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A New Method for Study of the Adsorption Function of an Adsorbate on an Adsorbent, Applied to the Study of the Adsorption Function of Isopropyl Alcohol on a Zinc Oxide Catalyst

I. Experimental Results

STEIN KOLBOE

From the Central Institute for Industrial Research, Oslo 3, Norway

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It is first shown that adsorption of isopropyl alcohol on a zinc oxide catalyst is essentially a reversible process. Secondly, quantitative thermodesorption curves of isopropyl alcohol under equilibrium conditions with negligible concentration gradient over the catalyst bed have been recorded. From these curves a complete adsorption function for adsorption of isopropyl alcohol on zinc oxide can be established. The detailed analysis is given in the following paper.

INTRODUCTION

One of the main assumptions in the Langmuir-Hinshelwood-Hougen-Watson scheme for establishing kinetic equations for heterogeneously catalyzed reactions is that all the active centers on a catalyst surface can be taken to have identical properties (*1*). The author has recently advanced the view that this assumption may be too restrictive, and that one should rather expect the catalyst surface to consist of several sets of active centers (*2*). This view was partly based upon the fact that there will in general be more than one crystal face exposed on the catalyst surface, and partly upon the fact that many adsorbing systems have been shown clearly to be heterogeneous. The model assuming more than one set of active centers on a catalyst has so far been successfully applied to two systems where the classical Hougen-Watson (*1*) equations were not in agreement with the experimental data: dehydrogenation of *sec*-butyl alcohol over a brass catalyst (*2*), and hydrogenation of propylene and isobutylene over a platinum catalyst (*3*). Reviews of older work assuming nonhomogeneous surfaces in heterogeneous catalysis have been given by Roginski and Constable (*18, 19*).

While working with zinc oxide as a catalyst for dehydrogenation of isopropyl alcohol it became clear that the observed kinetics could not be brought into agreement with the Hougen-Watson equations, but a model based on several sets of active centers appeared satisfactory (*4*). It is clear that the assumption of several sets of active centers on a catalyst cannot be maintained as a satisfactory model unless, at least in some cases, there exists a partial or complete relationship between the adsorption function in a system, and kinetic measurements in the same system. Studies of consistency between the adsorption function and rate measurements are therefore critical tests on the soundness of assuming that there may be more than one set of active centers on a catalyst.

The objective of this and the following article (*5*) is to present a complete analysis of the adsorption function of isopropyl alcohol on a zinc oxide catalyst. To reach this goal a new method for establishing the adsorption function of a system will be given.

Based on work by Wicke (*6*) and Zhabrova *et al.* (*7*) it has been widely maintained in the literature that the rate-determining step in isopropyl alcohol dehydrogenation is acetone desorption (*8–10*). If this is correct, it is to be expected that isopropyl alcohol adsorption will be only partially reversible, and the adsorption function for isopropyl alcohol cannot be expected to bear any relationship to kinetic measurements on the dehydrogenation reaction. Although results of kinetic measurements on the dehydrogenation reaction obtained fairly recently have weakened the case for acetone desorption being the slow step (*4, 11–13*), it was found necessary to investigate to what extent the adsorption is reversible before studying the adsorption function itself.

The first part of this article is concerned with experiments showing that adsorption of isopropyl alcohol on zinc oxide is to a large extent, or possibly fully, reversible. Then an experimental procedure for quantitative thermodesorption measurements under equilibrium conditions is indicated and some experimental curves for the system isopropyl alcohol/zinc oxide are given. A method for quantitative treatment and complete analysis of the experimental results is given in the following paper (*5*).

EXPERIMENTAL

Apparatus. The experiments were carried out using a flow system consisting of needle valve, manometer, flow meter, saturator for introducing isopropyl alcohol into a carrier gas stream, reactor, oven, sampling valve, and a gas chromatograph.

The gas leads were made of copper in the part before the flow meter, and the rest were of glass (Pyrex) with joints and stopcocks lubricated with Apiezon L or T.

The carrier gas flow was measured using a capillary differential pressure flow meter with silicon oil (Dow Corning 704) as manometer fluid. The saturator consisted simply of a container of isopropyl alcohol and was so constructed that the carrier gas was made to bubble through the fluid. Although not important for the present discussion tests have shown that the carrier gas was essentially saturated with isopropyl alcohol (at the temperature prevailing in the saturator) when leaving the saturator. The saturator was equipped with a four-way stopcock so that the carrier gas could be made to bypass the saturator by turning this stopcock.

