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Kinetic Measurements and XRD Investigations *in Situ* of a V_2O_5–SiO_2 Catalyst for the Vapor-Phase Oxidation of Tetrahydrofuran to γ-Butyrolactone

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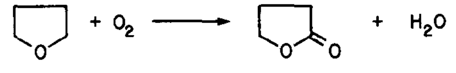
The kinetics of the oxidation of tetrahydrofuran (THF) to γ-butyrolactone over a V_2O_5–SiO_2 catalyst have been examined. An isothermal, fixed-bed reactor, operating at atmospheric pressure and temperatures between 170 and 215°C was used to obtain reaction rate data. X-Ray diffraction measurement *in situ* shows significant proportion of V(IV) on carrying out the oxidation of THF on the catalysts. Reduction in H_2 at temperatures above 170°C gives rise to V_4O_9, which is similar to the effect when the reduction is effected by THF. The rate data have been correlated by a rate equation developed on the basis of a two-step redox mechanism.

INTRODUCTION

V_2O_5-based catalysts are frequently used in the selective vapor-phase oxidation reactions of organic compounds. The vapor-phase reaction of tetrahydrofuran (THF) with oxygen may give a convenient route to the synthesis of γ-butyrolactone.



It is known that γ-butyrolactone is prepared by metallic ion-catalyzed decomposition of α-(hydroperoxy) tetrahydrofuran (*1–4*) and by the oxidation of THF by RuO_4 (*5–7*) or H_3PO_4 (*8*), but there is no systematic kinetic study on γ-butyrolactone formation by vapor-phase oxidation of THF.

It is important to investigate which phases of vanadium oxide are present in the catalysts under reaction conditions. Generally it is expected that under reaction conditions the catalyst will contain a certain amount of lower oxides formed by the reduction of the original V_2O_5 catalyst. Such oxidation-state changes have been described in the literature for a variety of reactions, for example, in recent papers concerning the oxidation of toluene on a V_2O_5/Al_2O_3 catalyst (*9*), the oxidation of alkylpyridines on V_2O_5/TiO_2 and V_2O_5/SnO_2 catalysts (*10, 11*), the ammoxidation of 3-picoline with V_2O_5/SnO_2 (*12*) and with other different vanadium oxides (*13, 14*), and ethylene oxidation to acetic acid with V_2O_5/Pd (*15*). The catalysts were calcined at 400°C when used for ethylene oxidation (*15*), at 450°C for toluene oxidation (*9*), and in the range of 1150–1250°C in other cases (*10–12*). Investigations of the structural dynamics of V_2O_5–SiO_2 catalysts when used for the oxidation of tetrahydrofuran have not been published previously. For this pur-

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pose, an especially designed temperature-programmed *in situ* X-ray diffractometry has been used to follow the oxidation-state changes of a V_2O_5–SiO_2 catalyst in the oxidation of THF. This technique is of value in obtaining information about the exact phases present in the catalysts during the reaction. For the purpose of comparison, we have also studied the reduction of the catalyst in H_2 at various temperatures.

In the study presented here, the active phase of the V_2O_5–SiO_2 system was examined in conjunction with kinetic measurements to elucidate the mechanism of THF oxidation over this catalyst. The present paper is limited to results when using a catalyst composition of 20% by weight of V_2O_5, and 80% by weight of silica, calcined at 450°C.

EXPERIMENTAL

Catalyst Preparation

Supported V_2O_5 (20%) catalysts were prepared by intermixing a colloidal silica sol with ammonium metavanadate powder. The resulting solution was vacuum-dried at 70°C and then calcined at 450°C for 6 hr.

Temperature-Programmed in Situ X-Ray Diffractometry

The *in situ* X-ray diffraction patterns of the catalysts and their base components—V_2O_5 and SiO_2—were obtained from an automated Rigaku Theta-Theta wide-angle goniometer run in horizontal mode and controlled by an INTEL 8-bit SBC 80/204 single-board computer with 48K of RAM. The INTEL 8080 microcomputer is supported by an RMX-80 real-time operating system, and comes with a Beehive keyboard and video display unit and two 8-in. single-density Data Systems floppy disks having 512-kbyte storage capacity. The goniometer stepper motor driver, a Fluke temperature indicator, and an ECS temperature controller and soft-start power pack are integrated into a versatile data acquisition and display system through interface hardware and PLM software. The hardware functions are controlled in a multitasking mode through an extensive library of programs called from dual disks. In-house software protocol provides easy data transfer to a host PDP-10 computer, from which data files are manipulated through interactive file editing and data smoothing routines in support of off-line nonlinear least-squares profile fitting, deconvolution, and plotting functions.

