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Letter to Editor

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In the recent article by Szmigiel and co-workers [1], the authors reported results in the ammonia synthesis using the barium-promoted ruthenium catalysts supported on boron nitride. They attributed the observed enhancement in the ammonia synthesis rates of the catalysts with modifying the supports at high temperature to the decrease of boron oxide, which might act as a deactivation agent. The authors invoked their X-ray photoelectron spectroscopic (XPS) data to conclude that the drop in an oxygen content in support materials. However, the explanation is unsatisfactory since the oxygen content reduced slightly but the rates increase significantly, for example, If HCV was heated at 700–800 °C for 120 h, the oxygen content decreased from 3.8 to 2.7 at%, while the rate of HCV_{NH_3} supported ruthenium catalyst increased by 60%.

The authors pointed that hexagonal boron nitride was the only detectable phase in all support materials according to the XRD patterns. However, BNS and BNS_{NH_3} might be identified as turbostratic BN, According to the results of Thomas *et al*. [2] and Pease *et al*. [3], the Bragg angles of (002) and (10) reflections in XRD pattern of the two-dimensional structure turbostratic BN are coincident with those of hexagonal boron nitride with three-dimensional crystal structures, but lacking of some types of reflections such as (102), (004). It is well known that heating the samples at high temperature would lead to the disordered boron nitride is converted to high ordered hexagonal BN [2–5].

The highly ordered graphitic structure might be responsible for the activity of the boron nitride supported ruthenium catalyst, which in good accordance with the results of Ru catalysts supported on active carbon [6–10]. There are few explanations the correlations between graphitization of support materials and activity, Song *et al*. [10] suggested that the growth of Ru on a graphite surface is epitaxial and has two orientations with the (0001) surface parallel to the graphite (0001) surface. Hansen *et al*. observed that the Ru crystals exhibited a hexagonal morphology *in situ* TEM studied of BN supported ruthenium catalysts [11].

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Therefore, the reported results of Szmigiel *et al*. [1] are more justifiably explained by the likely phase transition of boron nitride. When the support materials were modified by heating in ammonia, the disorder BN can be converted to highly ordered BN, as indicated by the sharpening of the (002) reflection in XRD diffraction pattern, thus the activity for ammonia synthesis was higher. The boron nitride transformation is promoted by the presence of boron oxide [2], thus the activity of BNS supported ruthenium catalyst increase more remarkably than that of HCV since the higher oxygen content of BNS. The phenomena that the activity increase as a result of the catalysts activation procedure also could be clarified by the influence of phase transition of boron nitride on the catalytic activity since the high pressure might be effective for transformation of turbostratic BN to hexagonal BN [12], thus activity of the catalyst was reduced with an ammonia rich mixture (10% NH_3 in H_2:N_2 = 3:1) flowing under high pressure of 90 bar higher than that pretreated in an ammonia free (H_2:N_2 = 3:1) gas under 1 bar.

Analyzing XRD patterns in the paper of Smigiel *et al*. more detailedly might be helpful to identifying the structure of boron nitride. Other characterizations such as high-resolution transmission electron microscopy (HRTEM) or scanning electro microcopy (SEM), which have been described previously [13,14], also could be used for helping to clarify the issue.

In summary, in addition to the conclusion that the high oxygen content due to the activity decrease, as proposed by Szmigiel *et al*., the effect of BN structure on the catalytic activity also is necessary to be considered. It may be possible to learn correlations between graphitization of the support materials and activity in detail since the BET surface areas of HCV with high-temperature treatment increased slightly.

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