Technical

Reactivation of Partially Poisoned Nickel Catalyst by Bleaching Earth

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ABSTRACT

The effect of activated bleaching earth on the hydrogenation kinetics of fats has been studied in a model system containing sodium soaps, phospholipids and allyl isothiocyanate. Both unsupported and supported catalysts were inactivated by these inhibitors. The optimal quantity of adsorbent, when added to the reaction system, caused a maximal increase of hydrogenation rate in the presence of these inhibitors. In the case of partial inactivation of a catalyst with these inhibitors, the addition of bleaching earth resulted in a regeneration of the catalyst's active surface and an immediate increase in the hydrogenation rate. The effectiveness of this interaction depended upon the inhibitor type, catalyst type and time of contact with catalyst inactivators. The results suggest the positive effect of activated bleaching earth during hydrogenation results from the sorption processes, inhibitor transformations on the adsorbent and direct interaction with the nickel catalyst.

INTRODUCTION

Inactivation of catalyst is a serious drawback during hydrogenation of oils containing catalyst inactivators (1-14). Sulfur and phosphorus compounds are extremely poisonous. It was proven that unsupported catalysts are generally inactivated to a greater extent than supported ones with the same level of inhibitor content in the reaction system. Catalyst inactivators also increase the induction periods, which are proportional to the amount of poisons present. Particularly long induction periods occur in the presence of sulfur compounds. Catalysts also are strongly poisoned by alkaline soaps. Oils subjected to hydration, neutralization and bleaching before hydrogenation still contain considerable amounts of poisons which inactivate catalysts to varying degrees (15-16). This information led us to the search for new catalytic systems with reduced susceptibility to the inhibitory effect of catalyst inactivators. We have pointed out in our studies (17) the possibility of using the montmorillonite-type silicate which are accessible and widely used in the fat industry. They belong to the group of active adsorbents with surfaces which also may be responsible for various types of catalytic reactions (18-26). Our preliminary studies indicate that the introduction of activated bleaching earth into the reaction system during hydrogenation of oils changes the reaction rate. There is an optimal quantity of adsorbent which when added to the system increases the hydrogenation rate to a maximum (27,28). When this quantity is exceeded, the reaction rate drops.

Further studies showed that the mechanism of adsorbent interaction is complex and depends upon the adsorbent, catalyst type and kind of oil (28). The comparison of the increased oil hydrogenation rate in the presence of activated bleaching earth over the rate without the adsorbent showed the bleaching earth more markedly interacts when the process is carried out with unsupported catalyst and when oil contains considerable quantities of inhibitors. Out of the group available and studied by us, the most active was Czech bleaching earth. In addition, it does not change the selectivity nor the *trans*-isomer content during hydrogenation (29).

In order to determine the nature of the interaction of Czech bleaching earth, the hydrogenation rates were compared for oil initially treated with adsorbents and oil hydrogenated in the presence of the bleaching earth (30). Conditions of the initial treating of oil with bleaching earth were the same as during hydrogenation. This oil was hydrogenated after the removal of adsorbent. The results show that a higher reaction rate is observed when bleaching earth is a component of the reaction system during hydrogenation. This means that it interacts not only with inhibitors present in oil by adsorbing them but also with the nickel catalyst. Therefore, it was relevant to determine the degree of interaction of bleaching earth toward a partially inactivated catalyst. The results of these studies are reported here.

MATERIALS AND METHODS

Kinetic studies were carried out in a "dead-end" type laboratory reactor which gave a constant recording of the volume of absorbed hydrogen. The model system consisted of refined soybean oil, inhibitors, formate-type nickel catalyst produced by the Fat Factory "Gen. W. Wróblewski" in Gdańsk, supported catalyst Nysel DM-3 produced by Harshaw Co. and Czech bleaching earth, Nobel type, of acidity 0.04% HCl and moisture content equal to 10.3% by weight. The following inhibitors were used: allyl isothiocyanate (AITC), phospholipids and sodium soaps. The method of preparation, introduction to the reaction system and the general characteristics were previously described (14). The content of poisons in oil was expressed as sulfur, phosphorus and sodium content. The reaction system was fed with poisons enough to reduce the catalyst activity by ca. 50% of their initial value. Concentrations are compiled in Table I.

