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Catalytic Dehydrogenation and Oxidation of Propanol-2 on Platinum

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The relative rates of various pathways for the dehydrogenation and oxidation of propanol-2 on a platinum foil catalyst were determined by means of ultrahigh vacuum techniques. A clean platinum surface, which is an active and specific catalyst for dehydrogenation of propanol-2 to acetone, is rapidly poisoned by preferential sorption of CO. Addition of oxygen has no effect on the catalyst dehydrogenation activity, but at sufficiently high pressures leads to heterogeneous oxidation of the propanol-2. The results indicate that development of a selective propanol-2 dehydrogenation catalyst hinges on the capability of limiting the poisoning effect of CO.

INTRODUCTION

Results from earlier studies (*1*) indicate that the rate of dehydrogenation of propanol-2 to acetone on a platinum wire catalyst at 112°C is enhanced by the addition of oxygen to the fed gas. This process appeared to be an example of an oxidative dehydrogenation, which deserved further study to determine the precise role of oxygen in such a reaction.

The dehydrogenation of propanol-2 in the liquid phase over various catalysts has been examined by several investigators (*2–4*), all of whom reported an inhibition by the ketone product, but none of whom indicated enhancement by oxygen or air.

In the presence of hydrogen at temperatures below 150°C, the equilibrium (*5*) between propanol-2 and acetone is decidedly on the side of the propanol-2:

$$CH_3\text{—}CHOH\text{—}CH_3 \rightleftarrows CH_3\text{—}CO\text{—}CH_3 + H_2. \quad (1)$$

It seems likely, therefore, that oxygen promotes the dehydrogenation rate by reacting with surface hydrogen to form water, consequently displacing the equilibrium to the right side of Eq. (1).

To examine the elementary steps associated with this reaction, it is essential to be able to measure reaction rates and products obtained from a clean platinum surface. For this reason we employed ultrahigh vacuum (UHV) techniques to carry out our study.

EXPERIMENTS

Apparatus and Catalyst

The apparatus was assembled from standard UHV fittings, components, and materials in such a way that it could be cleaned by baking at temperatures up to 350°C. The basic system (Fig. 1) consisted of four parts:

1. The reactor was a 1.5 in. diameter cylindrical Pyrex tube attached to the vacuum system with Kovar-glass seals. Tungsten wire lead-throughs to support the catalyst were fused in the reactor at one end. At the same end an inlet conductance and an ionization gauge were also attached. The opposite end of the reactor was partially closed with a copper disk containing a 0.25 in. diameter aperture at its center, which served as a limiting conductance for flow out of the reactor.

The catalyst was a 0.005-in. thick ribbon

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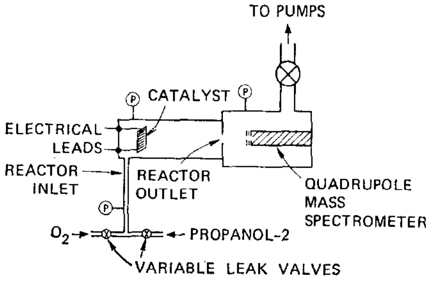

FIG. 1. Diagram of apparatus (P = ion gauge).

of 99.99% pure platinum with its ends spotwelded to the tungsten lead-throughs. Its total geometric surface area was 5 cm^2. The platinum ribbon could be heated up to ~1200°C by an electric current to desorb volatile surface impurities. The temperature of the catalyst was measured with a radiation thermometer using an appropriate emissivity correction.

2. The inlet system consisted of a tubular Pyrex conductance through which gaseous reactants could be metered into the reactor. Gas flow was controlled by adjusting the pressure at the upstream end of the inlet conductance with UHV variable leak valves. With this arrangement reactants could be admitted to the reactor at selected and constant mass flow rates. In all of our experiments, propanol-2 was admitted at a rate corresponding to an initial pressure of $(5 \pm 2) \times 10^{-8}$ Torr in the reactor.

3. The analytical device, used to give a continuous analysis of the products in the reactor effluent, was a quadrupole mass spectrometer. This unit was oriented so that the ionizing region was in line-of-sight alignment with the axis of the reactor and its outlet aperture.

