



# Insight into the suppressive effects of sulphony species on the NO–D<sub>2</sub> reaction on platinum surfaces: A surface science approach

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## ABSTRACT

The influence of S<sup>18</sup>O<sub>2</sub>, O<sub>2</sub> and their reaction products, surface sulphony species, on NO–D<sub>2</sub> reactions on the surface of stepped Pt(332) was studied. Oxidation of S<sup>18</sup>O<sub>2</sub> by O<sub>2</sub> proceeds to a very slight extent on Pt(332), taking place as the surface temperature is increased to 300 K and higher. The oxidation reaction gives rise to surface sulphony species (S<sup>18</sup>O<sub>x</sub>, x>2) that persist on the surface up to 500 K but desorb completely at 600 K. The surface sulphony species desorb mainly as S<sup>18</sup>O<sub>2</sub> (predominantly) and S<sup>18</sup>O<sub>3</sub>. On the other hand, co-adsorbed S<sup>18</sup>O<sub>2</sub> molecules render the desorption of O atoms, (which otherwise occurs at 700 K and higher from a clean Pt(332) surface), undetectable. Such oxygen desorption reappears and gains a considerable intensity as the sulphony species covered Pt(332) surface was further exposed to NO molecules. However, NO dissociation is suppressed in the presence of S<sup>18</sup>O<sub>2</sub>, O atoms and surface sulphony species; the suppressive effect from O atoms and surface sulphony species is much more significant than that from S<sup>18</sup>O<sub>2</sub>. No N<sub>2</sub> desorption resulting from NO dissociation is detected under some conditions.

The suppressive effect exerted by O atoms and surface sulphony species also holds for the NO–D reaction, but is highly dependent on the exposures of O<sub>2</sub> and S<sup>18</sup>O<sub>2</sub>. The NO–D reaction is not suppressed on the Pt(332) surface which has been pre-exposed to 0.4 L O<sub>2</sub> at 90 K and then annealed to 200 K, due to rapid removal of O atoms (including those from NO dissociation) as a result of the facile reaction between O and D. On the Pt(332) surface, pre-exposed to O<sub>2</sub> and S<sup>18</sup>O<sub>2</sub> and then annealed to 400 K, the efficiency of the NO–D reaction (manifested by N<sub>2</sub> production) is obviously lower than that on a clean surface (without surface sulphony species); however, the suppressive effect becomes significant only as the exposures of O<sub>2</sub> and S<sup>18</sup>O<sub>2</sub> are ≥0.4 L.

Surface sulphony species-induced suppression of the NO–D reaction on Pt(332) mainly results from NO–Pt interactions being weakened and a lack of D atom supply at the surface temperatures where NO dissociation becomes significant. D<sub>2</sub> desorption from the Pt(332) surface finishes at ~350 K, at which temperature surface sulphony species and O atoms persist and NO dissociation just becomes appreciable. As such, the NO–D reaction evolves into NO dissociation on the surface sulphony species covered Pt(332).

The present results also suggest that the site blocking effect of surface sulphony species and O atoms does not evidently contribute to their suppression of NO–D reaction.

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## 1. Introduction

Poisoning by sulfur oxides on the catalytic reduction of NO, regardless of the nature of reductants, has been one of the major problems in mitigating the emission of exhausts, especially from diesel powered engines. It is generally acknowledged that the presence of sulfur oxides inevitably leads to the efficiency of NO reduction being reduced [1–3]. However, more and more recent studies have discovered that under lean-burn (oxygen-rich) reaction conditions, the poisoning effect exerted by SO<sub>2</sub> on NO reduction is not

observable and under certain circumstances, coexistence of SO<sub>2</sub> and O<sub>2</sub> promotes the reduction of NO by CO (or H<sub>2</sub>) [4–9]. As such, reduction of NO in the presence of co-existing SO<sub>2</sub> and O<sub>2</sub> is considered a potential way to simultaneously remove NO and SO<sub>2</sub> from exhausts (SO<sub>2</sub> is also a harmful resource to the environment) [4–9]. The O<sub>2</sub> induced mitigation of the SO<sub>2</sub> poisoning effect was assumed to be a result of adsorbed SO<sub>2</sub> molecules being oxidized by O<sub>2</sub> [8,9]. This oxidation reaction scavenges SO<sub>2</sub> molecules, which are pre-adsorbed on the metal surface, leading to the active sites on the metal surface becoming available for the adsorption of NO and CO/or H. Nevertheless, this question is still open for further investigation, because the related studies were carried out on multi-component catalysts that are composed of both noble metal and metal oxides. Evidently, sulfur oxide molecules can be adsorbed both on noble metals and on metal oxides (actually react with them), rendering it

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difficult to delineate under reaction atmosphere: where sulfur oxide molecules are adsorbed, how sulfur oxide molecules interact with other kinds of reactant molecules (NO, CO (or H<sub>2</sub>) and O<sub>2</sub>) and how adsorption of NO is affected by sulfur oxide related species remain valid questions.