Inhibitors were added to the oil and bleaching earth was introduced into the reaction system either simultaneously with the catalyst or during hydrogenation. Hydrogenation was carried out using oil (50 g), 0.1% Ni (with respect to

TABLE I

Inhibitor Concentrations during Hydrogenation of Oils in the Presence of Activated Bleaching Earth

Catalyst used	Inhibitor concentration (μg/g) S	P	Na
Unsupported formate type	24	20	12
Supported Nysel DM-3	25	50	25

the mass of oil); temperature was set at 170 C ± 0.5 C, stirring rate was 2700 rpm and hydrogen pressure was atmospheric.

The catalyst was introduced into the oil after the stabilization of process conditions and the saturation of oil with hydrogen.

The relationship between the amount of hydrogen consumed and the reaction time, which was recorded automatically during hydrogenation, illustrated the kinetics of the process. Reaction rate constants k were calculated according to formula:

$$k = \frac{2,303}{t} \cdot \log\frac{IV_o}{IV_t}, \qquad [I]$$

where IV_o = initial iodine value of oil, IV_t = iodine value after hydrogenation time t and t = hydrogenation time.

On the basis of iodine values, which were calculated from the volume of absorbed hydrogen, the relationship between log IV and the reaction time was traced. It has linear characteristics in consecutive hydrogenation stages. The analysis of fatty acid composition indicated different reduction rates of poly- and monoenoic acids. The effect of bleaching earth addition on the kinetics of the process was determined for polyenoic acids hydrogenation, since this is the most interesting from an industrial point of view.

The effect of bleaching earth was determined as E_z, which was expressed as the percentage increase of the reaction rate constant:

$$E_z = \frac{k - k_o}{k_o} \cdot 100, \qquad [II]$$

where k = hydrogenation rate constant with bleaching earth and k_o = hydrogenation rate constant without bleaching earth.

To illustrate the effect of activated bleaching earth on partially poisoned nickel catalyst, the adsorbent (1.5%) was introduced into the reaction system at 0, 15, 30 and 60 min after the onset of the reaction (points 0, A, B and C on the graphs).

RESULTS AND DISCUSSION

On the basis of the results (Fig. 1), we determined there is an optimal quantity of bleaching earth which, when introduced to the reaction system containing particular inhibitors, causes a maximal increase in the hydrogenation rate. When this concentration was exceeded, the reaction rate decreased. The comparison of E_z values showed that the highest interaction of adsorbent in the system containing supported catalyst was observed for sodium soaps. The slightly less pronounced, but remarkable, effect of silicates was also observed during the hydrogenation of oil containing phospholipids. The least pronounced, but still significant, effect of the adsorbent was observed for AITC. The system containing these inhibitors during hydrogenation in the presence of unsupported catalyst behaved almost identically. The results show that the type of inhibitor has a great influence on the magnitude of the effect of bleaching earth in the reacting system. On the basis of data in the literature it is concluded that bleaching earth, because of its acidic character, decomposes soaps and liberates fatty acids which are not as toxic as soaps (14). Of course, the increased acidity of bleaching earth caused an increased reaction rate in some cases, particularly in the presence of sodium soaps (30). The transformation of the remaining inhibitors resulting from the interaction with adsorbent also may occur. A higher hydrogenation rate in the presence of bleaching earth also may indicate there is adsorption of catalyst inactivators on its surface, which were formed during the process. The high temperature of reaction and possible presence of water (during industrial hydrogenation) favors the formation of free fatty acids or other inhibitors resulting from pyrolytic decomposition. One also may assume that the transformations of some substances on the catalyst surface lead to the formation of catalyst inactivators and then activated bleaching earth interacts by removing these inhibitors from the surface of the catalyst.

The reduction of the reaction rate after the optimal bleaching earth content is exceeded probably depends on the ratio of the adsorbent to the active metal. When the quantity of bleaching earth is excessive, the mechanical blocking of the metal surface by the adsorbent (which hinders the access of substrates to its surface) or competitive adsorption of substrates may be factors affecting the total reaction rate.