The reactor. The catalyst was supported on a horizontal sintered glass disc melted into a vertical glass tube, 10-mm id, with a 5-mm od thermocouple well down the center, ending 1 mm above the sintered glass disc. The carrier gas entered at the top and left at the bottom. In the experiments where it was necessary to cool the catalyst below room temperature, the reactor tube was surrounded by a coiled copper tube ending about 5 cm below the sintered glass disc. Cooled air from an air cylinder entered through the copper coil and thus cooled down the reactor and the surrounding oven. In this way the reactor and catalyst could be cooled down to about −25°C.

Analytical equipment. Gas samples from the outlet of the reactor were taken to the chromatograph for analysis by a Perkin-Elmer gas-sampling valve. A Perkin-Elmer 820 gas chromatograph modified with a flame-ionization detector (S. Kolboe, unpublished) was used for carrying out the analyses. The analytical column was composed of two connected 1-m columns, one filled with 20% diglycerol on Chromosorb W and the other with 20% dinonylphthalate

TABLE 1
ANALYTICAL DATA OF THE CATALYSTS[a]

ZnO p.a. Merck	ZnO from $ZnCO_3$
Surface	
5.8 m^2/g	52 m^2/g
Impurities	
0.001% Pb	0.001% Pb
0.0001% Cu	0.001% Cu
	0.01% Ca
	0.003% Ni
	0.003% Mg
	0.001% Fe

[a] The analytical results given were obtained by emission spectroscopy and indicate order of magnitude only.

on Chromosorb W. Highly purified nitrogen (Norsk Hydro) was used as carrier gas in the gas chromatograph.

Materials. Two types of zinc oxide catalyst were tested: analytical reagent zinc oxide from Merck, and a zinc oxide made by heating zinc carbonate in air for 24 hr at 350°C. The main analytical data of the catalysts are given in Table 1.

British Drug House analytical reagent isopropyl alcohol was used with no further purification.

EXPERIMENTAL RESULTS AND DISCUSSION

Experiments to Obtain Information on Rate-Determining Step and Reversibility of Adsorption

It was reasoned that if desorption of acetone is the rate-controlling step for isopropyl alcohol dehydrogenation a fairly large part of the catalyst should be covered with acetone after some time if isopropyl alcohol is added to a zinc oxide catalyst. Experiments were therefore carried out where isopropyl alcohol was added to the catalyst and later desorbed and analyzed. One experiment will be described in detail.

One gram of ZnO from $ZnCO_3$ was put in the reactor and a carrier gas flow containing 40 torr of isopropyl alcohol was maintained for 3 days at 205°C at a flow rate of 8 ml/min. Under these conditions about 50% (rate 10^{-5} mole/min) of the alcohol was dehydrogenated and about 5% was dehydrated to propylene and diisopropyl ether. During this period the reaction rate fell about 75% due to aging of the catalyst. (Details about catalyst aging will be published later.) The objective of this catalyst pretreatment was twofold: to obtain results on an aged catalyst and to make certain that the catalyst had been operated under conditions where acetone and propylene formation took place.

At the end of the 3-day period the reactor temperature was lowered to 70°C where no measurable reaction took place. The real experiment was now started by turning the four-way stopcock of the saturator so that a gas stream of pure nitrogen flowed through the reactor. During the first few hours when the tail-gas composition was changing rapidly it was analyzed every few minutes. While the desorption was taking place at 70°C no measurable quantities of acetone or propylene were observed. The sensitivity of the apparatus would make concentrations of about 10^{-5} torr visible. (Extrapolation from rate measurements at higher temperatures indicates that the concentrations should be far below this value.) After 45 days at this temperature and a carrier gas flow of 35 ml/min essentially no desorption of isopropyl alcohol took place any more. The temperature was then raised to 100°C. The concentration of isopropyl alcohol in the tail gas then increased. But there was no sign of acetone except at very low carrier gas flows (2–3 ml/min) when a barely visible acetone peak was observed. After 3 days at this temperature the reactor temperature was slowly and intermittently increased while analyzing the tail gas at intervals. After 3 days a temperature of 150°C had been reached and there was no measurable desorption. The temperature was now raised to 400°C during about 2 hr and the tail gas was analyzed at 5-min intervals. A fairly large concentration of propylene and acetone was now obtained in the tail gas.

By summing up the products of flow rate and concentration of each component over the whole experiment the following quantities of desorbed gases were found after correcting the isopropyl alcohol result for the (negligible) contribution from the apparatus with empty reactor: isopropyl alcohol, 3×10^{-4} moles; acetone, 2×10^{-7} moles; propylene, 7×10^{-7} moles. Thus less than 0.07% of the surface was covered by acetone and less than 0.2% was covered by propylene at the beginning of the experiment.

