

NO_x storage over alkaline earth oxides supported on γ -Al₂O₃
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Introduction

Study of NO_x storage/release behavior is a key to NO_x trap research in order to improve the NO_x conversion and also to enhance our understanding of the mechanism of these reactions. Previous studies have demonstrated the importance of the storage material [1]. Studies in our laboratory have shown that nitration of barium containing catalysts results in the formation of a Ba(NO₃)₂ monolayer strongly interacting with the alumina support [2]. Furthermore, variation in the NO₂/NO ratio with Ba loading was also reported. In this work we investigated the behavior of four different alkaline earth oxides (BaO, CaO, MgO and SrO) on an alumina support. As the commercial catalysts (Toyota) contain about 20% barium oxide supported on Al₂O₃, we paid special attention to prepare these mixed oxide systems containing equimolar alkaline earth oxides.

Materials and Methods

The alkaline earth oxides on alumina catalysts used in this work, were all synthesized by the incipient wetness method. The loading was controlled to have the same molar ratio for all the alkaline earth oxides based on 20% BaO/Al₂O₃. The γ -alumina used as support has ~200 m²/g surface area after calcination at 500°C under air flow for 2 hours. Experiments were performed in an *in situ* IR cell and in a flow reactor. Surface species were analyzed by infrared spectroscopy using a Magna Nicolet IR 750 spectrometer in transmission mode. TPD experiments following sample saturation with NO₂ were conducted in both the *in situ* system, and the flow reactor. During the TPD runs gases were analyzed by a UTI 100C mass spectrometer (*in situ* system), and by a fluorescent NO_x analyzer (flow reactor). The oxides were first pre-heated at 973 K to eliminate impurities. NO₂ saturation was carried out at room temperature, followed by evacuation.

Results and Discussion

After the initial small doses of NO₂ on all of the alkaline earth oxides, the infrared spectra show bands that we attribute to nitrite species, which are followed by, at higher doses, the appearance of features characteristic of different types of nitrate species.

The IR spectra of Fig. 1 show that after adsorption of NO₂ and subsequent evacuation, two sets of features are present: the first one include bands located around 1650 and 1250 cm⁻¹ that we attribute to surface nitrate species on alkaline earth oxides. The second ones (bands centered at ~ 1450 - 1520 cm⁻¹) can be assigned to bulk nitrates. There is a clear correlation between the nature of the nitrate species formed, and the basicity of the alkaline earth oxide. With increasing basicity the intensities of the IR features representing bulk nitrates (~1430-1500 cm⁻¹) increase, and concomitantly, that of the surface nitrates decrease. Practically no bulk nitrate features are seen on MgO/ γ -Al₂O₃, only those of surface nitrates, similarly to the alumina support. As the basicity of the alkali metal increases the intensities of the bulk nitrate bands increase. The TPD results shown in Fig. 2 (obtained in the flow reaction) confirm the trends observed in the IR experiments. For the MgO/Al₂O₃ system only

an NO₂ desorption feature is seen, in concert with the decomposition of surface nitrates that release only NO₂. For the other three alkaline earth oxides, both NO₂ and NO desorption features are observed, supporting the previous observation that in these systems both surface and bulk nitrates form upon their exposure to NO₂. Furthermore, the ratio of surface-to-bulk nitrates (integrated intensity ratio of the NO₂ and NO desorption features) decrease going from CaO to BaO.

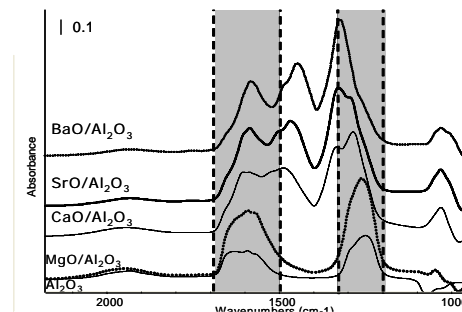


Fig. 1. Comparison of IR spectra from Al₂O₃ and alkaline earth oxides supported on alumina (CaO/Al₂O₃, BaO/Al₂O₃, SrO/Al₂O₃, MgO/Al₂O₃) after NO₂ adsorption at room temperature.

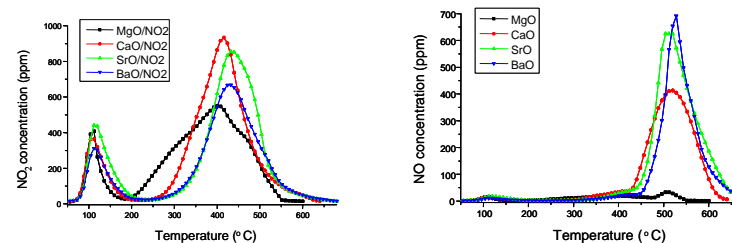


Fig. 2. TPD spectra from CaO/Al₂O₃, BaO/Al₂O₃, SrO/Al₂O₃ and MgO/Al₂O₃ after NO₂ saturation at 300K.

Significance

The result presented here demonstrate how the surface to bulk nitrate ratio over alkaline earth oxides changes with basicity, and that can have significant implication on the choice of material used in practical applications.

References

1. Szanyi, J., Kwak, J.H., Hanson, J., Wang, C. and Peden, C.F., *J. Phys. Chem. B* 109, 7339 (2005).
2. Szanyi, J., Kwak, J.H., Kim, D.H., Burton, S.D. and Peden, C.F., *J. Phys. Chem. B* 109, 27 (2005).