The positive effect of activated bleaching earth during hydrogenation is probably caused by sorption processes, transformations of inhibitors on the adsorbent and direct interaction with the nickel catalyst. Dissociation of hydrogen and the conjugation of ethylene bonds of unsaturated fatty acids on the active surface of silicate also may be responsible for the hydrogenation rate increase (31, 32). The adsorbent also interacts with partially poisoned nickel catalyst. The analysis of kinetic curves given in Figures 2-6 shows that the interaction of the adsorbent causes an immediate increase in hydrogenation rate. The strongest interaction similar for both catalysts was observed in the inactivation with sodium soaps (Figs. 2 and 3). The effect of bleaching earth in the experiment with unsupported catalyst was so great that hydrogenation rates approached those obtained in the presence of active catalyst with an

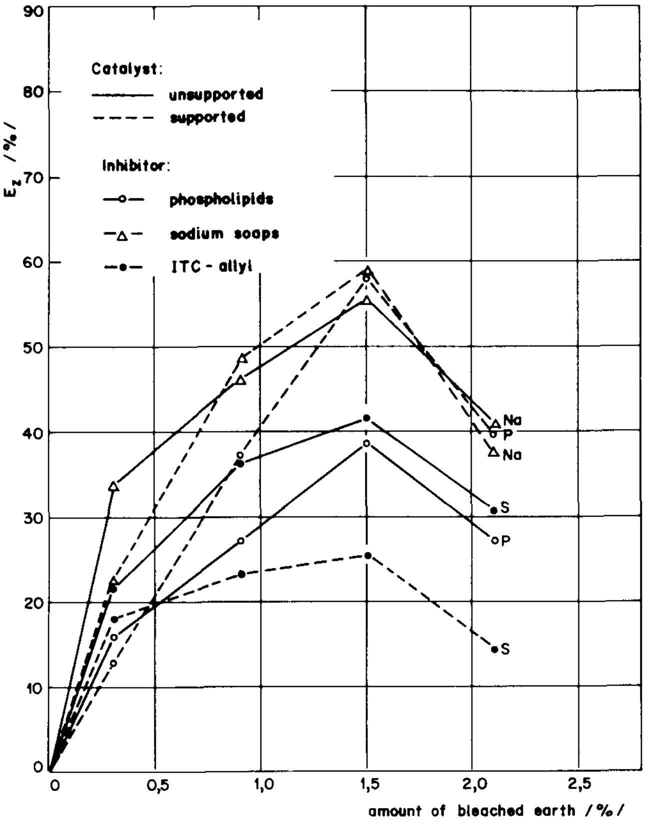

FIG. 1. Effect of the concentration of activated bleaching earth on value E_Z during hydrogenation of soybean oil containing various inhibitors.

oil containing neither inhibitors nor the adsorbent (Fig. 2). The results prove catalyst poisoning with sodium soaps is reversible. The interaction of bleaching earth in the system containing catalyst partially inactivated with phospholipids was qualitatively similar to the system with sodium soaps (Figs. 4 and 5). The positive effect of the adsorbent was, however, less pronounced as the time of contact between catalyst and inhibitor was increased. These results suggest stronger adsorption of this inhibitor on the active metal surface.

In experiments with oil containing AITC, the positive effect of bleaching earth was evident with the unsupported catalyst only (Fig. 6), whereas the supported catalyst was not affected (Fig. 7). The interaction of the adsorbent after the simultaneous addition with catalyst was also insignificant.

The results of these studies have shown the possibility of reactivating a catalyst partially inactivated with the

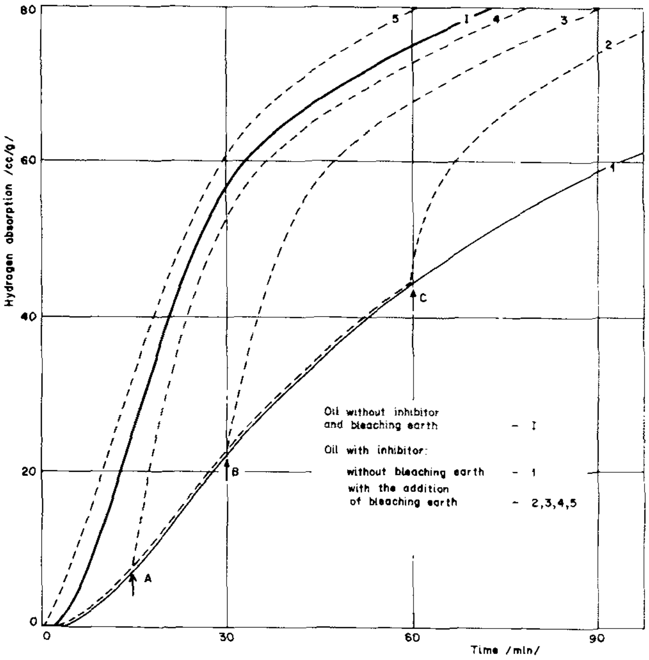

FIG. 2. Kinetic curves for hydrogenation of soybean oil in the presence of sodium soaps and bleaching earth introduced into the system at different reaction times (unsupported catalyst).

