

Solid state ^{27}Al NMR study of $\text{BaO}/\text{Al}_2\text{O}_3$ catalysts: BaAl_2O_4 formation and decomposition

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Introduction

The control of NO_x (NO and NO_2) emissions from combustion processes, including those occurring in vehicle engines, remains a challenge particularly for systems operating at high air-to-fuel ratios (so-called 'lean' combustion). In the mid 1990's, alkali and alkaline earth oxide-based NO_x storage/reduction catalysts (especially Pt-Rh/ $\text{BaO}/\text{Al}_2\text{O}_3$) were developed by Toyota, and have shown promising activities for lean- NO_x reduction. Although there are extensive studies on the NO_x storage/reduction mechanism, a fundamental question still remains concerning which barium phases are most favorable for storing and releasing NO_x . It has been reported that BaO and Al_2O_3 react at high temperatures ($> 800^\circ\text{C}$) to form a less active aluminate phase, BaAl_2O_4 . We have also reported the effects of thermal aging and H_2O treatment on the formation and decomposition of $\text{BaO}/\text{Al}_2\text{O}_3$ [1].

In this report, the results of an investigation on the formation and decomposition of a BaAl_2O_4 phase for $\text{BaO}(x)/\text{Al}_2\text{O}_3$ ($x = 8$ and 20 wt%) catalysts using XRD and solid state ^{27}Al MAS NMR are presented.

Experimental

The $\text{BaO}/\text{Al}_2\text{O}_3$ samples were prepared by the incipient wetness method, using $\text{Ba}(\text{NO}_3)_2$ solutions and γ -alumina to yield nominally 8 and 20 wt% BaO -containing materials. After impregnation, the catalysts were activated via calcination at 500°C in flowing air for 2h. To investigate the effects of high temperature treatments on the structure, calcinations at 1000°C were carried out in a muffle furnace for 10 h. Solid state ^{27}Al -NMR spectra were acquired on a Varian/Chemagnetic CMX Infinity 300 MHz instrument with a sample spinning rate of 5 kHz and 1 s recycle delay.

Results and Discussion

Figure 1 shows that BaAl_2O_4 formation was dependent upon the BaO loading. Curves (a) and (b) are solid state ^{27}Al -NMR spectra of γ - Al_2O_3 and BaAl_2O_4 standard samples (Aldrich, after 1000°C 10h treatment). The spectrum of the Al_2O_3 sample in Fig. 1(a) contains peaks at ~ 0 ppm and at ~ 60 ppm, which are typically assigned to octahedrally and tetrahedrally coordinated Al ions, respectively. The spectrum for the BaAl_2O_4 sample has a peak at ~ 70 ppm which has been assigned to aluminum species with tetragonal coordination in the BaAl_2O_4 phase. Spectra (c) and (d) were obtained after calcination at 1000°C for 10h of the 8 and 20% $\text{BaO}/\text{Al}_2\text{O}_3$ samples, respectively. The spectrum of the 20% $\text{BaO}/\text{Al}_2\text{O}_3$ sample clearly shows the presence of a significant amount of BaAl_2O_4 after the high temperature calcination, while that of the 8% $\text{BaO}/\text{Al}_2\text{O}_3$ sample displayed the same features as the original alumina. These results are consistent with our previous reports [2] which showed that a surface (monolayer) BaO phase is quite stable against thermal aging and does not form a crystalline BaAl_2O_4 phase upon high temperature calcination.

After the formation of BaAl_2O_4 on the 20 wt.% sample by high temperature thermal treatment, we investigated the phase changes of the resultant BaAl_2O_4 material by NO_2 and/or

H_2O adsorption. NO_2 adsorption does not result in any change in either the ^{27}Al -NMR or XRD spectra. However, upon water adsorption on 20% $\text{BaO}/\text{Al}_2\text{O}_3$ at room temperature, all of the aluminum species from the BaAl_2O_4 phase disappear and a new species, $\text{Al}(\text{OH})_4^-$, forms, displaying a feature in the NMR spectrum at 79 ppm [3]. These results were confirmed by water treatment of the standard BaAl_2O_4 material (Aldrich). H_2O treatment of BaAl_2O_4 at RT results in the formation of tetrahedral and octahedral aluminum species, as well as $\text{Al}(\text{OH})_4^-$. The development of tetrahedral and octahedral aluminum peaks prove the formation of alumina as a result of water-induced decomposition of BaAl_2O_4 . The $\text{Al}(\text{OH})_4^-$ species disappear readily when the sample is dried in an oven at 120°C and the Ba-containing samples before the BaAl_2O_4 formation by high temperature thermal treatment. These results clearly demonstrate the water-induced decomposition of BaAl_2O_4 into separate Al- and Ba-containing phases (BaO and/or $\text{Ba}(\text{OH})_2$).

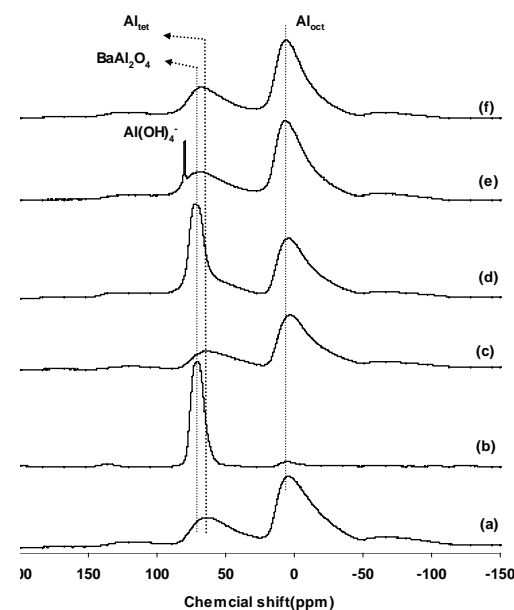


Fig.1 Solid state ^{27}Al -NMR spectra for: (a) alumina; (b) BaAl_2O_4 (1000°C , 10h); (c) 8% $\text{BaO}/\text{Al}_2\text{O}_3$ (1000°C , 10 h); (d) 20% $\text{BaO}/\text{Al}_2\text{O}_3$ (1000°C , 10 h); (e) H_2O treatment of (d); and (f) 120°C dry for (e).

Significance

The results of this solid state ^{27}Al NMR study clearly show the formation and decomposition of a BaAl_2O_4 phase which can result in the thermal deactivation of NO_x storage-reduction catalyst.

References

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3. D.H. Kim, J.H. Kwak, J. Szanyi, and C.H.F. Peden, *Appl. Catal. B in press*.