Cracking patterns for all of the compounds encountered in this study were determined empirically using samples of the pure substances. The sensitivity of the mass spectrometer was calibrated for oxygen and for carbon monoxide using the ion gages to evaluate gas density. An absolute calibration for the organic components was not carried out.

4. The pumping system comprised a 50 liter/sec ion-getter pump with a titanium sublimation booster pump. The apparatus was rough-pumped from atmospheric pressure with a mechanical pump isolated from the system with a liquid nitrogen-cooled molecular-sieve trap. Base pressure in the system was less than 10^{-9} torr.

Procedure

Prior to each experiment the platinum ribbon catalyst was heated to ~1200°C for several minutes under vacuum. Upon cooling to the desired reaction temperature, the catalyst could be pretreated with oxygen or exposed to the reactant by appropriate manipulation of the inlet valves. In either case, a continuous analysis of the reactor effluent was recorded by the mass spectrometer. The mass range 1–60 was scanned repetitively with a period of approximately 1 min.

The propanol-2 employed was reagent grade material, dried by passage through a column of 4A molecular sieves, and vacuum distilled. The oxygen was research grade gas, 99.999% pure.

As is typical of all UHV systems, the major residual impurity in our system was CO. During periods of inactivity between experiments, this gaseous component would chemisorb on the reactor surfaces and on the catalyst. We measured the sticking probability of CO on our platinum ribbon and found it to adsorb at a nearly constant rate independent of pressure up to approximately half coverage of the surface (Fig. 2). With the catalyst saturated with chemisorbed CO, we introduced propanol-2 to the reactor. In this "blank" experiment at 25°C, no decomposition products were observed, thus demonstrating the absence of catalytic activity on any of the exposed surfaces in the reactor other than the clean Pt catalyst. Catalytic activity was restored to the platinum by thermal cleaning. During all experiments the ion-gauge filaments were extinguished to reduce CO pressure and to eliminate thermal decomposition reactions which might occur on the incandescent tungsten wires.

All experiments were carried out in the molecular flow region where the Knudsen number (mean-free-path/reactor-radius) is of ample magnitude to ensure a negligible

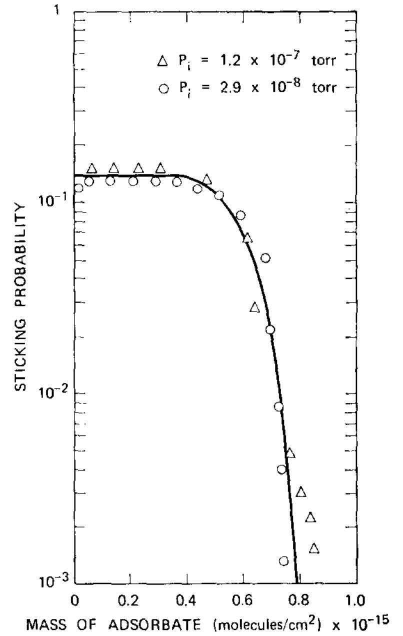

FIG. 2. Sticking probability of CO on Pt as a function of surface coverage at 25°C.

contribution due to homogeneous reaction by gas-phase collisions.

RESULTS

The freshly cleaned catalyst exhibited a high initial activity and specificity for the dehydrogenation of propanol-2 to acetone. In the catalyst temperature range from 25 to 400°C, only insignificant traces of organic vapors other than acetone and propanol-2 were observed in the reactor effluent. The initial high activity, however, diminished with time at variable rates. The time variations of activity in terms of the fractional yield of acetone in the reactor effluent are shown in Figs. 3 and 4 for typical experiments at 25 and 150°C.

