

The Effect of CO₂ on NO_x Storage/Reduction Catalysts

Christelle Verrier¹, Ja Hun Kwak¹, Do Heui Kim¹, Chundi Cao, Charles H.F. Peden¹,
Guillaume Clet², and János Szanyi^{1*}

¹Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, WA,
99352, USA

²Laboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, Caen,
France

*janos.szanyi@pnl.gov

Introduction

BaO-based NO_x storage-reduction (NSR) catalysts have been considered as leading candidates for treating automotive exhaust gases of lean burn engines [1,2]. Although, these catalysts have shown high efficiencies for NO_x reduction, their performances were negatively influenced by the presence of other gas constituents in the exhaust stream (e.g. H₂O, CO_x, SO_x). Despite the extensive studies on these NSR catalysts, there are several issues related to the effect of CO₂ [3,4] that have not been understood unambiguously (nature of carbonates species formed, the mechanism of carbonate species, the conversion of nitrates to carbonates and visa versa, the stabilities of carbonate species). In this contribution we will present results on the effect of CO₂ on the decomposition of nitrates from a NO₂-saturated 20 wt% BaO/γ-Al₂O₃ sample using TPD, TR-XRD and Raman techniques.

Materials and Methods

A 20 wt% BaO/γ-Al₂O₃ sample was prepared by the incipient wetness method using aqueous Ba(NO₃)₂ solution and a 200 m²/g specific surface γ-Al₂O₃ support material. The NO₂ uptake and TPD experiments were conducted in a fixed bed quartz reactor under continuous flow. The catalyst is first saturated with NO₂ at 293 K using a NO₂ (5000 ppm) on a Ar flow on 100 mg of 773 K calcined sample. After nitration TPD was performed from room temperature to 973 K under CO₂-containing flow at 8 K/min heating rate. The evolution of NO_x species (NO and NO₂) were monitored with a chemiluminescence NO_x analyzer. The Raman measurements were carried out at LCS ENSICAEN, using a LABRAM spectrometer equipped with a LINKAM CCR 1000 in situ Raman cell. TR-XRD studies were carried out at line X7B at Brookhaven National Laboratory.

Results and Discussion

The effect of CO₂ on the properties of a 20 wt% BaO/γ-Al₂O₃ NO_x storage material was investigated in two systems: in a flow through reactor where the NO₂ uptake and NO_x release properties were studied, and in an *in situ* Raman cell where the nature of the adsorbed species were investigated. Prior to TPD experiments the 20 wt% BaO/γ-Al₂O₃ sample was saturated with NO₂ at room temperature. TPD was then carried out in gas streams containing CO₂ in varying amounts. The addition of CO₂ to the Ar carrier gas resulted in the modification of the nitrate decomposition pattern, i.e. a new desorption feature appeared at a temperature that is higher than the one we have seen for surface nitrate decomposition, but lower than the one of bulk nitrates. The intensity of the original surface nitrate decomposition peak was not affected by the presence of CO₂ in the purge gas, while that of the bulk nitrate decreased.

Interestingly, this new desorption state represented NO₂ desorption. The results of these TPD experiments are summarized in Fig. 1. Note that the NO_x that was desorbed as NO₂ increased with the increase in the CO₂ concentration concomitant with the decrease in the amount of NO desorbed. A series of Raman spectra collected during a TPD experiment in 25 % CO₂/N₂ gas mixture following the room temperature NO₂ saturation of the sample is shown in Fig. 2. The formation of BaCO₃ sets in after most of the nitrates are decomposed.

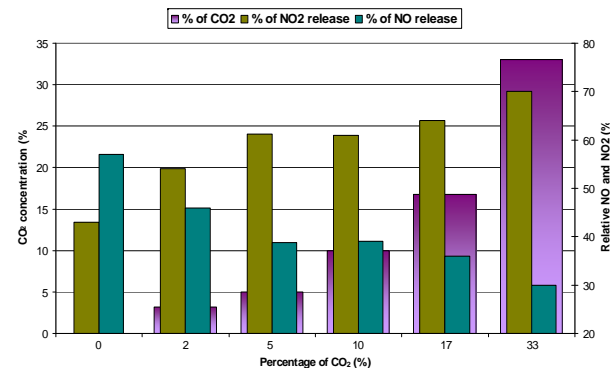
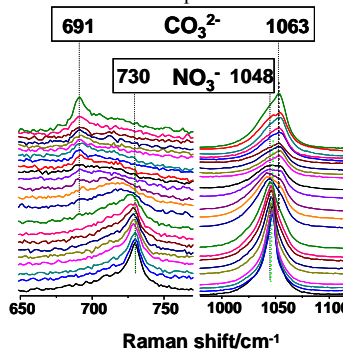


Figure 1. Summary of the relative amount of NO and NO₂ (in %) released during TPD under CO₂ flow on pre-nitrated BaO(20 wt%)/γ-Al₂O₃.



There is no evidence of gradual replacement of nitrates by carbonates. Interestingly, nitrates can form on this high temperature-carbonated sample even at room temperature, suggesting the coexistence of the carbonate and nitrate phases. In this presentation we will discuss the details of the CO₂ effect on the NO_x uptake and release on BaO/γ-Al₂O₃ NO_x storage materials, and its consequences to the operation of real NSR catalysts.

Figure 2. Raman spectra collected during TPD on a NO₂-saturated BaO(20 wt%)/γ-Al₂O₃ sample in 25 % CO₂/N₂ flow.

Significance

The fundamental understanding of the effect of CO₂ on the NO_x uptake and release properties of NSR

catalysts is critical for the design of better catalyst systems

References

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