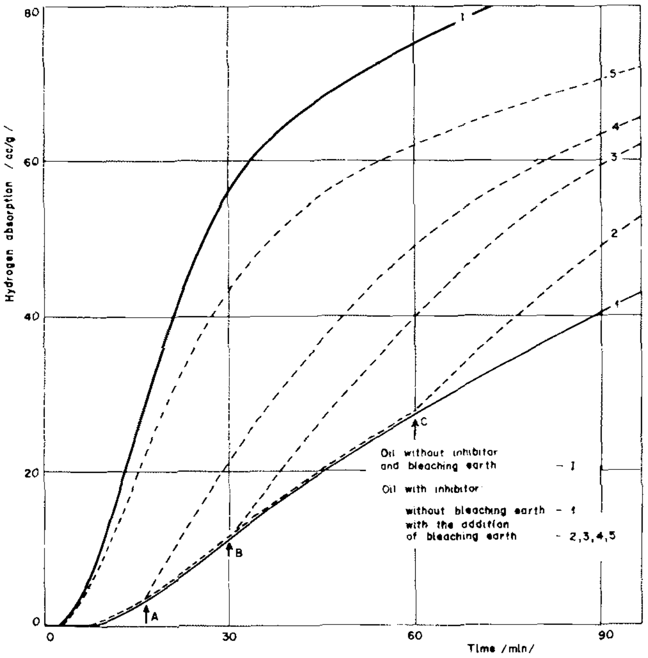

FIG. 4. Kinetic curves for hydrogenation of soybean oil in the presence of phospholipids and bleaching earth introduced into the system at different reaction times (unsupported catalyst).

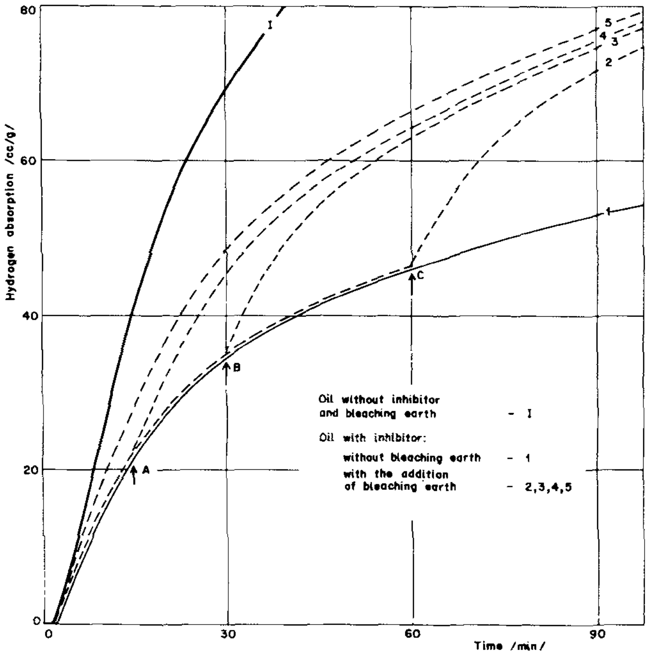

FIG. 3. Kinetic curves for hydrogenation of soybean oil in the presence of sodium soaps and bleaching earth introduced into the system at different reaction times (supported catalyst).