The wide-angle diffractometer is equipped with a long fine focus copper target, driven by a 3KW Rigaku generator. All scans were collected at 40 kV and 25 mA with 2° divergence slits and 0.30-mm receiving slits.

The *in situ* reactor/furnace was fitted with a specially designed fixed-bed reactor floated in the trough of an open-end, three-component radiative-type serial-heating element with stainless-steel reflector plates, and mated to an evacuable aluminized canister. The water-cooled reactor/heater was powered to approximately 700°C in a multisegment, programmable temperature control mode through a variable proportional-integral-differential algorithm. Two stainless-steel sheathed iron–constantan thermocouples were used as sensors for the temperature controller.

Reagent-grade tetrahydrofuran was transported in vapor phase via helium carrier to the reactor from a 500-ml gas washing bottle heated to approximately 50°C. Metered helium carrier gas containing THF was then directed into a 10-ft copper helical coil immersed in a constant-temperature—40°C—bath. Flowthrough of reactant was maintained at approximately 0.08 liter/m and 28–30°C at the entry port of the reactor. Hydrogen flow was metered at less than 0.01 liter/m after canister evacuation and nitrogen purge. Similar experiments were conducted with oxygen, but at flow rates between 0.05 and 0.10 liter/m.

Kinetics

Reactions were carried out in a fixed-bed-type reactor with a continuous-flow system at atmospheric pressure. The apparatus was similar to that used by Athappan and Srivastava (*16*) in the decomposition of cyclohexanol. However, some of the details of the equipment vary between experiments. A brief description of the equipment used in this study is necessary. THF was fed by the calibrated metering pump into a preheater. These vapors were picked up by an incoming oxygen stream and the oxygen-feed mixture was lead to the reactor. The reaction products were passed through a water trap and ice water condensers and were analyzed by GLC using PEG 20M and PORAPAK QS columns.

During the runs, the reciprocal of space velocity was varied by changing the amount of catalyst. The experimental conditions were so chosen by preliminary investigation that the reaction rate was not influenced by external and internal diffusion. A temperature range of 170–215°C was covered, and the reaction temperature reported is the average bed temperature and is accurate to ±1°C. The average size of the granules was $(-8+10)$-mesh size.

The experimental data were taken under steady-state conditions, in which a minimum of seven runs was made in 30-min intervals after steady state had been attained. The standard deviation was less than 1.5%. The average of the last two values of these analyses was used for estimation of conversion. Fresh catalyst was used in each run.

RESULTS AND DISCUSSION

X-Ray Diffraction Investigations of Catalysts

In situ X-ray diffraction measurements of V_2O_5, SiO_2, and V_2O_5 on SiO_2 support were made at programmed 2θ and temperature intervals under different gas exposures. The initial gas flow experiment was conducted with hydrogen and the catalyst base component V_2O_5, mainly to identify phases formed at the designated temperatures under conditions simulating the THF experiment. Figure 1 shows the gradual reduction of V_2O_5 in hydrogen as the sample was heated from 25 to 300°C. A mixture of two phases—V_2O_5 and V_4O_9—is evident at 200°C after a previous 3-hr exposure to hydrogen at 100°C. V_4O_9 is the arrested stage of reduction at 300°C, with a minor amount of retained V_2O_5. Bragg reflections consistent with Powder Diffraction File card 23-720 (V_4O_9) confirm the steady-state phase formation. Unidentified peaks in the 300°C run are apparent at $3.6\bar{3}$ ($2\theta = 24.50$), $3.5\bar{1}$ ($2\theta = 25.36$), and $2.97\bar{8}$ ($2\theta = 29.98$) Å. No structural changes were observed in the SiO_2 catalyst support upon flow exposures to H_2, THF, or O_2, and at programmed temperature stages of 100, 200, and 300°C, in similar manner to V_2O_5. Both materials showed no structural changes upon air exposure at successive temperature segments. All intensity units in Figs. 1–4 are arbitrary for convenience of presentation.

