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Comment

Comment on Weber et al. Mayenite-Based Electride C12A7e$^-$: A Reactivity and Stability Study. *Catalysts* 2021, *11*, 334

Yasunori Inoue [1], Masaaki Kitano [2] and Hideo Hosono [2,*]

[1] Catalyst Section, R & D Department, Tsubame-BHB Co., Ltd., 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan; y.inoue@tsubame-bhb.co.jp
[2] Materials Research Center for Element Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan; kitano.m.aa@m.titech.ac.jp
* Correspondence: hosono@mces.titech.ac.jp

In 2012, we reported that C12A7 electride (C12A7: e$^-$) significantly promotes the catalytic activity of Ru nanoparticles for ammonia synthesis through the electron donation from the C12A7: e$^-$ with a low work function (2.4 eV) to Ru [1]. Recently, Weber et al. [2] reported in this journal that the application of Ru/C12A7e$^-$ catalysts at the industrial scale is limited prospects due to irreversible hydride formation at high pressures >1 MPa. According to their study, the catalytic activity of Ru/C12A7: e$^-$ disappeared immediately above 1 MPa, which is totally different from our previous result [1]. Figure 1 summarizes the relevant data in [1,2]. Such a large difference may be caused by the difference in electron concentration (N_e) of C12A7: e$^-$ used. In [2], the plasma arc melting synthesized C12A7: e$^-$ (aluminum solid reductant) samples are of dark green color and the is N_e is explained to be in the range of 0.1 to 1.2 $\times$ 10^{21} cm^{-3}. As we reported in [3], the catalytic performance of Ru/C12A7: e$^-$ critically depends on the electron concentration (N_e) of C12A7: e$^-$, e.g., Ru/C12A7: e$^-$ with N_e > 1.0 $\times$ 10^{21} cm^{-3} exhibits an order of magnitude higher activity for ammonia synthesis than those with low N_e (<5.0 $\times$ 10^{20} cm^{-3}). We consider that the electron concentration of the plasma-synthesized C12A7: e$^-$ sample is obviously lower than 1.0 $\times$ 10^{21} cm^{-3}. Kammert et al. also prepared C12A7: e$^-$ by a similar method using aluminum as a solid reductant, and N_e of the obtained C12A7: e$^-$ was determined to be 4.0 $\times$ 10^{20} cm^{-3} by iodometric titration method [4]. Such an insufficient N_e is not effective for the promotion of Ru catalyst in ammonia synthesis. Green sample color means electron concentration does not reach 1 $\times$ 10^{21} cm^{-3} in our accumulated data. Quantitative relation between N_e and the peak position of absorption band due to electron trapped in the cages are already reported in [5]. We examined the application of the modified Ru/C12A7: e$^-$ catalysts in ammonia synthesis at high pressures up to 5 MPa. As shown in Figure 1, the ammonia synthesis activity of the modified Ru/C12A7: e$^-$ catalyst increases with reaction pressure above 3 MPa. Furthermore, the modified Ru/C12A7: e$^-$ catalyst exhibited excellent stability for almost 2 years at high pressure condition (5 MPa). Therefore, we demonstrate that the Ru/C12A7: e$^-$-based catalyst has great potential as a practical catalyst for ammonia synthesis.

Based on the above results, we disagree with the conclusions by Weber et al. that the application potential of C12A7 electride under industrially relevant conditions is limited. We would like to emphasize that the catalytic performance of Ru/C12A7: e$^-$ changes drastically by electronic structure of C12A7: e$^-$ controlled by N_e and Ru-support interface structure [6]. A comprehensive review on electrides and their applications focusing on catalyst for NH_3 synthesis was recently published [7]. We hope this review is helpful for understanding our concept and approach.

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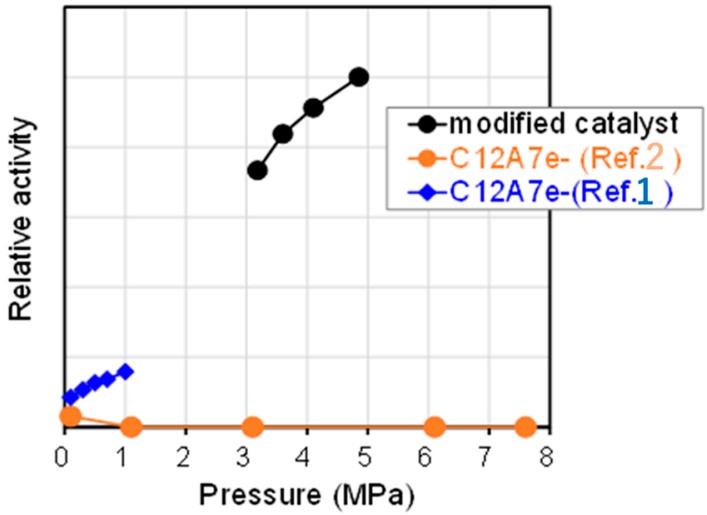

Figure 1. Relative activity of various Ru/C12A7: e^- catalysts as a function of reaction pressure. Temperature: ~360 °C.

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