• *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.

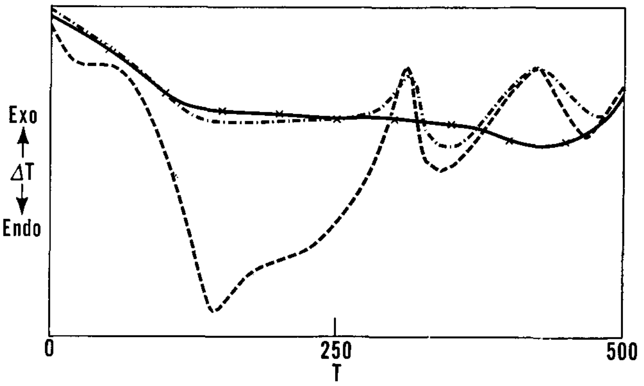

FIG. 1. Thermograms of a copper-chromium-barium catalyst as received (before heat treatment) (------), after vacuum drying (-.-.-.), and after heat treatment at 350C (———). The rescan profile (xxxx) of the catalyst as received coincides with the initial profile of the heat-treated catalyst.

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).

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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

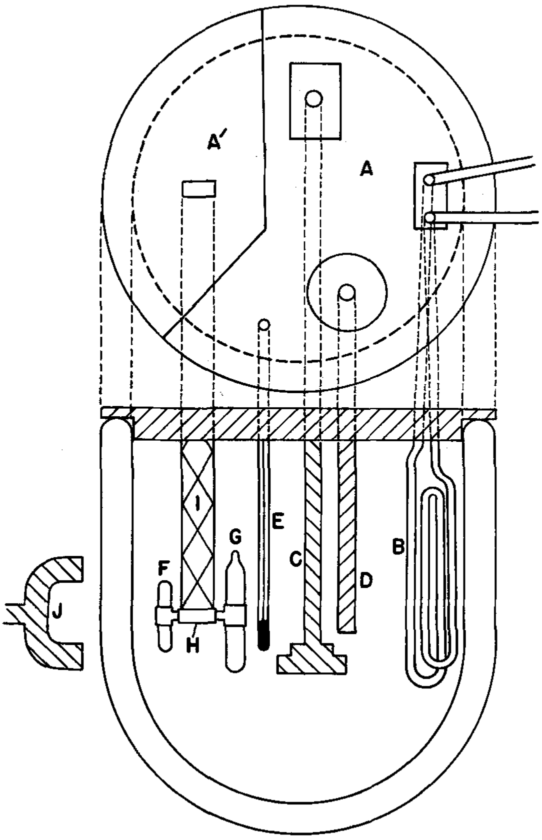

FIG. 1. Schematic diagram of bath section of low-temperature solubility apparatus.

of the synthetic method, i.e., using slowly rising temperature. It is also more generally applicable and usually more reliable than the analytical method, which depends upon the existence of a sufficiently accurate method of analysis and is therefore often unusable.

In the course of the development of methods of correlation and prediction of solubilities for homologous and analogous long-chain compounds, the need arose for a means of determining consistently accurate solubility data covering extreme ranges of concentration and extending down to very low temperatures. An apparatus was therefore designed and constructed which extends the temperature range of the thermostatic sealed tube method down to −60C and the concentration range down to 0.001 mole per cent. The apparatus can be used for any system in which crystals can be caused to form, and also to determine solubilities of liquids. It is especially suited for low-temperature determinations, since no protection of the sample from contamination by moisture condensation is necessary. It is particularly useful for the detection and investigation of polymorphic forms, because of the visibility of the crystalline phase, ease of temperature manipulation, and because the sample can readily be removed from the bath for shock chilling or other thermal treatments required to form the different crystal modifications.

The apparatus is illustrated schematically in Fig. 1. The constant-temperature bath is contained in a 10-liter unsilvered Dewar flask (ca. 10 in. inside diameter by 11 in. deep). A lid of 1-in.-thick transite with a lip is partially recessed into the top of the flask. A rubber gasket is inserted between the cover lip and the flask for protection and thermal sealing. The lid is constructed in two parts, one of which is permanently attached to the flask. Mounted on the permanently attached lid section (A) are the bath-cooling coil (B), the centrifugal stirring mechanism (C) for the bath (a circulating pump of 5 to 6 gal/min capacity), the bimetallic thermoregulator (D), and the thermometer (E). A precision total immersion thallium-mercury thermometer with a range of from +5C to −60C graduated to 0.2C was used. A calibrated thermocouple also can be used.

The sample rotation assembly is rigidly attached to the removable section of the lid (A′), which is supplied with a lifting handle and a metal flange resting on A. This assembly consists of a 2-in. Teflon-covered magnetic stirring bar (F) and a clip for holding the sample tube (G) mounted on opposite ends of a 0.25 by 1.5-in. stainless steel shaft. The shaft extends through a 0.75-in.-long Teflon sleeve-bearing (H) mounted at the bottom of the stainless steel support (I). The sample tube (ca. 10 mm inside diameter by 9 cm) is caused to turn end over end by a rotating No. 7 horsehoe magnet (J), external to the system about 3 in. from F, driven by an electric motor (Bodine KYC-25) with a geared output shaft operating at 25 rpm. A focusable microscope light is positioned behind the apparatus so as to shine through the sample tube, to aid the visual observation of the solute crystals.

In the heat exchange system, a low-capacity electric pump operated by a relay and controlled by the bath thermoregulator circulates the coolant liquid (95% ethanol) from a reservoir through the bath coils to an external heat exchanger and back to the reservoir. A dry ice–acetone mixture is used in the external heat exchanger (Haake, model K-60). The bath coils consist of about 75 in. of 0.375-in.-in-diameter copper tubing.

Depending upon the operating temperature, the temperature fluctuation in the bath ranges from ±0.1C to ±0.2C. For operations above room temperature a 300-w hairpin electric heater is used, and distilled water is used as the bath liquid instead of 95% ethanol.

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