A similar flow experiment was conducted with the catalyst—V_2O_5/SiO_2—heated to 100, 170, and 300°C, while maintaining a hydrogen flow rate of 0.01 liter/m. The results are shown in Fig. 2. As expected, V_4O_9 is the major phase formed at 300°C upon exposure to hydrogen. Unidentified lines are evident at 3.05 ($2\theta = 29.25$) and 2.95 ($2\theta = 30.28$) Å.

The object experiment of catalyst exposure to tetrahydrofuran was conducted over a period of 16 hr. The result of the V_2O_5/SiO_2 partial reduction to V_4O_9 at 170°C, and more extensive reduction at 200°C, is shown in Fig. 3. All peaks are identifiable as V_4O_9 (major phase) or residual V_2O_5. Unlike the hydrogen experiment, all peaks are related to V_4O_9 or V_2O_5 at 100, 170, 200, 225, and 300°C.

A final experiment was conducted to investigate the steady-state composition of the V_2O_5/SiO_2 catalyst at 200°C after heating the catalyst in air, evacuating the canister to 100 mm Hg for 30 min, and backfilling with helium. The catalyst was then exposed to flowing THF/O_2/helium for 16 hr. As indicated, no reduction was observed in air; however, expectedly, on carrying out the

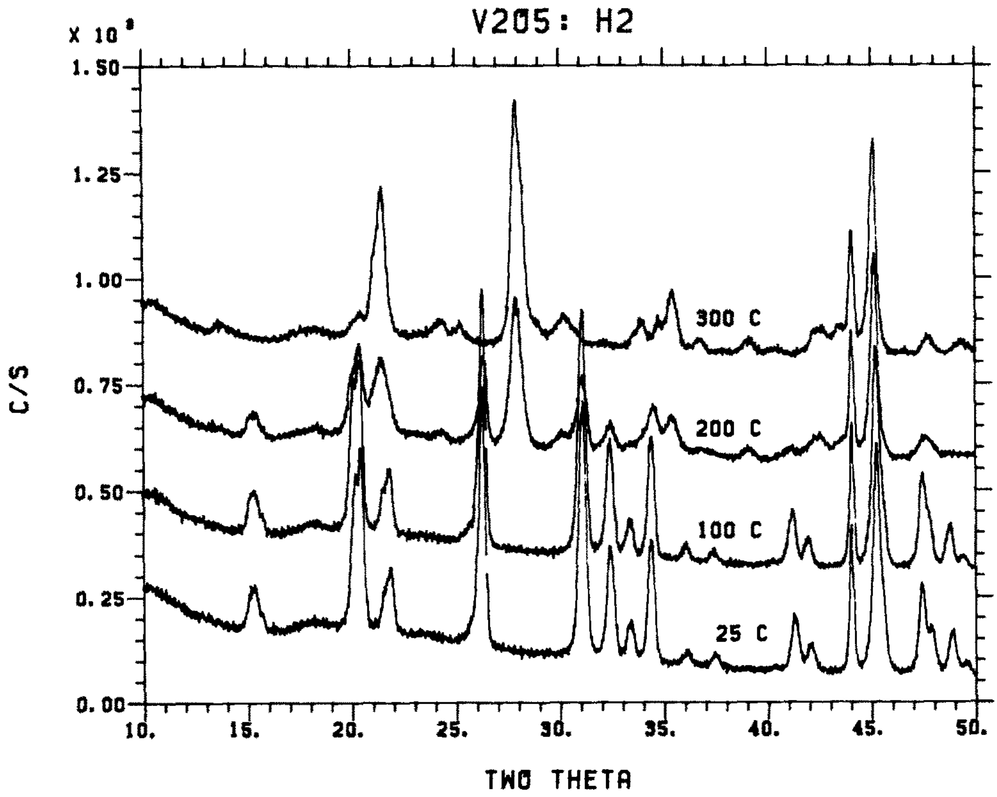


FIG. 1. *In situ* X-ray diffraction patterns of V_2O_5 in H_2 at various temperatures.

oxidation of THF we find that V_4O_9 is predominant with a small amount of V_2O_5. Both exposures in Fig. 4 represent steady-state conditions. Oxygen flow for the next 16 hr—with diffraction patterns collected intermittently—did not completely restore the reduced state to the V(V) state. The rate of reoxidation was slower than that of reduction.

