• *Short Communication*

Differential Thermal Analysis for Evaluation of Copper-Chromium Oxide Catalysts

Some copper-chromium catalysts have been reported to be highly efficient for selectively lowering the linolenate content of soybean oil (1,6). To gain benefit from this selectivity, the catalyst must be in an active form. Commercial copper-chromium catalysts may vary considerably both in selectivity and activity under a standard set of hydrogenation conditions. During our early work, heat treatment of catalysts was frequently necessary to improve their activity. We find differential thermal analysis (DTA) to be helpful for qualitatively predicting the activity of a new batch of a specific type of catalyst that has previously been proved to be active and selective. A thermogram is made for each sample under a standard set of conditions. Upon completion of a scan, the sample is immediately cooled by liquid nitrogen. A second (rescan) thermogram is then obtained for each sample by programming under the same standard conditions.

Figure 1 illustrates the thermograms obtained with a representative copper-chromium-barium catalyst before and after heat treatments. As received, this catalyst showed absolutely no catalytic activity for reduction of linolenate. After vacuum drying, the catalyst was still inactive. However, it became active when heated at 350C for 6 hr.

The first, very broad, endothermic peak in the thermogram for the catalyst as received is believed to result from dehydration of the catalyst. The DTA thermogram for the vacuum dried catalyst did not have this initial endothermic peak, but at higher temperatures still had a profile similar to the catalyst as received. The rescan thermogram of the catalyst as received was identical to the initial thermogram of the heat treated catalyst.

In our studies, active catalysts of the Cu-Cr-Ba type have consistently given both initial and rescan thermograms with a positive slope near 500C. Excessive heat treatment will give a less active catalyst with zero or negative slope. Optimum conditions for heat treatment vary from catalyst to catalyst.

The DTA thermograms were obtained on a duPont 900 Thermal Analyzer. Samples were tightly packed to a depth of 4 mm in the macro sample tube and the thermocouple inserted. A similar depth of 180 mesh silican carbide was used for the reference. After it had been purged with dry nitrogen, the cell was cooled to −50C with liquid nitrogen. The samples were programmed to 485C at 15C/min. With the temperature differential scale (ΔT in Fig. 1) set at 0.2C/in, heating at a programmed rate of 15C/min appears to be optimum. Hydrogenation data will be published at a later date (6).

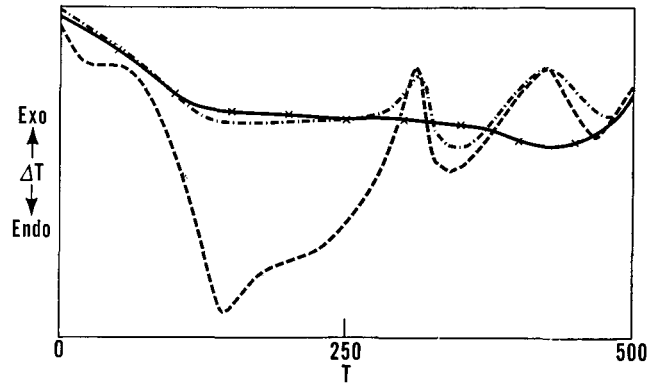

FIG. 1. Thermograms of a copper-chromium-barium catalyst as received (before heat treatment) (------), after vacuum drying (-.-.-.), and after heat treatment at 350C (———). The rescan profile (xxxx) of the catalyst as received coincides with the initial profile of the heat-treated catalyst.

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Apparatus for Low-Temperature Solubility and Freezing-Point Determinations by the Thermostatic Sealed Tube Method

METHODS FOR DETERMINING the solid-liquid phase relations of binary and ternary systems or solubilities fall into two general categories: analytical methods and synthetic methods (1). A synthetic method is usually required in the construction of freezing-point diagrams of binary and ternary systems. The static form of the synthetic method, the thermostatic sealed tube method (2), apparently was first developed in this Laboratory. The freezing-point or solubility temperature is taken as the average of two temperatures a few tenths of a degree apart, one at which the last crystals just disappear and the other at which a few crystals remain after prolonged agitation. Satterfield and Haulard (3) have recently shown that the thermostatic form gives more accurate results than the usual (dynamic) form