Radical Chemistry in Oxidative Dehydrogenation of Propane over Boron Nitride

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Propylene is a crucial industrial building block for producing acrolein, polypropylene, acrylonitrile, propylene oxide etc. [1]. The recent shift from steam crackers of oil-based naphtha to shale-based ethane has resulted in a huge gap between the supply of propylene and rising global demand [2]. Therefore, new technologies to meet the increasing propylene demand are highly desired. Oxidative dehydrogenation of propane (OHDP) on boron nitride (BN) has been one of the most promising strategies since 2016 [3]. Previous reaction kinetics and theoretical studies implied the existence of gas-phase radical reactions in ODHP over BN [4], which still lacks direct experimental evidence. Here, we carry out ODHP over BN and reference V-based catalysts via *operando* synchrotron photoelectron photoion coincidence (PEPICO) spectroscopy. On V-based catalyst, CO_x (CO and CO_2) are the major byproducts in addition to the main product, propylene. In contrast, gas-phase radicals (methyl, propyl, allyl etc.) are only observed over BN together with enols, ketenes and higher olefins. This confirms active gas-phase radical chemistry over the BN catalyst. The relatively favorable desorption of these radicals from BN surface not only prevents overoxidation to CO_x, but also provides additional gas-phase formation routes to propylene and ethylene. This explains why the selectivity to olefins in ODHP over BN is significantly higher than that over V-based catalyst, which sheds light on the importance of coupling homogenous gas-phase reactions and heterogeneous surface catalysis in practical industrial applications.

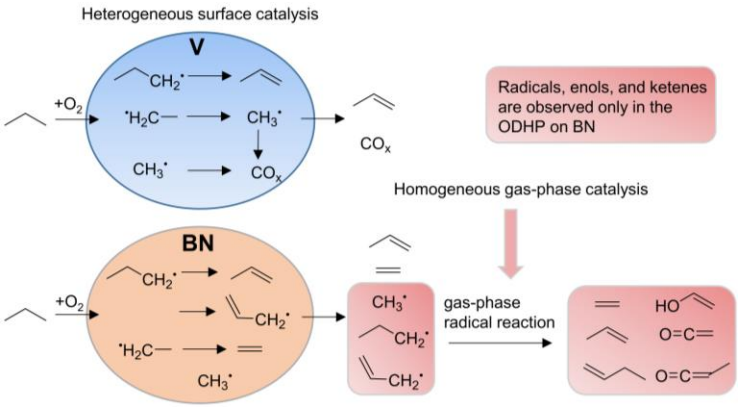

Figure 1: ODHP reaction routes over V-based and BN catalysts, including homogenous gas-phase radical reactions and heterogeneous catalysis on the catalyst surface.

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