It has also been reported by Seoane *et al.* (*15*) that V_4O_9 is the only reduced phase existing at the steady state, as in our catalyst. Their catalyst also comprises some remaining unreduced vanadium pentoxide in their studies of ethylene oxidation to acetic acid. This phase was characterized by the weight loss of V_2O_5, and by X-ray diffraction for the final catalysts. Pd added to V_2O_5 only enhanced the reducibility of this oxide. ESCA studies on V_2O_5–Al_2O_3 also showed significant proportion of V(IV) on carrying out the oxidation of toluene (*9*).

Kinetics of the Reaction

The effect of various variables, reactant mole fraction, $\bar{R}$ = THF/O_2; reaction temperature, T; the reciprocal space velocity, W/F (g-cat hr/mole), on the conversion were investigated. Figure 5 presents the conversion as a function of space velocity at 200°C for $\bar{R} = 0.5$. It is seen that though the conversion increases with a $W/F = 10$, the change from 10 to 18 was very small.

Reaction kinetics were examined at the temperatures of 170, 185, 200, and 215°C in a low W/F condition. The feed rate for THF was between 0.78 and 2.83 g · mole/hr. The products contained unreacted THF, γ-butyrolactone, and water. Among by-products, only traces of succinic acid were confirmed; they were not included in the kinetic analyses. Rate calculations were based on conversion to γ-butyrolactone. Figure 6 shows the effect of feed ratios ($\bar{R}$)

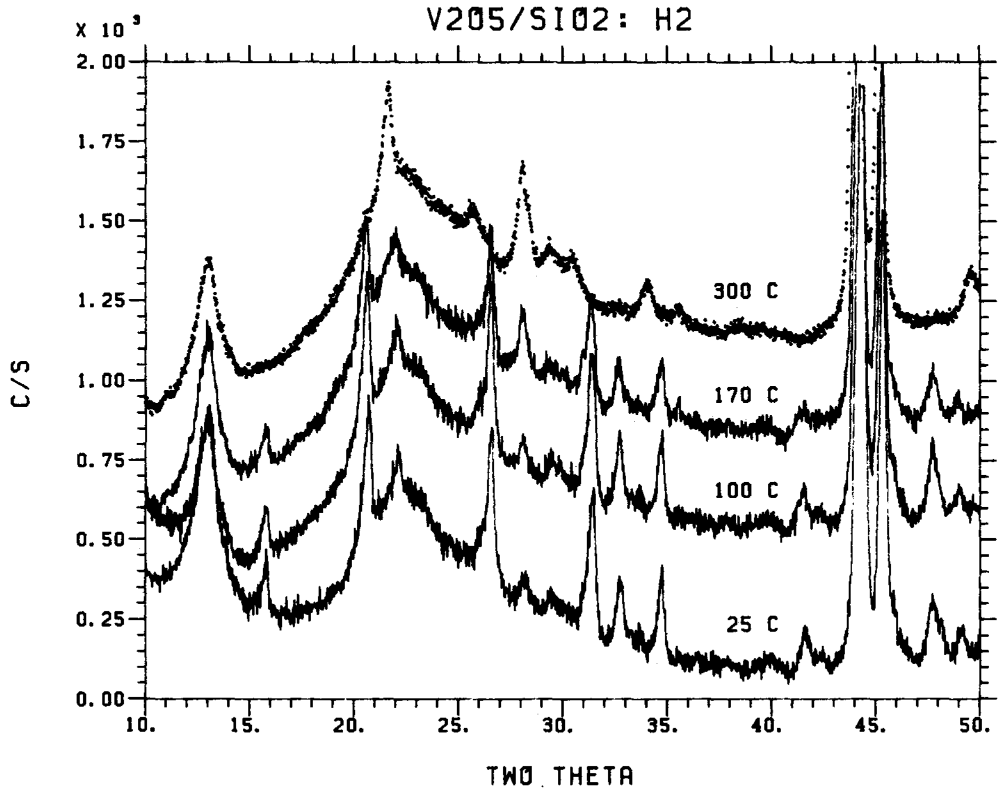


FIG. 2. *In situ* X-ray diffraction patterns of V_2O_5–SiO_2 in H_2 at various temperatures.

on the reaction rate for a $W/F = 9.0$.

