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Catalytic Dehydrogenation of 2-Butanol with ZnO and CuO

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The kinetics of the catalytic gas-phase dehydrogenation reaction of 2-butanol have been studied in the 189–248°C temperature range for ZnO and in the 129–200°C temperature range for CuO, using a gas-flow system. The effect of oxygen pretreatment of these semiconducting catalysts on the reaction rate and activation energy supports a reaction mechanism for the rate-limiting step involving oxygen surface states and hole charge transfer to the adsorbed alcohol at the catalyst surface. In the temperature ranges studied the only significant reaction of 2-butanol was dehydrogenation to 2-butanone.

INTRODUCTION

Recent advances have been made in the theory of the surface electronic properties of semiconducting catalysts (*1*, *2*) and the relation of these electronic properties to kinetic parameters such as activation energy (*3*). In the present work we compare the reaction kinetics of the gas-phase dehydrogenation of 2-butanol for the bulk *n*-type semiconductor catalyst ZnO with the bulk *p*-type semiconductor catalyst CuO, particularly the effect of oxygen pretreatment on reaction kinetics. Previous workers have considered this gas-phase reaction particularly with respect to yields obtained at higher temperatures where the competing dehydration reaction was significant (*4–6*), from an equilibria standpoint (*7*), and by a static method as a function of the orientation of the catalyst germanium (*8*).

Analysis of catalysis on semiconducting surfaces, where the reaction rate is assumed to be dependent on charge transfer between reactant adsorbate and semiconductor adsorbent leads to a consideration of the catalyst's energy band model. In particular, control of the relative positions of the band edges at the surface of the catalyst by suitable pretreatment, is of interest, since these surface band edge positions are related to the density of surface holes p_s and electrons n_s which may be involved in the charge transfer (*1*, *9*). The hole density at the surface of the semiconducting catalyst is related to the upper edge of the valence band at the catalyst surface E_{VS} and the Fermi reference level E_F by the equation:

$$p_s = N_V e^{(E_{VS}-E_F)}/kT, \qquad (1)$$

where N_V represents the density of states in the valence band. If hole transfer takes place, in the rate-limiting step of a reaction, to the reactant adsorbate at the catalyst surface, the rate of the adsorption reaction can be expected to be dependent on p_S. Equation (1) indicates that the magnitude of E_F, which is determined by the bulk electronic character of the catalyst, can also affect p_S, dependent on the relative magnitudes of E_{VS} and E_F; E_F remaining constant with respect to surface pretreatment. If oxygen, an acceptor adsorbate, is adsorbed on the catalytic surface during pretreatment, localized electronic surface-state energy levels due to the adsorbed oxygen accepting electrons from the bulk of the catalyst must be considered. Because charge neutrality at the catalytic surface is not maintained such oxygen surface

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states cause E_{VS} to increase, therefore, increasing p_s.

For an extrinsic *n*-type semiconductor, such as ZnO, where holes are minority charge carriers at the surface prior to oxygen pretreatment, $E_F > E_{VS}$, and oxygen pretreatment can be expected to influence p_s due to the increase in the term $(E_{VS} - E_F)$ in (1). For an extrinsic *p*-type semiconductor, such as CuO, holes are the majority charge carriers; $E_F < E_{VS}$, and p_s can be expected to be of great magnitude even without oxygen pretreatment. Such electronic energy band considerations do not, of course, exclude other rate-determining factors which may be involved due to oxygen pretreatment, such as chemical reactions which may remove catalytic inhibitors (*10, 11*).

EXPERIMENTAL DETAILS

The flow reactor used consisted of a 36 mm i.d. × 32 in. long outer quartz reaction tube with an inner quartz reaction tube 16 mm i.d. × 9 in. long, the latter containing about 10 g of ZnO or 35 g of CuO held in place by quartz wool plugs; the inner tube was centered in the outer tube. The inner tube with catalyst could be positioned in and out of the reaction temperature zone by use of a quick-disconnect fitting. Catalyst temperature was measured with a thermocouple in a quartz tube which was positioned to be in direct contact with the catalyst by use of a quick-disconnect fitting. Furnace temperature was controlled to within ±0.5° by use of an experimental proportional controller.

