Thermal Stability and Structure of the Fe-Ba/γ-Al_2O_3 Mixed-Oxide Systems as NO_x Storage Materials

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Introduction

Over the past several years, the global environmental protection efforts resulted in stringent emission legislation regarding NO_x emissions originating from stationary as well as mobile sources. Among the variety of approaches, the NO_x storage-reduction (NSR) technology[1] is one of the most promising catalyst technologies that are capable of reducing the NO_x in excess oxygen. The contradictory results from numerous studies[2,3] indicated that the phase composition and the preparation method have a significant effect on the sulfur tolerance and on the interaction between the active storage (BaO) and the reduction (Pt) component in the NSR Pt-Ba/γ-Al_2O_3 catalytic system containing iron. Therefore in the current study the effect of introducing of Fe containing component on the structural and the morphological alterations and the thermal stability of the nitrates during heat treatment of freshly prepared Ba/Fe/γ-Al_2O_3 samples, which can be viewed as model systems that imitate realistic model NO_x storage materials, was established.

Materials and Methods

A series of Ba, Fe and Ba-Fe containing mixed oxide samples were synthesized by conventional incipient wetness impregnation of γ-Al_2O_3. The influence of Fe (5 - 10 wt. % Fe) and Ba (8 - 20 wt. % BaO) components on the nature of the crystallographic phases, thermal stability and the dispersion of the formed mixed-oxide (or nitrate) domains was investigated in the temperature interval of 423 – 1273 K. Synthesized nitrate storage materials were analyzed in detail by means of X-ray diffraction (XRD), Raman spectroscopy (RS), Scanning Electron Microscopy (SEM) and Energy Dispersive X- ray (EDX) analysis.

Results and Discussion

Selected Raman spectroscopic results presented in Fig. 1 showed that the presence of 5 wt. % Fe (mainly in the form of α-Fe_2O_3, hematite) in the Ba-Fe/γ-Al_2O_3 system results in the formation of thermally stable, bulk-like $Ba(NO_3)_2$ domains on the surface. The decomposition temperature of these nitrates is about 250 K higher than that of the Ba/γ-Al_2O_3 counterpart which lacks Fe. Above 1073 K, the existence of α-Fe_2O_3 in the Fe/γ-Al_2O_3 system facilitates the γ-Al_2O_3 → α-Al_2O_3 phase transformation by decreasing the transition temperature.

The XRD studies indicated that in the Ba/Fe/γ-Al_2O_3 system, the crystallinity of the formed α-Al_2O_3 phase is lowered due to the presence of the Ba component, particularly for high Ba loadings. Fe was also found to suppress the $BaAl_2O_4$ formation to a certain extent in the Ba/Fe/γ-Al_2O_3 system at elevated temperatures. Morphological changes and alterations of the elemental distributions as a function of thermal treatments and compositional variations were also qualitatively investigated using a combination of SEM and EDX - techniques.

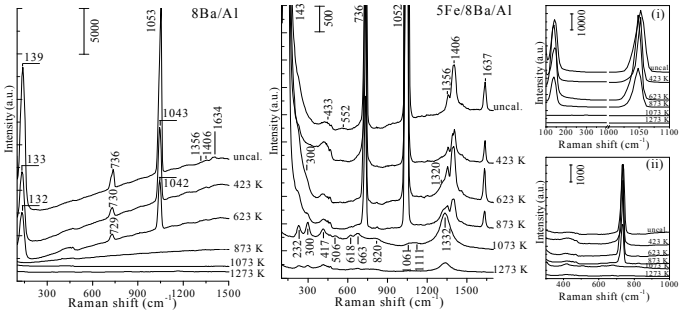

Figure 1. Temperature dependent ex-situ Raman spectra corresponding to the calcined (423 - 1273 K) and uncalcined Ba/Al with 8 wt. % BaO loading and Fe/Ba/Al mixed oxide NO_x-storage materials with 5 wt. % Fe and 8 wt. % BaO loadings.

Fig. 2 (a, b and c) presents a set of selected representative SEM-EDX of the 8Ba/Al and 5Fe/(8 or 20BaO)/γ-Al_2O_3 samples calcined at 623 K. It is apparent that increasing the Fe loading results in bigger Fe domains and leads to a slightly negative influence on the homogeneity of the surface distribution of the Ba domains.

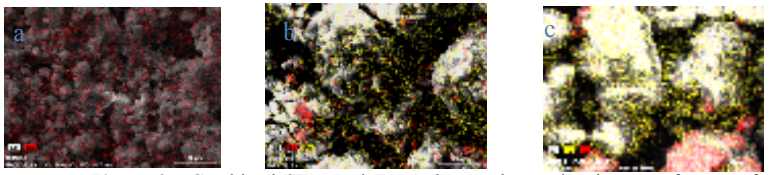

Figure 2. Combined SEM and EDX elemental mapping images of some of the representative Ba/Al, and Fe/Ba/Al samples thermally treated at 623 K. (a) 8Ba/Al, (b) 5Fe/8Ba/Al and (c) 5Fe/20Ba/Al.

On the basis of the structural and the spectroscopic results, it can be concluded that the crystallinity and the thermal stability of the Ba-nitrates on the support surface strongly depend on their interaction with the γ-alumina support material and the presence of Fe species as an additive into the Ba/Al system.

Acknowledgments

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