In a similar experiment where isobutyl alcohol was added to the catalyst to displace the isopropyl alcohol similar results were obtained, but the maximum coverage of acetone and propylene was then 0.02% for both compounds. Significantly the propylene and acetone in these desorption experiments came off at considerably higher temperatures than normally necessary for a substantial production of both. This is exemplified by the conversion indicated above at 205°C.

If 0.02% of the catalyst surface is covered by acetone at low temperatures it can therefore hardly be on the sites leading to acetone production at, say, 200°C, and these (possibly) acetone-covered sites are not the ones which give rise to acetone production in this temperature region. Experiments on the analytical reagent zinc oxide gave very similar results. It also appears to be of no importance whether a fresh or an aged catalyst sample is used for the experiments.

It may thus be concluded that isopropyl alcohol adsorption on zinc oxide is essentially a reversible process, and the results indicate strongly that acetone desorption is not the rate-determining process. This is also in agreement with recent kinetic measurements which indicate that the surface reaction is rate-determining (*11–13*).

Experiments to Determine the Adsorption Function

The experiments to be described here show a basic similarity to the experiments described by Amenomiya and Cvetanovic (*14*). They were carried out in the following way. Carrier gas containing isopropyl alcohol at a partial pressure of 8 torr was passed through the reactor which contained 32 mg of ZnO from $ZnCO_3$. In the experiments described here the catalyst had not been subjected to any aging pretreatment before carrying out the experiments. The exact details of the experimental procedure depended on the particular experimental conditions which were wanted. In Experiment I the temperature was first lowered to about 0°C by means of the cooling coil, and the carrier gas flow was then set to about 1 ml/min. The conditions were then kept unaltered until a temperature of about -10°C had been reached, at which time the four-way stopcock on the saturator was turned so that pure carrier gas only flowed through the reactor at a flow rate of about 1 ml/min. (The low flow was maintained in order to minimize desorption at high temperatures.) Conditions were now kept unchanged until a temperature of $-20°$ to -25°C had been reached (the lowest temperature which could be reached with the experimental setup used). At this temperature the flow rate of carrier gas was increased to about 20 ml/min and kept constant at this value for the rest of the time needed for the experiment. After about 1 hr at $-20°$ to -25°C when the isopropyl alcohol pressure in the tail gas had fallen to about 10^{-2} torr, the cooling was stopped and heating of the oven containing the reactor was started. Separate experiments with the empty reactor had shown that after this time the contribution from the reactor and glass tubes was insignificant and that all isopropyl alcohol left in the apparatus was adsorbed on the catalyst.

Although it is not essential for the interpretation of the results, the voltage over the oven was so adjusted (linear increase with time) that a fairly regular temperature increase was obtained (second derivative nearly constant). In this way the temperature in the reactor was measured by means of the thermocouple in the thermocouple well. Due to finite thermal conductivities the thermocouple temperature will not be equal to the temperature in the reactor when the temperature is changing. The following approximate equation is, however, easily established

$$\frac{dT_R}{dt} = \frac{dT_{tc}}{dt} + K\frac{d^2T_{tc}}{dt^2}$$

where T_R is reactor temperature, T_{tc} is the thermocouple temperature, t is time, and K is the time constant of the system, which was found to be about 3 min in this system. By means of this equation, corrected temperature readings are obtained. A sample of the tail gas was taken for analysis every 60 sec. Temperature measurements were taken at the same intervals. In this way isopropyl alcohol pressures and temperatures are obtained as functions of time.

The chemisorption process is usually a fast process and auxiliary experiments on the isopropyl alcohol/zinc oxide system showed that the adsorption of isopropyl alcohol is indeed a fast process. It is therefore clear that the desorption was essentially an equilibrium process. For the subsequent treatment of the results the concentration profile of the carrier gas in the catalyst bed is important. If there is no longitudinal diffusion (or rather if it is negligible compared to the carrier gas flow) complicated differential equations arise. The reactor which was used here was very shallow, however (about 1 mm deep) and the experiments have been carried out using low carrier gas flows (typically 0.25 cm/sec). There has then been only a small concentration gradient over the catalyst bed. By assuming that all isopropyl alcohol production took place in a plane perpendicular to the gas flow, and that the diffusion coefficient of isopropyl alcohol in nitrogen could be put equal to the diffusion coefficient of ethyl alcohol in air, it was found that the isopropyl alcohol concentrations would be only 20% lower in a plane 1 mm above. As desorption was taking place over the entire bed, the concentration difference must have been less than 20%. The simplifying assumption is then made that there was no concentration gradient over the catalyst bed.

