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Response to Letter to the Editor

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Early studies of the Aika's group have shown [1] that the support is an integral component of the unpromoted ruthenium catalysts for ammonia synthesis. For instance, the TOF values of NH_3 synthesis for Ru/MgO or Ru/CaO proved to be several dozen times higher than TOFs determined for Ru/Al_2O_3 or Ru/AC [1]. Based on the kinetic experiments performed with Ru/C, $Ru/MgAl_2O_4$ and Si_3N_4, Jacobsen et al. [2] have suggested that the support plays a decisive role in controlling the morphology of the Ru crystals and, thereby, the number of super active B_5-type sites. It can not be excluded, therefore, that well crystallized boron nitride would be a more advantageous support for ruthenium than poorly organized BN, as suggested by the authors of the letter.

Compared to unpromoted systems, those promoted with barium are considerably more active in NH_3 synthesis. One can even say that the activity of ruthenium is dominated by the presence of the promoter [3–7]. Consequently, the differences in the surface-based reaction rates observed for the Ba-promoted catalysts deposited on various supports [8, 9], including our Ba–Ru/BN systems [10], were ascribed to different promotional effects of Ba. Clearly, the properties of the support material are assumed to control the distribution of the promoter between the ruthenium surface and the support surface [8] or, more generally, the coverages of ruthenium by the promoter species (promotion) and the support material or its component (site blocking) are dependent on the kind of the support [9, 10]. That is general philosophy of interpreting the correlations obtained for various ruthenium catalysts promoted with Ba.

To evaluate the alternative proposed by the authors of the letter (the proposal is addressed exclusively to the Ba–Ru/BN catalysts), a reference should be given to the XRD data characterizing the BN supports used in our studies [10] (see Fig. 1). To facilitate the discussion and to avoid misunderstanding, the form of Fig. 1 should precisely be the same as that presented in [10] and this has been done. It is clearly seen in Fig. 1 that all the BN materials exhibit a turbostratic structure. This was also stressed in [10]. It is seen as well that the structure of both starting nitrides (BNS and HCV) is fully resistant to overheating in an ammonia stream at 700–800 °C for 120 h. In contrast to what the authors of the letter claim, there is no reason to suppose that "disordered BN can be converted to highly ordered BN" when heating in NH_3. Such a conversion would result in the formation of new peaks that were characteristic for the 3D hexagonal structure of BN. This, however, was not the case (see Fig. 1). The sharpening of the (002) reflections in the patterns corresponding to the overheated specimens would indicate only that the thicknesses of the stacks increased. Close inspection of the (002) peaks demonstrates, however, that even such an effect was not observed – line broadening for the fresh material is identical to that overheated in ammonia, both for HCV and BNS (see HCV versus HCV_{NH_3} and BNS versus BNS_{NH_3}, respectively). As the changes in the BN structure are expected to be the stronger the higher the temperature, activation of the Ba–Ru/BN catalysts at 550 °C for 5 h (90 bar, ammonia rich H_2+N_2 mixture) certainly would not lead to noticeable structural changes of the BN support, as suggested by Lin et al. in their letter. To summarize, the concept proposed by the

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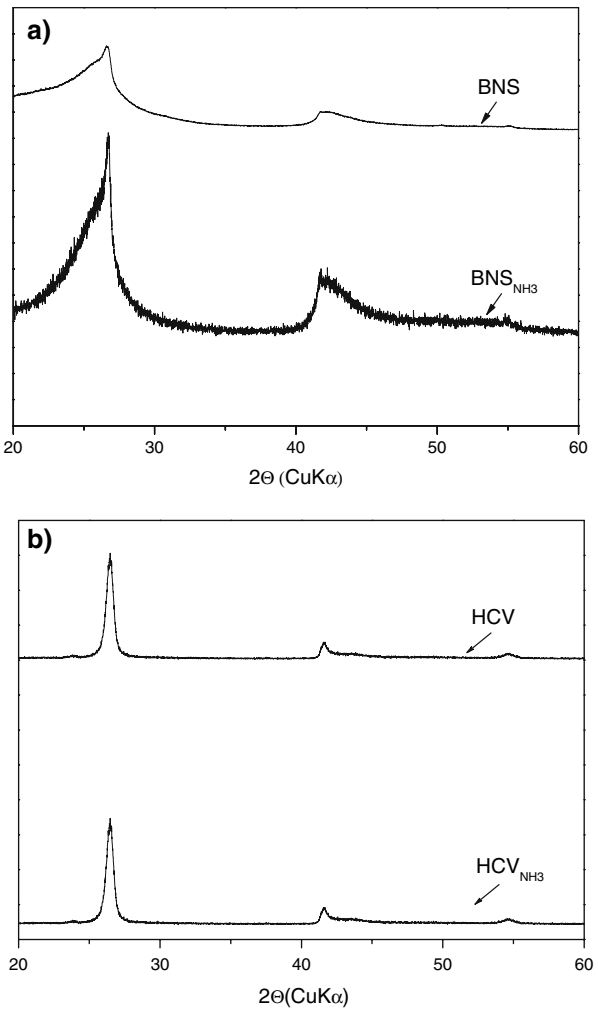

Fig. 1 XRD patterns of the boron nitride supports; (**a**) BNS, BNS_{NH_3}; (**b**) HCV, HCV_{NH_3}

Chinese group does not find support in our studies and should rather be rejected.

References

1. Aika K, Ohya A, Ozaki A, Inoue Y, Yasumori I (1985) J Catal 92:305
2. Jacobsen CJH, Dahl S, Hansen PL, Tornqvist E, Jansen L, Topsoe H, Prip DV, Moenshaug PB, Chorkendorff I (2000) J Mol Catal A: Chem 163:19
3. Kowalczyk Z, Krukowski M, Raróg-Pilecka W, Szmigiel D, Zieliński J (2003) Appl Catal A: Gen 248:67
4. Bielawa H, Hinrichsen O, Birkner A, Muhler M (2001) Angew Chemie Int Ed 40(6):1061
5. Szmigiel D, Bielawa H, Kurtz M, Hinrichsen O, Muhler M, Raróg W, Jodzis S, Kowalczyk Z, Znak L, Zieliński J (2002) J Catal 205:205
6. Fastrup B (1997) Catal Lett 48:111
7. Siporin SE, Davis RJ (2003) J Catal 222:315
8. Hansen TW, Hansen PL, Dahl S, Jacobsen CJH (2002) Catal Lett 84:7
9. Szmigiel D, Raróg-Pilecka W, Miskiewicz E, Gliński M, Kielak M, Kaszkur Z, Kowalczyk Z (2004) Appl Calal A Gen 273:105
10. Szmigiel D, Raróg-Pilecka W, Miskiewicz E, Maciejewska E, Kaszkur Z, Sobczak JW, Kowalczyk Z (2005) Catal Lett 100:79