With regard to these questions, this study, employing surface science technology, attempts to describe the NO–H<sub>2</sub> reaction in the presence of both SO<sub>2</sub> and O<sub>2</sub> on the surface of stepped Pt(332) at a molecular level. Pt(332) is a stepped surface with a 6(111) × (111) structure. The (111) plane predominates in practical metal-containing catalysts for deNOx because of its low surface energy. The surface can therefore serve as a model for simulating the surface of true catalysts. So far, to our knowledge, there is no surface science study of the effect of SOx on NOx reduction. A considerable amount of disagreement also exists within the literatures on the surface chemistry of SOx, NOx and even O<sub>2</sub> on stepped Pt surfaces. While this makes the “surface science” study of the NO–SO<sub>2</sub>–O<sub>2</sub>–H<sub>2</sub> reaction a system that is relatively more complex than other systems related to NO reduction, this also makes this topic a worthwhile area of study. Special attention is paid to clarifying: (1) how oxidation of SO<sub>2</sub> proceeds on a stepped Pt surface; (2) how adsorption of NO molecules on a stepped Pt surface is affected by surface sulphy species that result from the reaction between SO<sub>2</sub> and O<sub>2</sub> at various temperatures; (3) how the efficiency of NO–H (H<sub>2</sub> is dissociatively adsorbed on Pt surfaces) reaction is changed in the presence of SO<sub>2</sub> or surface sulphy species; and consequently, (4) providing an explanation for the O<sub>2</sub> induced mitigation of SO<sub>2</sub> poisoning effects on the NO–H<sub>2</sub> reaction.

## 2. Experiment

All the experiments were carried out in a standard UHV system described elsewhere [10,11]. Briefly, a stainless steel UHV chamber is pumped by a turbo-molecular pump, which is in turn backed by an oil diffusion pump. A base pressure of  $1 \times 10^{-10}$  Torr is routinely attained. The chamber is fitted with potassium chloride windows for grazing incidence surface IR spectroscopy.

The Pt(332) crystal was cleaned by repeated cycles of Ar<sup>+</sup> ion bombardment and oxidation. The final cleanliness was judged by the CO infra red spectrum, which is sensitive to the cleanliness and the state of perfection of the surface [12,13]. IR spectra were obtained in a single reflection geometry at 7° grazing incidence by using a Digilab FTS 7000 spectrometer. 1000 scans, which take less than 2 min, were coadded at a resolution of 8 cm<sup>-1</sup>. A narrow band mercury cadmium telluride (MCT) detector was used throughout, with a cut-off around 1000 cm<sup>-1</sup>. Although some IR data is shown extending down to 800 cm<sup>-1</sup>, the steep spectral function (cut-off) in the frequency region 800–950 cm<sup>-1</sup> makes the data unreliable below about 950 cm<sup>-1</sup>.

S<sup>18</sup>O<sub>2</sub>, O<sub>2</sub>, D<sub>2</sub> and NO were introduced into the chamber by backfilling. The highly efficient pumping system can restore the background to workable levels quickly. Thermal desorption spectra were achieved by resistively heating the crystal at a linear rate of 4 K/s.

Thermal desorption data for any single species are internally consistent in terms of sensitivity and scale. However, absolute coverages of species are not known, and relative coverages of species by comparison of thermal desorption areas are not attempted here as there are too many unknown scaling factors.

## 3. Results and discussions

### 3.1. S<sup>18</sup>O<sub>2</sub>–<sup>16</sup>O<sub>2</sub> reactions

#### 3.1.1. IR spectra

S<sup>18</sup>O<sub>2</sub>–<sup>16</sup>O<sub>2</sub> reactions on the surface of Pt(332) are interrogated using IR spectroscopy. The Pt(332), exposed at 90 K to 2.4 L <sup>16</sup>O<sub>2</sub> and then 1.6 L S<sup>18</sup>O<sub>2</sub>, was annealed to various target temperatures. IR spectra were taken after cooling the crystal down to 90 K. There is no