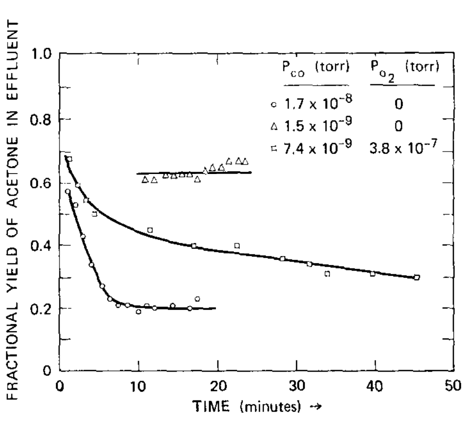

FIG. 3. Rate of formation of acetone from propanol-2 on Pt catalyst as a function of time after thermal cleaning. Catalyst temp: 25°C.

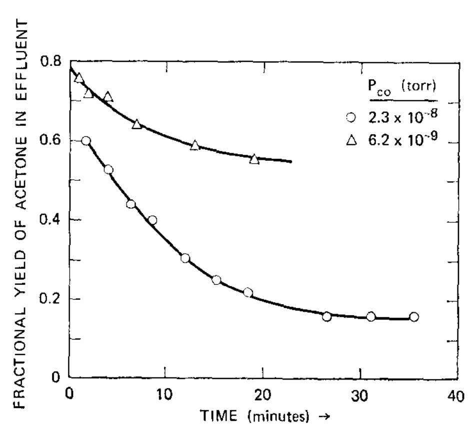

FIG. 4. Rate of formation of acetone from propanol-2 on Pt catalyst as a function of time after thermal cleaning. Catalyst temp: 150°C.

Pretreatment of the catalyst with oxygen appeared to diminish the catalytic activity, but in an unpredictable manner. The same was true when small quantities of oxygen were added to the propanol-2 feed stream (compare yields indicated by squares and by triangles in Fig. 3). The addition of larger quantities of oxygen, however, caused significant modification in the effluent composition. The variation in products and yield over a fivefold increase in oxygen pressure is shown in Fig. 5.

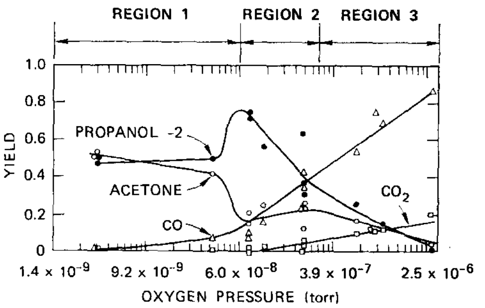

FIG. 5. Effect of oxygen on the reaction of propanol-2 on platinum at 150°C. $P_{CO(background)} \sim 6 \times 10^{-9}$ Torr.

Discussion

We were at first inclined to attribute the observed time decay of dehydrogenation activity of the catalyst (Figs. 3 and 4) to the accumulation of product (*4*) or an organic intermediate on the platinum surface. It has been demonstrated (*6*) that alkanes and olefins decompose on platinum by loss of hydrogen, leaving on the surface a carbonaceous residue.

However, Kemball and Stoddart (*7*) showed quite conclusively that the carbon skeleton in acetone remains unbroached in a platinum catalyst during hydrogenation to propanol-2. In our own experiments, we noted that the loss in propanol-2 dehydrogenation activity was related neither to the length of time the catalyst was exposed to reactant and product, nor to the magnitude of the initial yield of acetone (Figs. 3 and 4). Consequently, we dismissed acetone or an adsorbed intermediate as inhibiting agents.

Careful scrutiny of our data revealed that the pressure of residual CO varied substantially from one experiment to another. Qualitatively, the rate of decay of activity of the catalyst appeared to be proportional to the residual CO pressure (Figs. 3 and 4). Since we had a direct measure of the rate of adsorption of CO on platinum (Fig. 2), and since this rate was constant up to half-coverage, we could compute for each dehydrogenation experiment the period of time τ required to half-cover the catalyst surface with chemisorbed CO following thermal cleaning. The results of this computation (Table 1) show that the observed acetone-yield decay rates, represented by the initial slope of the curve in Figs. 3 and 4, have an inverse relationship to τ.