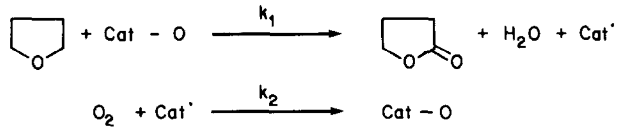
Experiments were also carried out with mixed feed to study product inhibition. The products of this reaction do not poison, for the addition of 5 mole% of water or γ-butyrolactone or the efficiency of the reaction.

Reaction Mechanism

It is generally assumed that in the oxidation reactions a reduction–oxidation mechanism is valid. This mechanism was first proposed by Mars and Van Krevelen (*17*) for the oxidation of naphthalene catalyzed by V_2O_5, and was later confirmed for many oxidation reactions (*18–24*).

We could show that THF is able to reduce vanadium (V) to (IV) as the major crystalline components. In order to introduce the redox mechanism, the following model may be considered. THF is chemisorbed on the oxidized sites V(V). This chemisorbed THF is transformed into chemisorbed lactone by the underlying lattice oxygen. After this step, the lactone is found chemisorbed on reduced sites V(IV). This chemisorbed lactone can desorb to the gas phase, thus liberating the reduced sites. The molecular oxygen is chemisorbed on the reduced sites V(IV), oxidizing them by incorporation into the crystalline lattice of vanadium oxide.

The degree of reduction at steady state depends on the kinetics of the following two types of reaction,



(1)

(2)

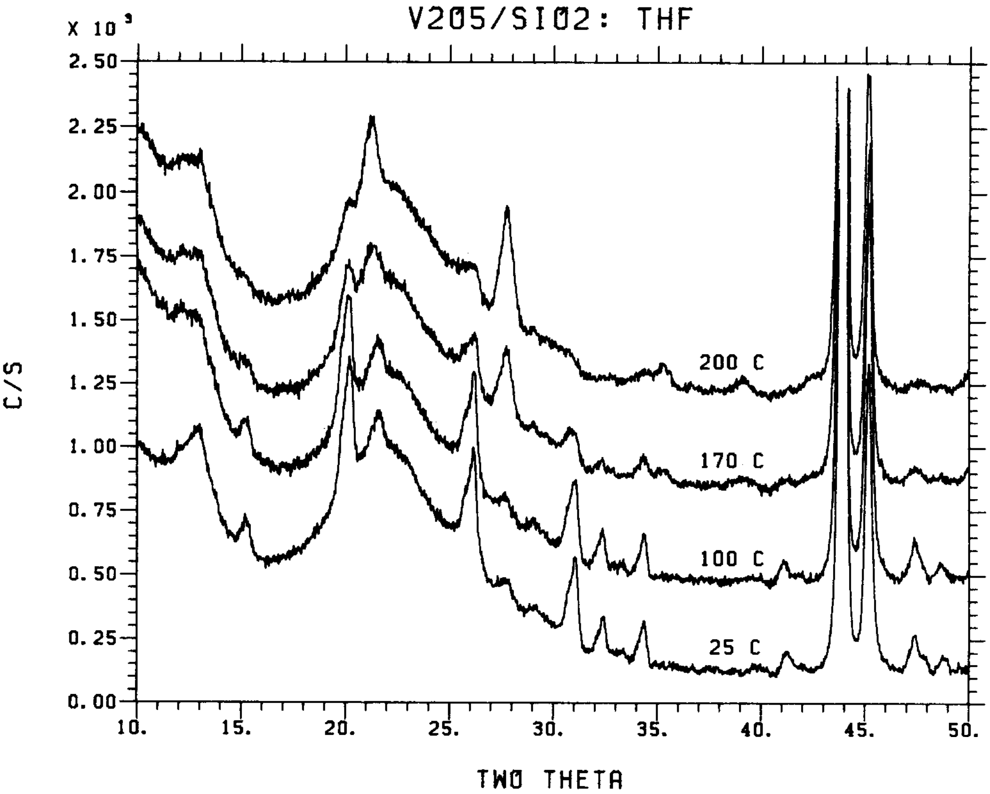


FIG. 3. *In situ* X-ray diffraction patterns of V_2O_5–SiO_2 in THF at various temperatures.