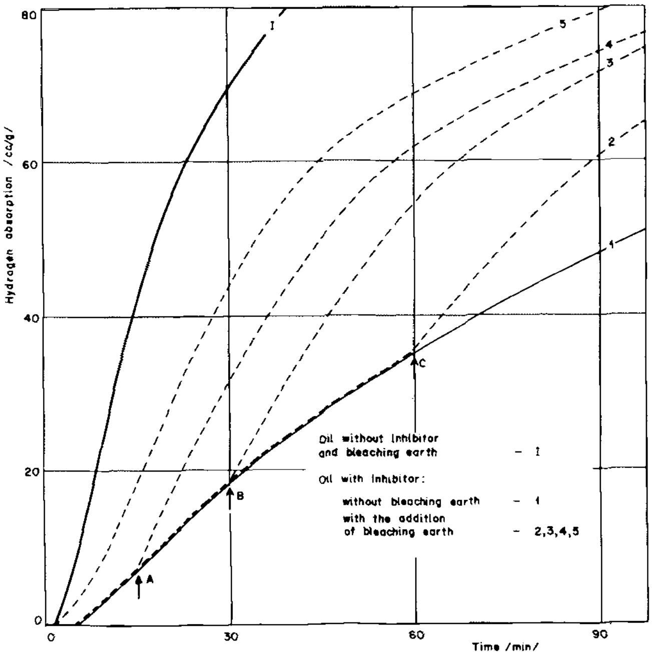

FIG. 5. Kinetic curves for hydrogenation of soybean oil in the presence of phospholipids and bleaching earth introduced into the system at different reaction times (supported catalyst).

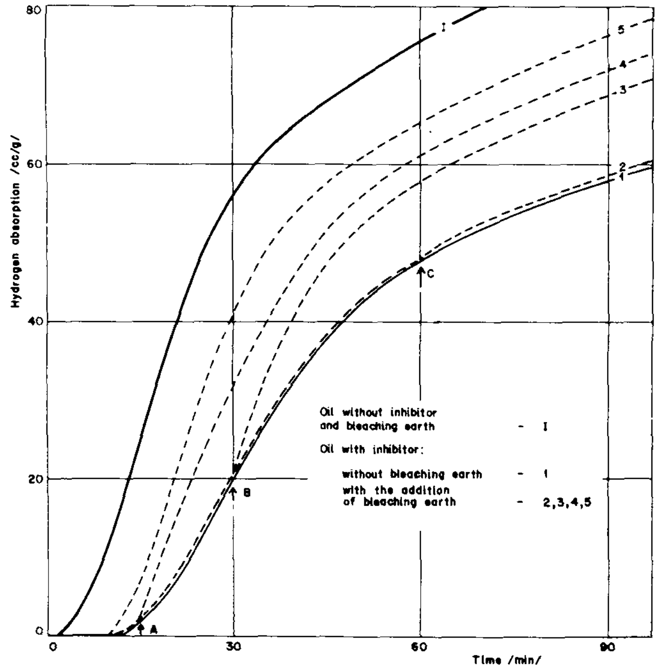

FIG. 6. Kinetic curves for hydrogenation of soybean oil in the presence of AITC and bleaching earth introduced into the system at different reaction times (unsupported catalyst).

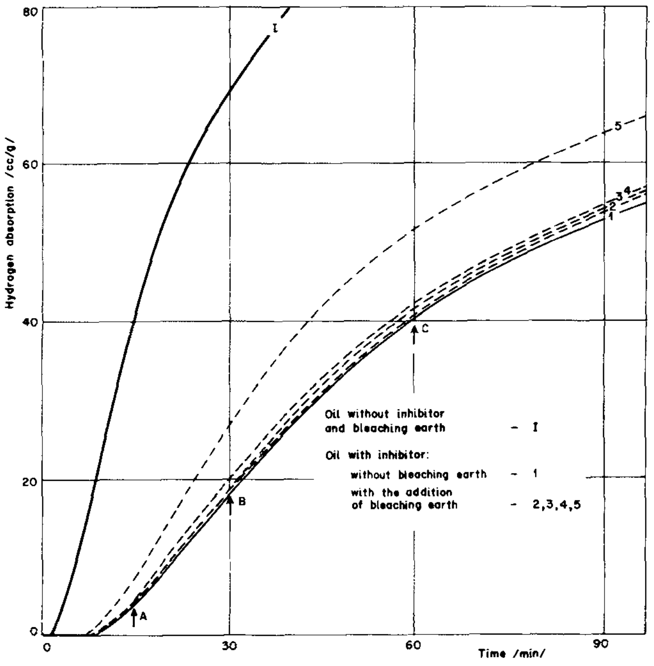

FIG. 7. Kinetic curves for hydrogenation of soybean oil in the presence of AITC and bleaching earth introduced into the system at different reaction times (supported catalyst).

inhibitors described here by adding activated bleaching earth to the reacting system.

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