discernable spectral change following anneals to temperatures between 200 K and 250 K. At 300 K, two peaks appear at ~1305 cm<sup>-1</sup> and 1345 cm<sup>-1</sup> respectively. Both peaks achieve higher intensities at 400 K, which persist to 500 K, as shown in Fig. 1. These two peaks can be assigned to the asymmetric vibrational modes of SO<sub>4</sub>(ads.) species as a result of an isotope effect, i.e., the 1305 cm<sup>-1</sup> peak is associated with S<sup>18</sup>O bonds and the 1345 cm<sup>-1</sup> peak to S<sup>16</sup>O bonds, respectively [14]. Moreover, in this annealing temperature range (400–500 K), another two peaks, which have relatively weaker intensities than those at ~1305 cm<sup>-1</sup> and 1345 cm<sup>-1</sup>, appear at ~1210 cm<sup>-1</sup> and 1250 cm<sup>-1</sup>, respectively. The ~1210 cm<sup>-1</sup> peak was observed in the S<sup>18</sup>O<sub>2</sub> spectrum (without co-adsorbates) between 90 K and 300 K; the 1250 cm<sup>-1</sup> peak was observed both in the S<sup>16</sup>O<sub>2</sub> spectrum (without co-adsorbates) and in the spectrum of 100 L <sup>16</sup>O<sub>2</sub> + 50 L S<sup>16</sup>O<sub>2</sub> co-adsorbate that is annealed to 270 K on Pt(111) [14–16]. Both peaks can be assigned to the asymmetric vibrational modes of surface sulphy species (SO<sub>x</sub>, x > 2), again due to an isotope effect. None of the peaks are detectable when the annealing temperature is increased to 600 K.

So far, there are few vibrational spectroscopic studies of the surface chemistry of sulfur oxide species on metal single crystals [14–16]. In one study, SO<sub>2</sub>–metal complex structures were proposed by White et al. [15]. The existing studies have not achieved consensus on the assignments of the IR peaks to characteristic vibrational modes of surface sulphy species (SO<sub>x</sub>, 4 ≥ x ≥ 1) because the frequencies of these species overlap significantly. To this end, this paper is not engaged in identifying the specific surface sulphy species either. On the other hand, the existing data have unambiguously confirmed that SO<sub>2</sub> is easily dissociated and oxidized by O<sub>2</sub> on Pt surfaces to produce surface sulphy species (SO<sub>x</sub>, x ≥ 2), which desorb as SO<sub>2</sub> (predominantly) and SO<sub>3</sub>. The present IR results in Fig. 1 are fairly consistent with previous studies, i.e., on the Pt(332) surface, S<sup>18</sup>O<sub>2</sub> is oxidized to sulphy species (SO<sub>x</sub>, x ≥ 2) by <sup>16</sup>O<sub>2</sub> when the surface temperature is increased to 300 K. The sulphy species can remain on the surface at temperatures up to 500 K but desorb completely at 600 K. Noticeably, the extent of dissociation and oxidation of SO<sub>2</sub> on Pt surfaces has never been qualified before. This is to be addressed in the next part.

### 3.2. Thermal desorption spectra

Fig. 2(a) shows thermal desorption spectra of various species that may be produced from the co-adsorbate, for which 0.8 L O<sub>2</sub> was pre-

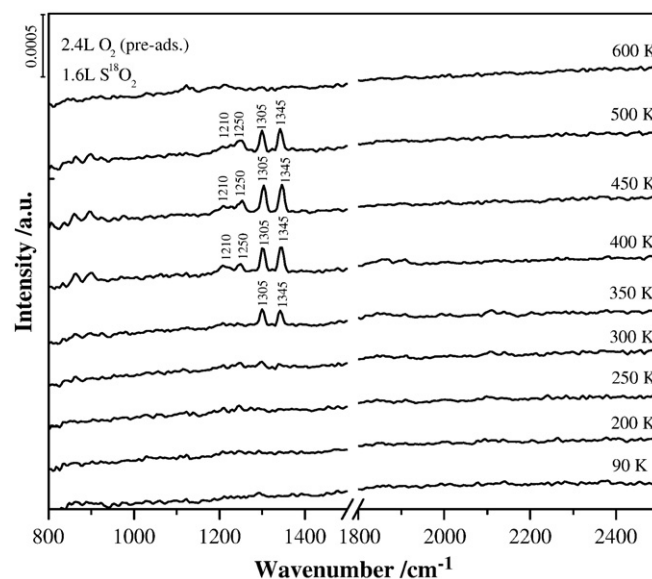


Fig. 1. IR spectra following anneals of the Pt(332), exposed to 2.4 L O<sub>2</sub> and then 1.6 L S<sup>18</sup>O<sub>2</sub> at 90 K, to various target temperatures. Spectra were always recorded after cooling the crystal down to 90 K after each anneal.

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