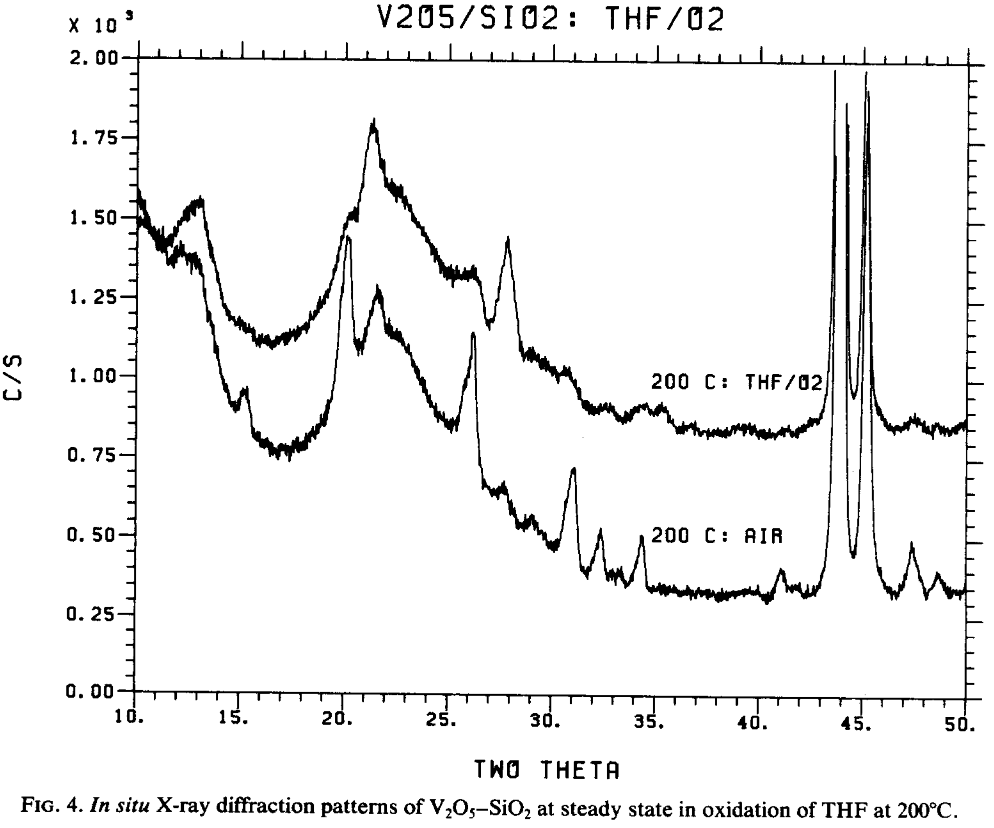


FIG. 4. *In situ* X-ray diffraction patterns of V_2O_5–SiO_2 at steady state in oxidation of THF at 200°C.

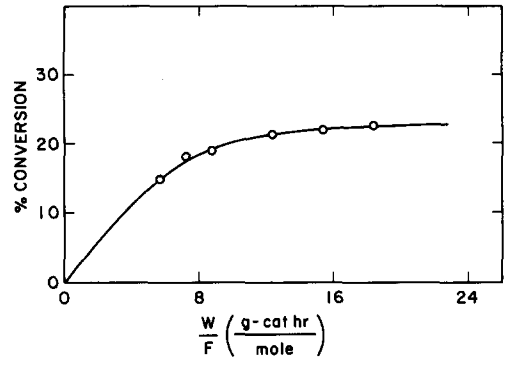


FIG. 5. Variation of the conversion of THF with W/F at 200°C; $\bar{R} = 0.5$.

