Selectivity and kinetics of methyl crotonate hydrogenation over Pt/Al$_2$O$_3$

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Supporting information

Fig. S1. (a) DSC and (b) evolution of gas-phase products from the thermal decomposition of the Pt precursor of the as-prepared Pt/Al$_2$O$_3$ sample.
Fig. S1a shows the DSC profile during thermal decomposition of the platinum precursor of the as-prepared Pt/Al$_2$O$_3$ sample, and the evolution of gas species as a function of time/temperature is shown in Fig. S1b. The DSC profile shows three apparent endothermic peaks in the temperature range from 25 to 500 °C. The first endothermic peak at 92 °C can be attributed to the loss of physisorbed water from the sample, as indicated by the corresponding water evolution (Fig. S1b). In the temperature range between 100 and 230 °C, NO and NO$_2$ besides H$_2$O were detected, indicating both hydrate and nitrate decomposition. In this stage the water may be from the water of crystallization which exists in the crystalline framework of platinum nitrate. The third endothermic peak located at about 300 °C can be ascribed to further decomposition of platinum nitrate, as seen in the NO$_x$ evolution profiles. The thermal analysis results indicate that the nitrogen species in the precursor can possibly be removed after calcination at 500 °C. Actually, it was found that the color of the catalyst treated at 400 °C for 4 h was grey while that of the sample obtained at 500 °C was black.
Due to the chemisorption of H₂ on the Pt surface, H₂O was used as the indicator for the reduction process. As shown in Fig. S2, all the samples show a broad peak in the temperature range of 50 to 400 °C. Besides H₂O, a small amount of N₂O was observed for the three samples, indicating that even a high calcination temperature of 700 °C was not enough to completely remove NOₓ species from the catalyst. A pretreatment of the sample by H₂ at 400 °C is required to remove all nitrate species and to reduce the catalysts.
Fig. S3. Typical GC spectra under different magnifications for analysis all the products.
Fig. S4. (a) and (b) the GC peak areas of the minor species at different retention times and (c) carbon balance as a function of reaction temperature for MC hydrogenation on the Pt/Al$_2$O$_3$ catalysts calcined at 500-700 °C.
Fig. S5. Carbon balance of MC hydrogenation on the Pt/Al₂O₃-500 catalyst at different MC concentrations.
Fig. S6. Carbon balance of the catalytic kinetics of MC hydrogenation on the Pt/Al₂O₃ treated at (a) 500 and (b) 700 °C.