Reagent grade 2-butanol was obtained from Eastman Kodak Company and was further purified by standard procedures (*12*) including fractional distillation. The refractive index of the purified 2-butanol was 1.3946 at 25°C.

Reagent grade ZnO and CuO were obtained from Matheson Coleman and Bell; surface areas of these reagents were determined before and after reaction and oxygen pretreatment by the McFearin nitrogen adsorption method using a Perkin-Elmer Shell Sorptometer.

Nitrogen was used as a carrier gas for 2-butanol and was prepurified grade. Oxygen used for pretreatment was ultrahigh purity grade. These gases were obtained from Matheson Company. Initial constant partial pressures of 2-butanol were controlled by thermostating the alcohol in a Pyrex saturator through which nitrogen carrier gas was bubbled at a 100 $\text{cm}^3\ \text{min}^{-1}$ flow rate. Flow rates were measured with a Fischer-Porter Company flowmeter.

Overall reaction rates were obtained for reaction times of 3–5 hr. Reaction products were condensed in a dry ice–acetone cold trap and analyzed by gas chromatographic and refractive index measurements. Standard solutions were used to construct calibration curves for both of these methods of analysis. Gas chromatographic analysis showed less than 1% of the reaction product was other than 2-butanone and unreacted 2-butanol.

Catalyst pretreatment was effected *in situ* (*13, 14*) by flowing 50 $\text{cm}^3\ \text{min}^{-1}$ oxygen at 1 atm pressure through the catalyst charge held at 410°C, for about 30 min. Dehydrogenation reactions proceeded when reaction temperatures were established.

CALCULATION OF REACTION RATES

The overall, idealized, dehydrogenation reaction of 2-butanol taking place below 250°C, with ZnO or CuO as catalyst may be represented by the equation:

$$C_2H_5\text{—CHOH—}CH_3(g) \rightarrow C_2H_5\text{—CO—}CH_3(g) + H_2(g). \quad (2)$$

The inflowing gaseous moles of alcohol, n_i, to the reactor for unit time t is n_i/t, and can be expressed by the ideal gas equation:

$$n_i/t = (p_i/RT)(V/t) \text{ moles sec}^{-1}. \quad (3)$$

In Eq. (3), p_i is the partial pressure of alcohol in the inflowing gas stream, R the gas constant, T the temperature in degrees Kelvin at the flowmeter and (V/t) the gas flow rate ($\text{cm}^3\ \text{sec}^{-1}$).

Steady state moles of alcohol n_{alc} may be obtained from the equation:

$$n_{\text{alc}} = n_i - n_{\text{ket}}, \quad (4)$$

where n_{ket} represents steady state moles of ketone. The steady state moles of hydrogen and ketone formed by Eq. (2) are equal. These conditions, therefore, lead to the equation for the steady state mole fraction of ketone, X_{ket}:

$$X_{\text{ket}} = \frac{n_{\text{ket}}}{(n_i + n_{\text{ket}})}. \qquad (5)$$

Rearranging (5) and dividing by the catalyst surface area $A(\text{cm}^2)$, the overall reaction rate may be expressed in terms of moles of ketone formed per unit time per unit catalyst surface area by the equation:

$$n_{\text{ket}}/A \cdot t = [X_{\text{ket}}/A(1 - X_{\text{ket}})](n_i/t) \quad \text{moles sec}^{-1}\ \text{cm}^{-2} \qquad (6)$$

Equations (3) and (6) were combined and X_{ket} was evaluated by analysis of the condensed product 2-butanone and 2-butanol to determine the overall reaction rates. Conversion (100%) of alcohol to ketone corresponds to $X_{\text{ket}} = 0.5$ for the condensed ketone–alcohol mixture since moles of hydrogen gas formed equals moles of ketone formed.

RESULTS AND DISCUSSION

Effective activation energies $\Delta H^{\ddagger}_{\text{eff}}$ for oxygen pretreated catalysts ZnO and CuO have been found to be 1.8 and 6.7 kcal mole^{-1}, respectively, as evaluated from the Arrhenius-type plots shown in Fig. 1. The effective activation energies of the reaction for ZnO and CuO catalysts without oxygen pretreatment have been found to be 28.9 and 4.6 kcal mole^{-1}, respectively, as evaluated from the Arrhenius-type plots shown in Fig. 2.

