Effect of boron promotion on coke formation during propane dehydrogenation over Pt/γ-Al2O3 catalysts

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Introduction:

Coke formation continues to be an important challenge for Pt-based catalysts during propane dehydrogenation (PDH)[1]. Boron promotion drastically reduces coke formation on nickel[2] during steam reforming and on cobalt[3] during Fischer-Tropsch synthesis. DFT calculations and catalyst characterization indicate that reduced boron atoms selectively block step and/or subsurface sites, thus preventing nucleation and growth of deactivating carbon[2,3].

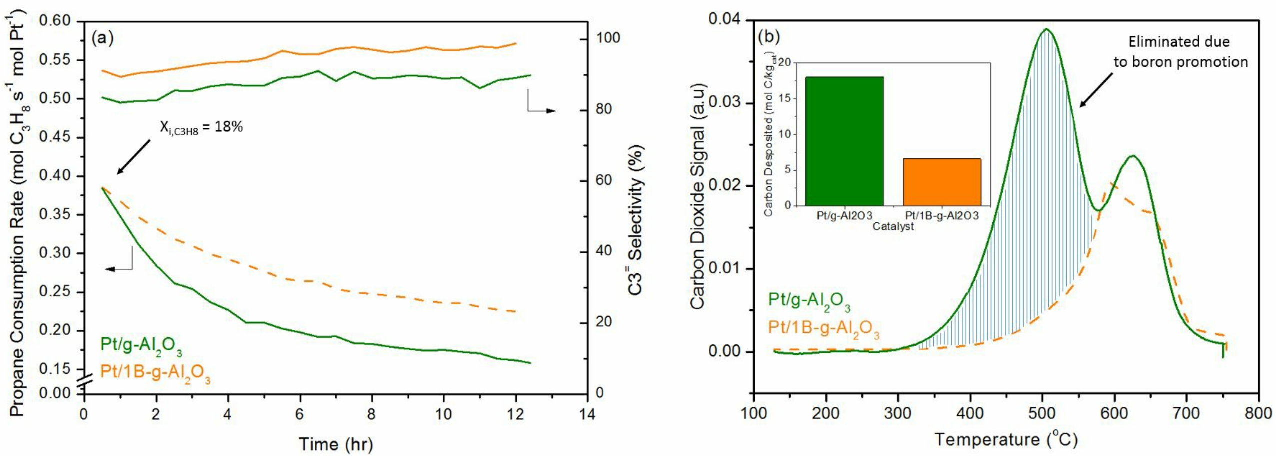
In this work, boron is introduced to enhance the catalytic performance of Pt/γ-Al_2O_3 catalysts during PDH. A series of catalysts with different boron loadings was prepared following various impregnation sequences. Detailed characterization and DFT calculations help identify boron's location and state (alloy/amorphous oxide).

Results:

XB-γ-Al_2O_3 support materials (X=wt.%B) were prepared via wet impregnation of H_3BO_3 onto commercial γ-Al_2O_3. Three different synthesis routes were followed: (a) Pt/XB-γ-Al_2O_3 catalysts were prepared via wet impregnation of H_2PtCl_6 onto XB-γ-Al_2O_3. (b) 1B/Pt-γ-Al_2O_3 was prepared via wet impregnation of H_3BO_3 onto Pt/γ-Al_2O_3 i.e., an inverse sequential impregnation. (c) Pt-1B-γ-Al_2O_3 was prepared by co-impregnation. Pt/γ-Al_2O_3 was prepared as a reference. The platinum loading was fixed at 3wt.% to facilitate characterization and obtain B/Pt (mol) ratios from 1-10.

Effects of boron loading and impregnation sequence were investigated during short-term (20 min) PDH tests at 600°C and a C_3H_8/H_2 ratio of one. Unlike with nickel and cobalt,[2,3] the promoting effect of boron was only observed when boron was introduced *before* the active metal. The Pt/1B-γ-Al_2O_3 catalyst showed only a minor reduction in activity during the short-term experiment but achieved a 2.6-fold reduction in the amount of deposited carbon for an optimal loading of 1wt.% B. Long-term experiments (12 hr) confirmed the improved stability and selectivity of Pt/1B-γ-Al_2O_3, *(Fig.1a)* with a 3.2-fold reduction in deposited carbon and an increase in propylene selectivity from 92 to 98%. TPO-profiles *(Fig.1b)* of spent catalysts show that boron promotion eliminates and reduces the low- and high-temperature carbon oxidation peaks, respectively. Propylene decomposition experiments on pure and boron-modified γ-Al_2O_3 relate the low-temperature peak to carbon formed on the support.

NH_3-TPD experiments indicate that boron modifies the number and strength of the support acid sites. In-situ XRD experiments under H_2 at 600°C exclude the formation of a Pt-B alloy. TEM-EDS shows a uniform distribution of boron over the material. DFT calculations support the formation of boron oxide rather than a Pt-B alloy. Testing and characterization thus indicate that boron modifies both the active-metal *and* the support. Clearly, the promoting effect of boron is more complex than often assumed[4].



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