

Insight into the Nitrilation Reaction as Catalyzed by Titanium Dioxide

Matthew V. Hickson, Ryota Osuga, Bart Van Meerbeek, Damien P. Debecker, Kiyotaka Nakajima, Ekaterina V. Makshina, Bert F. Sels

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Graphical Abstract

Polymorphism of titanium dioxide heavily influences its catalytic activity for the nitrilation reaction. Two reactions are displayed – the nitrilation of ethyl acrylate to acrylonitrile and of ethyl propionate to propionitrile. Deactivation noted when utilizing the acrylate is linked to acrylonitrile polymerization. Under stable conditions with the propionate, the anatase polymorph is shown to outperform the rutile polymorph substantially.

Abstract

While titanium dioxide has displayed excellent capabilities as a catalyst for the nitrilation reaction, the role that catalyst polymorphism plays in this reaction has remained largely unexplored. Herein, the catalytic capabilities of the anatase and rutile polymorphs regarding the nitrilation reaction are explored. In efforts to clarify structure–activity correlations, sets of these two polymorphs are characterized to determine their polymorphic purity, surface areas, and acidic properties. Initial catalytic investigations encounter considerable challenges, as substantial deactivation is observed when employing ethyl acrylate as a substrate - an issue attributed to the polymerization of the generated acrylonitrile. Stable catalyst performance is achieved using the saturated substrate and ethyl propionate. Investigating the nitrilation reaction using this saturated substrate displays significantly higher catalytic activity on the anatase polymorphs compared to the rutile. The catalytic activity correlated well with the total acid density, and correlations occur independently for both anatase and rutile, emphasizing the impact the catalyst polymorph has on this reaction. Finally, the superior catalytic performance of anatase is rationalized through in situ fourier transform infrared spectroscopy (FTIR) investigation of adsorbed ethyl propionate.