where Cat-O and Cat' denote active site and reduced site, respectively. When the rates of both processes (Eqs. (1) and (2)) are equal, it is possible to derive an expression for the oxidation of THF, similar to one proposed by Sharma and Srivastava (*22*) for the oxidation of toluene and methanol:

$$\gamma = \frac{k_1 p_{\mathrm{THF}}}{[1 + (k_1/k_2)(p_{\mathrm{THF}}/p_{\mathrm{O_2}})]} \tag{3}$$

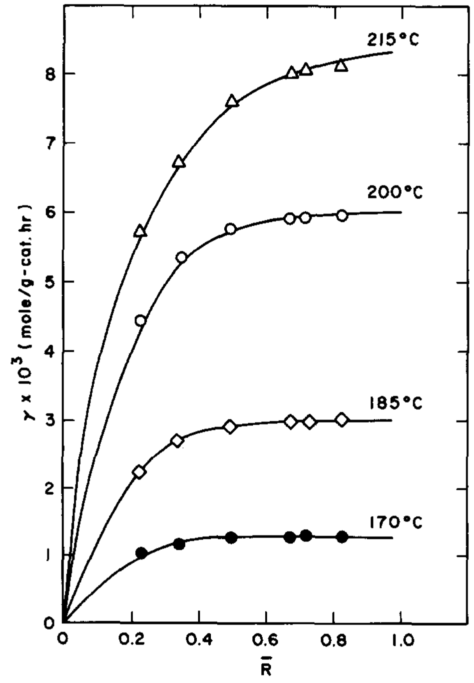


FIG. 6. Dependence of the reaction rate on $\bar{R}$ at various temperatures; $W/F = 9.0$.

TABLE 1

Rate Constants at Various Temperatures

Temperature (°C)	k_1 (gmole · hr^{-1} · g^{-1} · atm^{-1})	k_2 (gmole · hr^{-1} · g^{-1} · atm^{-1})
170	1.1×10^{-2}	2.8×10^{-3}
185	2.1×10^{-2}	5.8×10^{-3}
200	3.3×10^{-2}	10.0×10^{-3}
215	6.3×10^{-2}	22.4×10^{-3}
	$\Delta E_1 = 15$ (kcal/mole)	$\Delta E_2 = 18$ (kcal/mole)

which on rearrangement gives

$$\frac{p_{\mathrm{THF}}}{\gamma} = \frac{1}{k_1} + \frac{1}{k_2}\left(\frac{p_{\mathrm{THF}}}{p_{\mathrm{O_2}}}\right). \tag{4}$$

This equation could be checked using data of Fig. 6, as shown in Fig. 7. The estimated values of k_1 and k_2 at the reaction temperatures of 170, 185, 200, and 215°C are summarized in Table 1. From the dependence of the values of k on the reaction temperature, the activation energy of the reduction step is estimated as 15 kcal/mole, while that for the reoxidation is calculated as 18 kcal/mole, indicating a satisfactory temperature relationship.

It is therefore concluded that the oxidation of THF over the V_2O_5–SiO_2 catalyst may proceed via the oxidation–reduction cycle V(V) $\rightleftarrows$ V(IV). In addition to data interpretation, the resulting rate equation was based on insight into the true physicochemical nature of the process.

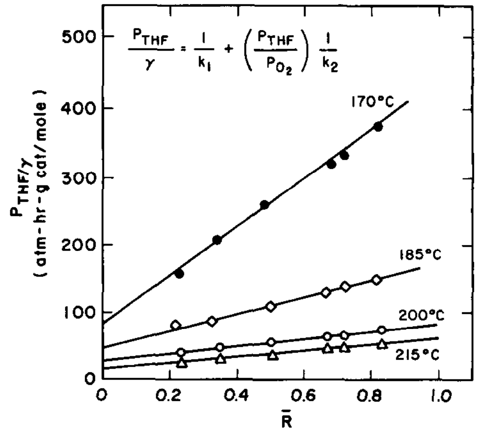


FIG. 7. $p_{\mathrm{THF}/\gamma}$ – vs – $\bar{R}$ plot.

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