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Note

Study of the heterogeneously catalyzed dehydrogenation of secondary alcohols using gas chromatography

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A technique was described¹ in which kinetics of heterogeneously catalyzed reactions could be studied using a simple gas chromatographic (GC) setup. The dehydrogenation of 2-propanol on manganese(II) oxide, a model reaction whose kinetics are well known, was chosen to determine the validity of this method. Results obtained from that study agreed well with literature values^{2,3}. As an extension of this work the dehydrogenation of other secondary alcohols on manganese oxides was chosen for investigation.

EXPERIMENTAL

A small amount of catalyst was placed in the front section of a chromatographic column. The injection port, a stainless-steel tube cast in a well-insulated aluminium heat cone, controlled the temperature of the catalyst bed. The catalyst bed was followed immediately by an analytical column for the separation of product from unreacted starting material. In this case the analytical column was a 12 ft. × 0.25 in. O.D. glass column packed with 20% SP2401 + 0.1% Carbowax 1500 on Chromosorb W AW DMCS (60–80 mesh) from Supelco (Bellefonte, PA, U.S.A.). The sieved (60–80 mesh) catalysts, manganese(II) oxide (99%+) and manganese(IV) oxide (99%+) were obtained from Chemetals Corporation (Baltimore, MD, U.S.A.). These were placed in the section of the glass column in the injection port. The temperature of the catalyst bed was monitored by a thermocouple pyrometer with parallax correction mirror. For measurements of retention volume of the reactants on the catalysts, a 15 in. × 2 mm I.D. glass column packed with the respective catalysts was used. A Varian Model 1840-1 gas chromatograph equipped with dual flame ionization detectors was connected to a Vidar Autolab digital integrator. The helium carrier gas was dried and purified over molecular sieve 5A and indicating calcium chloride, and regulated by a differential flow controller.

The reactants, 2-butanol and 2-pentanol and their respective dehydrogenation products, 2-butanone and 2-pentanone, were obtained from J. T. Baker (Phillipsburg, NJ, U.S.A.). The same headspace sampling technique as was described previously¹ was used for obtaining samples for injection.

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RESULTS AND DISCUSSION

Bassett and Habgood⁴ outlined a treatment for analysis of chromatographic data obtained from on-column catalysis experiments. For a rate-controlled surface reaction it can be shown that

$$\ln [1/(1-x)] = \frac{RTW}{F} \cdot kK \quad (1)$$

where x is the extent of conversion (calculated from chromatographic peaks for reactant and product), R is the gas constant, T is the temperature ($^{\circ}\text{K}$) of the catalyst bed, W is the total weight of catalyst in grams, F is the flow-rate (ml/sec) of carrier gas in the reactor, k is the rate constant of the surface reaction and K is the adsorption equilibrium constant. Thus, a plot of $\ln [1/(1-x)]$ vs. $1/F$ will yield a straight line whose slope is proportional to the product of the rate constant for the surface reaction and the adsorption equilibrium constant. The value of K is needed so that k can be calculated. Values of K and ΔH_{ads} are obtained from retention volume measurements at a number of different temperatures. This data is subsequently plotted in the form of a van 't Hoff plot. The apparent activation energy, E_a , may be obtained from the slope of a plot of $\ln kK$ vs. $1/T$, and at constant flow-rate this is equivalent to a plot of $\ln [\ln 1/(1-x)]$ vs. $1/T$. The value of the activation energy of the surface reaction is obtained by summing the apparent activation energy and the heat of adsorption.

The catalysis reactions for 2-butanol and 2-pentanol on MnO were carried out at five different flow-rates from 10 to 40 ml/min of helium at a constant injector temperature (192°C).

The catalysis reactions on MnO_2 were carried out at similar flow-rates, but at a temperature of 245°C . For each flow-rate the extent of conversion of each alcohol to its corresponding ketone was calculated from calibration curve and the known amount of reactant injected. Measurements of extents of reaction were also made at constant flow-rate but at different temperatures. For the reactions on MnO the temperature range was $140\text{--}200^{\circ}\text{C}$ at a flow-rate of 27.0 ml/min, while for those on MnO_2 the range was $175\text{--}300^{\circ}\text{C}$ at a flow-rate of 28.0 ml/min. It is felt that rate constants obtained from constant temperature *versus* variable flow-rate experiments are less reliable than those obtained from constant flow-rate *vs.* variable temperature experiments. The limited range of flow-rates due to (1) back pressure from a 12-ft. packed column and (2) the flame detector not staying lighted at high flow-rates is the basis of this reasoning. Results of the constant flow-rate *versus* variable temperature experiments are summarized in Table I.

In addition to the abovementioned alcohols all the primary alcohols through 1-octanol, including 2-methyl-1-propanol (isobutanol), were injected to determine if any of these would undergo dehydrogenation on MnO and MnO_2 to form the corresponding aldehydes. No reaction was observed in any of these cases ($T = 192^{\circ}\text{C}$, flow-rate = 27.0 ml/min for MnO ; $T = 245^{\circ}\text{C}$, flow-rate = 28.0 ml/min for MnO_2). The secondary alcohols, 2-propanol and 3-pentanol, were also injected under the same conditions. As was mentioned earlier¹ the dehydrogenation of 2-propanol is a well-known reaction, and indeed, dehydrogenation was observed on both MnO and

TABLE I
RESULTS OF CONSTANT FLOW-RATE VERSUS VARIABLE TEMPERATURE EXPERIMENTS

Reactant	ΔH_{ads} (kcal/mole)	E_a (kcal/mole)	$E_{Surface}$ (kcal/mole)	$k(sec^{-1})$
2-Butanol/MnO	-2.23	11.7	13.9	$2.05 \cdot 10^5 e^{-13,900/RT}$
2-Pentanol/MnO	-2.53	13.4	15.9	$1.25 \cdot 10^6 e^{-15,900/RT}$
2-Butanol/MnO ₂	-1.44	21.5	22.9	$1.61 \cdot 10^8 e^{-22,900/RT}$
2-Pentanol-MnO ₂	-2.32	25.4	27.7	$5.34 \cdot 10^9 e^{-27,700 RT}$

MnO₂. However, no reaction was observed in either case for 3-pentanol. Its structure

OH
|
corresponds to R₁-C-R₂ where R₁ = R₂ = -CH₂CH₃. The other secondary al-
|
H

cohols studied, but which do undergo dehydrogenation have a structure R¹-C-CH₃
OH
|
R¹-C-CH₃
|
H

Experiments on other secondary alcohols with structures corresponding to those above may provide an interesting area of study in which structure may be correlated with activity in catalytic reactions.

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