TABLE 1
Relationship of Loss of Dehydrogenation Activity to CO Coverage

Catalyst temp (°C)	Inverse of yield decay rate (initial slopes from Figs. 3 and 4) (min)	Time for 1/2 · coverage by CO τ (min)
25	13	12
	20	25
	∞	125
150	25	8[a]
	50	30[a]

[a] Based on CO sorption rate at 25°C.

Further evidence for the involvement of CO in the inhibition of catalytic activity is the observed lower limit of acetone yield at 25°C (Fig. 3). It is tempting to suggest that this limit in yield of 0.2 corresponds to the activity of the platinum surface covered to the extent of 80% by CO on which the rate of adsorption of additional CO (at 25°C) is extremely slow (Fig. 2). The close correspondence of the lower-limit acetone yield with the fraction of CO-free platinum surface may well be fortuitous, but the total weight of evidence obtained in these experiments points unmistakably to chemisorbed CO as the inhibiting agent in the catalytic dehydrogenation of propanol-2.

Pretreatment of the catalyst with oxygen or the addition of small quantities of oxygen to the propanol-2 feed (up to a propanol-2/oxygen ratio of ~1) has no apparent effect on the CO inhibition (Region 1 in Fig. 5). This is not surprising, for although oxygen chemisorbs on platinum at fractional coverages up to 0.5, subsequent exposure of the surface to CO will result in displacement of the chemisorbed oxygen by the CO, even at room temperature (*8*).

Examination of the product yield as a function of oxygen pressure (Fig. 5) shows that relatively large quantities of added oxygen never restore the clean-surface dehydrogenation activity of the platinum. However, the metal surface does exhibit activity as an oxidation catalyst.

In the region where the O_2/propanol-2 ratio is in the range 1 to 5 (Region 2 in Fig. 5) propanol-2 oxidation to CO occurs preferentially relative to acetone oxidation to CO. At the same time the lower limit of dehydrogenation activity of the catalyst seems to be unaffected, for the yield of acetone is sustained. At higher oxygen pressures (Region 3 in Fig. 5) conversion of all organics to CO and CO_2 predominates.

These observations suggest four distinct reactions paths:

$$CH_3\text{—}CHOH\text{—}CH_3 \rightarrow CH_3\text{—}CO\text{—}CH_3 + H_2, \quad (A)$$

$$CH_3\text{—}CHOH\text{—}CH_3 + 3O_2 \rightarrow 3CO + 4H_2O, \quad (B)$$

$$CH_3\text{—}CO\text{—}CH_3 + 5/2O_2 \rightarrow 3CO + 3H_2O, \quad (C)$$

$$2CO + O_2 \rightarrow 2CO_2. \quad (D)$$

Reaction (A) predominates on clean platinum but is progressively inhibited by the accumulation of chemisorbed CO down to a limiting minimum activity. This reaction is unaffected by added oxygen except indirectly by the CO generated from concurrent oxidation of propanol-2 (Fig. 5, Region 1). Reaction (B) attains kinetic significance when the O_2/propanol-2 ratio has a value near unity and shows a marked increase in rate with increase in oxygen pressure. At O_2/propanol-2 ratios up to about 5, acetone is oxidation stable. [This fact was noted in earlier, higher pressure experiments (*1*) also.] Consequently, in this range of oxygen pressure (Fig. 5, Region 2), acetone yield shows a net increase as a function of P_{O_2}. At higher oxygen pressures, reactions (C) and (D) become of kinetic importance, and eventually CO and CO_2 are the only products of reaction (Fig. 5, Region 3).

We suggest that the modest oxygen enhancement of acetone yield from propanol-2 observed in earlier higher pressure experiments (*1*) was a manifestation of the competition between oxidation and dehydrogenation of the alcohol on platinum. We conclude that oxygen is not a promoter for the catalytic dehydrogenation of propanol-2. On the contrary, an oxygen-free, carbon monoxide-free catalyst exhibits both high activity and high selectivity for this reaction. The development of such a catalyst for higher-pressure systems may well be a worthy endeavor. The use of a hydrogen permeable membrane catalyst (*9*) may be particularly adaptable to this reaction, since it provides a sink for hydrogen without adding another reactive species (such as O_2) to the reaction mixture.

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