂ O ₃	2.6	2.4	83	1.1	1.0	-0.9	0.7
Pt/Al ₂ O ₃	6.7	3.8	81	1.1	0.7	-0.9	3
Pt/SBA-15	1.9	-	74	1.0	1.0	-0.8	2.9
Pt/SBA-15	3.8	4.2	76	1.1	0.7	-1.0	77
Pt/SBA-15	9.1	9.1	74	0.9	0.6	-1.1	140

*TOR at 250°C, 300 ppm NO, 170 ppm NO₂, 10% O₂, balance N₂

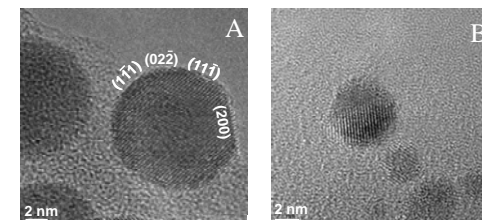


Figure 1. High resolution TEM images showing representative Pt clusters on (A) 9.1 nm Pt/SBA-15, (B) 3.8 nm Pt/SBA-15

References

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