

***In situ* FTIR and TPD studies on the interaction of NO_x with CeO₂**

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Introduction

Current and upcoming environmental policy in the developed countries is imposing significant decreases in NO_x emissions from combustion processes such as vehicle engines. Traditional three-way catalysts are ineffective under O₂ rich atmosphere lean-burn engines operate under. Lean NO_x trap (LNT) technology developed for treating lean automotive exhaust emission is considered one of the most promising NO_x reduction technologies.

CeO₂ is an important component of currently used three-way catalysts due to its high oxygen storage capacity and stability to maintaining high metal dispersion on the support [1] in LNT catalysts. In addition, the role of CeO₂ in improving the sulfur resistance of LNT catalysts has been well established. The explanation for this is that SO₂ can be stored as cerium sulfate which may prevent the formation of a more stable sulfur compound by interacting with storage component (BaO) [2]. The addition of CeO₂ to several catalyst systems proved to be effective in improving the performance of these catalysts [3,4]. In this study, the interaction of NO and NO₂ with oxidized and reduced, high surface area CeO₂ were investigated.

Materials and Methods

The CeO₂ catalyst used in this study was prepared using a solution-based hydrothermal method. The sample was treated under different gas environment (oxidized with O₂, reduced with H₂) to show different initial states. Stepwise adsorption of NO or NO₂ was performed on the catalysts at room temperature. Upon completion of adsorption experiments, the IR cell was evacuated at 300 K and TPD experiments were carried out from 300–973 K at a linear heating rate of 0.2 K/s. Infrared spectra were obtained during adsorption and desorption process in transmission mode on a Nicolet Magna-IR Spectrometer (model 750) at a spectral resolution of 4 cm⁻¹. Gas phase components were monitored by a UTI 100C mass spectrometer connected to the IR cell through a gate valve.

Results and Discussion

A series of infrared spectra collected during heating the sample under vacuum after NO adsorption at room temperature on oxidized CeO₂ is shown in Fig. 1. With increasing temperature, the initially weak peaks at 1629, 1611, 1462, and 1399 cm⁻¹ assigned to different types of nitrate species decreased. In the mean time, the peaks at 1265, 1167, 1103, and 823 cm⁻¹ assigned to different types of nitrite species also decreased progressively. At around 720K, these features totally disappeared. However, these nitrite species are not just desorbed from the catalyst. Part of them was transformed into nitrates during the heating process indicating that more oxygen species were becoming available to interact with nitrite. This transformation was evidenced by the increase of the nitrate peaks at 1548, 1516, 1424, 1231, and 992 cm⁻¹. These nitrate species are very stable and tend to desorb at very high temperature.

TPD profile of adsorbed species formed after NO adsorption on the same oxidized CeO₂ is shown in Fig. 2. The TPD results are consistent with IR results. Three stages of desorption occurred with increasing temperature. The nitrate species formed from initial NO adsorption at room temperature is the one disappeared first with increasing temperature. These initially formed nitrate may be the result of direct interaction between NO and the oxygen species associated with Ce(IV) centers. Apparently, these species are weakly bonded. They desorbed at very low temperatures characterized by the first peak at around 400 K. However, the nitrates that formed during the heating are very stable. As shown in the TPD profile, the highest desorption rate for these species is at 850 K shown as the third peak in the figure. Desorption of these species accompanied by large extent of O₂ desorption. The formation of these species may be from the interaction of nitrite with the oxygen species in the bulk. The second peak is assigned to desorption of nitrite species. The tail of the peak ends at around 740 K, which agrees with the fully disappearance of nitrite species peaks in IR results. The results from the study indicated that there were two different path ways for nitrate formation during the interaction of NO with oxidized CeO₂. As a result, two types of nitrates were formed. One is unstable and the other ones are bonded tightly with the adsorbed center.

Significance

Current study will provide significant insight on the reaction mechanism of NO_x reduction reaction on the CeO₂ promoted NSR catalysts.

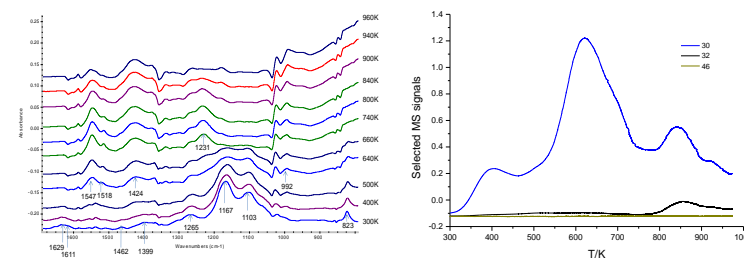


Figure 1. Evolution of adsorbed species of NO adsorption on oxidized CeO₂ with temperature.

Figure 2. TPD of adsorbed species of NO adsorption on oxidized CeO₂ with temperature.

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