The other experiments were carried out in a similar way to Experiment I, but the predesorptions (before starting the temperature rise) were carried out at higher temperatures. In all experiments the predesorption times were about 1 hr, at carrier gas flow rates about 20 ml/min.

The results of the four experiments reported here are shown in Fig. 1. In order to allow an easy comparison between the four curves the desorption rates have been plotted against temperature. For the theoretical treatment of the results time must be considered the independent variable, however.

Qualitative Discussion of the Results

By looking at the curves it becomes clear that the results cannot be interpreted on the basis of ordinary Langmuir adsorption for a homogeneous surface. The surface must clearly be heterogeneous. Several examples of adsorption on heterogeneous surfaces have been reported in the literature, and it is now clear that most surfaces are heterogeneous (*14–17*).

Visual inspection of the curves indicated that there were five different adsorption sites and these might give their main contribution at the temperatures where the triangles have been put on the abscissa. The exact positions of these triangles are not important as they will only be used for finding reasonable initial parameter estimates. The possibility

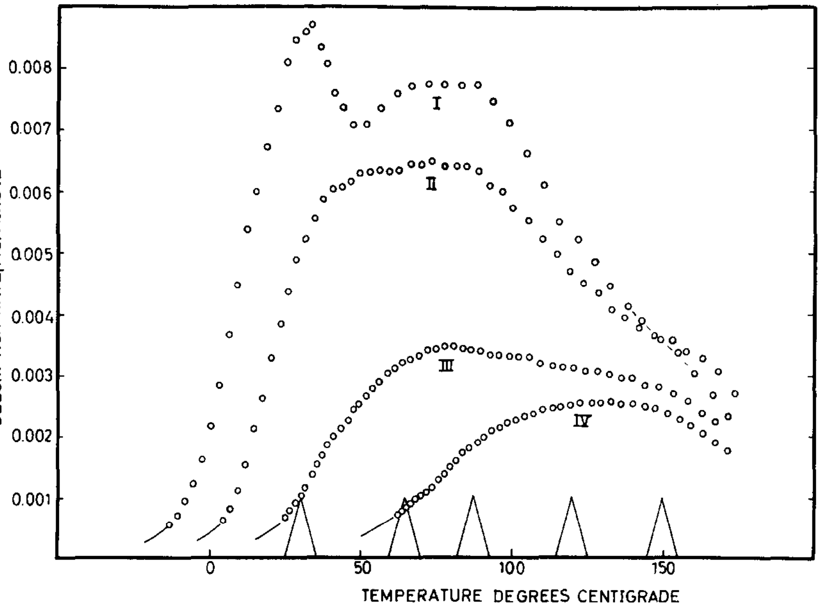

FIG. 1. Desorption rates plotted against temperature for the four experiments, which are described in the text. All four experiments have been performed on 32 mg of catalyst. The predesorption temperatures were as follows: Experiment I, −20°C; Experiment II, 5°C; Experiment III, 20°C; Experiment IV, 60°C.

that there may be other distributions, notably a continuous one, will be discussed in the following article (*5*).

It is apparent from Fig. 1 that the analytical precision in the determination of isopropyl alcohol concentrations in the emerging gas, from which the desorption rates have been calculated, is quite good. The standard deviation is 1% to 2%. Although the analytical precision is satisfactory the curves are somewhat uncertain at the high-temperature ends, which are known to be too low because the dehydrogenation of isopropyl alcohol to acetone is becoming quite important at the higher temperatures. This reaction is becoming visible at about 140°C, where a couple of percent of the isopropyl alcohol is converted to acetone. At 170°C about 50% is converted to acetone. It was shown above that essentially all the isopropyl alcohol can be desorbed as isopropyl alcohol, so the acetone which is found is evidently formed from the isopropyl alcohol shortly before it is swept out of the reactor. The reaction is not likely to affect the adsorption equilibrium between the catalyst and the gas phase, but it will have the effect of depleting the catalyst too quickly. The position of the most energetic adsorption site will then not be influenced so much (the effect of the reaction will be to move the peak towards lower temperature), but the amount adsorbed on the site will be estimated too low.

Preliminary experiments carried out with aged catalysts indicate that the desorption curves are influenced by aging, but quantitative results have not been obtained so far. A quantitative discussion of the results obtained here is given in the following paper (*5*), where it is shown how a complete analysis of the experimental results can be carried through.

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