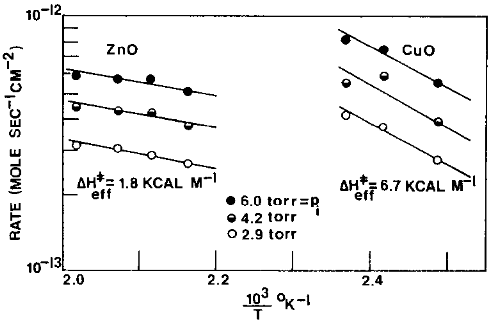

FIG. 1. Reaction rate as a function of temperature and p_i, the partial pressure of inflowing 2-butanol, for ZnO and CuO catalysts with oxygen pretreatment (activation).

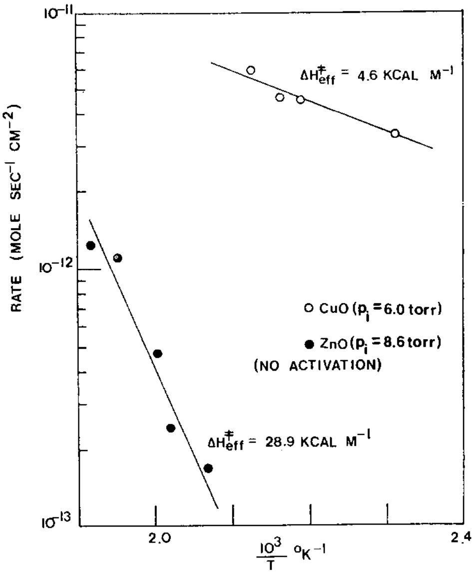

FIG. 2. Reaction rate as a function of temperature for ZnO and CuO catalysts without oxygen pretreatment (activation).

Reaction activation energy for ZnO with oxygen pretreatment as catalyst, of 1.8 kcal mole^{-1} compared to 28.9 kcal mole^{-1} without oxygen pretreatment supports the theory that catalyst surface-hole density p_s plays a part in the rate-limiting adsorption step. As discussed above semiconductor energy-band considerations indicate that oxygen pretreatment causes p_s to increase, therefore the observed increase in reaction rates and decrease in activation energy with such pretreatment indicate p_s determines the degree of charge transfer in chemisorption in the rate-limiting step, for ZnO as reaction catalyst.

The activation energy of the reaction for CuO with oxygen pretreatment of 6.7 kcal mole^{-1} compared to 4.6 kcal mole^{-1} without oxygen pretreatment indicates that pretreatment has little effect on the reaction kinetics since for a p-type semiconductor catalyst p_s is already of great magnitude. The latter theory is also supported by the greater reaction rates for CuO compared with ZnO as catalyst.

Because variation of the reaction rate

and activation energy support charge transfer by holes at ZnO and CuO semiconductor surfaces, chemisorption with hole charge transfer is proposed for the rate-limiting step in the temperature ranges studied. Because of steric effects involving chemisorption of the alcohol it is assumed that hole charge transfer involves hydrogen to a greater extent than for the adsorbed alcohol molecule. The dissociative, rate-limiting chemisorption step proposed is:

$$C_2H_5\text{—}CHOH\text{—}CH_3(g) + p_s \rightarrow C_2H_5\text{—}\underset{|}{C}OH\text{—}CH_3(ads) + H^+(ads), \quad (7)$$

followed by the reactions:

$$p_s + C_2H_5\text{—}\underset{|}{C}OH\text{—}CH_3(ads) \rightarrow C_2H_5\text{—}CO\text{—}CH_3(ads) + H^+(ads), \quad (8)$$

$$C_2H_5\text{—}CO\text{—}CH_3(ads) \rightarrow C_2H_5\text{—}CO\text{—}CH_3(g), \quad (9)$$

$$2H^+(ads) \rightarrow H_2(g) + 2p_s. \quad (10)$$

For the rate-limiting adsorption reaction (*7*) we propose that the hydrogen atom attached to the secondary carbon atom is the initial hydrogen adsorbed as indicated by previous workers (*15*) on similar systems.

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