JOURNAL OF CATALYSIS 60, 216–227 (1979)

Conversions of Isopropanol by Processed Coal Minerals and Pyrite

JEAN-PIERRE JOLY[1] AND DAVID OLLIS

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

Received November 25, 1977; revised March 2, 1979

Pyridine-extracted residues from coal liquefaction processes catalyze the conversion of isopropanol into acetone and propene, as do samples prepared from powdered pyrite. At 350°C and conversions above 10%, the ratio of (propene/acetone) is near to the equilibrium value for all coal- or pyrite-derived samples, independent of the degree of isopropanol conversion. This result suggests that all samples studied directly catalyze the reaction (propene + H_2O) $\rightleftarrows$ (acetone + H_2). As all tests for such a direct path were negative, the direct path does not exist for this latter reaction. Possible conversion paths for isopropanol are indicated.

INTRODUCTION

A catalytic role of natural coal minerals under liquefaction conditions has been suggested for decades, but convincing experimental evidence has only begun to appear recently. Wright and Severson (*1*) showed that addition of coal minerals and especially pyrite aided the hydrogenation conversion of coal with anthracene oil, apparently by assisting the rehydrogenation of the spent solvent. These authors also suggested that the alkali content of lignite appears to be related to the catalytic activity for coal hydrogenation with carbon monoxide and water.

Mukherjee and Chowdhury (*2*) used a density difference technique to separate ground coal into fractions of varying mineral content. Using high vitrinite samples which were also high in sulfur and relatively low in ash, they observed that conversions by hydrogenation (400°C, 3 hr, 100 kg/cm^2 pressure H_2) were increased from about 22 to 83% as the grams of natural mineral matter per 100 g organic matter increased from zero to nearly 58%. Incorporation of organic sulfur in samples which contained more than half of the iron in nonpyritic forms also increased the conversions. Some nonstoichiometric iron monosulfides formed during hydrogen pretreatment were believed to be the active catalyst but no definitive phase identification was presented. Impregnation with titanium hydroxide also increased conversion. Finally, these workers noted that addition of kaolinite also led to greater conversion of coal to gas and benzene soluble products, suggesting a cracking catalyst behavior.

Recently, Hodek and Kühn (*3*) confirmed that pyrite addition has a clear catalytic effect in hard coal hydrogenation using methylnaphthalene solvent, the active phase appearing to be a decomposi-

---

[1] Address: Ecole Superieure de Chimie Industrielle de Lyon, Université Claude Bernard, 43 Blvd 11 Nov 1918, Lyon I, 69621 Villeurbanne, France.

0021-9517/79/140216-12$02.00/0

tion product of pyrite. These authors suggested that high pyrite coals which have an otherwise tolerable mineral content were, in principle, well suited for hydrogenation at liquefaction conditions.

The catalytic importance in liquefaction of added mineral matter which closely resembles coal minerals being established, the pertinent questions are:

(i) What catalytically active phases may be identified in coal materials?

(ii) What role do these phases play under liquefaction conditions?

A fundamental elucidation of the first question will more likely arise with simpler reactants than coal. In particular, the use of model reactants to probe for separate kinds of activity appears fruitful here as in other areas of catalysis. For example, Morooka and Hamrin (*4*) studied thiophene desulfurization over coal mineral matter which had been obtained by low temperature ashing of ground, unprocessed coals using an ambient oxygen discharge. When their results are considered on a surface area basis (rather than weight used by the authors), the most active presulfided (H_2S treatment) minerals were about 3% as active as a commercial HDS cobalt molybdenum catalyst. Ashed coal minerals also equilibrated isomers for the easier reaction of butene isomerization, yet the butane/butene ration was far less than the equilibrium value at 400°C and total pressure of 103 kN/m^2 (*4*).

The present paper describes conversion of the model compound, isopropanol, over processed coal mineral matter concentrated from liquefaction bottoms by pyridine extraction. As minerals, especially pyrites and hydrated clays, are altered under the relatively mild temperatures of liquefaction, the study of the extracted *residue* would appear to provide a more meaningful guide to possible *in situ* liquefaction activity than an examination of minerals from unprocessed coals cited in the previous paragraph.

The isopropanol decomposition test reaction (*5*) was chosen because: (i) it is an easily catalyzed reaction (even weak catalytic activities would be noticeable), (ii) both dehydration and dehydrogenation activity may be probed in the same experiment, and (iii) the selectivity with which these two conversions occur may be useful in the identification of the active phases. Specifically, while solid acids are useful for dehydration, and metals usually provide only (de)hydrogenation activity, semiconductor phases may be expected a priori to yield products of both reactions classes with selectivity characteristic of each active particular phase and method of preparation.

The use in the present study of coal minerals of different geographic origins, which presumably contain a variety of oxides and several sulfur phases, might be expected to produce a range of selectivities in catalytic conversions of isopropanol if a number of different active phases are present (assuming that the reaction products are not equilibrated with each other).

MINERAL SAMPLES

Pyridine-extracted mineral samples derived from coal liquefaction bottoms were provided by Dr. Duane Whitehurst of Mobil Research and Development Corporation. As seen in Table 1, the coals processed were from three different US locales. Crystalline pyrite mineral was a gift of Prof. David Crerar. Pyrite powders were prepared by hand grinding in a ceramic mortar.

EXPERIMENTAL

The apparatus design for the isopropanol studies is that of de Mourgues (*6*) which is shown in Fig. 1. Helium passing through the saturators carries the desired partial pressure of isopropanol into the reactor.

TABLE 1

Catalyst Samples

Sample (m^2/g)[a]	Coal	Liquefaction treatment (min)
52 (9.9)	1LL6BS	393
62[b] (**)	1LL6MT	0.75
67 (37.1)	WKY14	2.0
70 (11.9)	1LL6MT	90.
83 (13.9)	1LL6BS	1.1
89 (9.15)	WYODAK	2.0

[a] Specific area of pyridine extracted material.

[b] Sample too small.

Under the entire range of flow rates of this study (10–270 cm^3/min), the isopropanol partial pressures entering the reactor depended only on the temperature of the final saturator and showed no dependence with flow rate. The latter saturator temperature was typically 19.9 ± 0.1°C, just under ambient temperature to avoid downstream condensation in the apparatus.

A 4-mm (i.d.) U tube reactor was completely filled with catalyst and/or quartz chips in order to minimize any homogeneous reactions. The catalytic section of 8 cm length in the center of the oven typically contained several tenths of a gram of mineral matter. The forced air chromatograph oven allowed temperature control to ±1°C. A mercury partial immersion thermometer, the reservoir of which was located near the reactor, provided temperature indications within 1°C of that shown on the oven indicator. The maximum total pressure drop across the packed bed was a few millimeters Hg.

The reacted mixtures of propene, acetone, water, and isopropanol were separated with a Perkin Elmer 820 gas chromatograph using a 12-ft, $\frac{1}{8}$-in.-diameter column of Poropak 180–100 mesh at 150°C, a 1-cm^3 sampling valve, and a thermal conductivity detector. Calibration volumes versus peak areas were linear, water was not determined, and a base line correction was applied to the propene peak. A sample analysis required

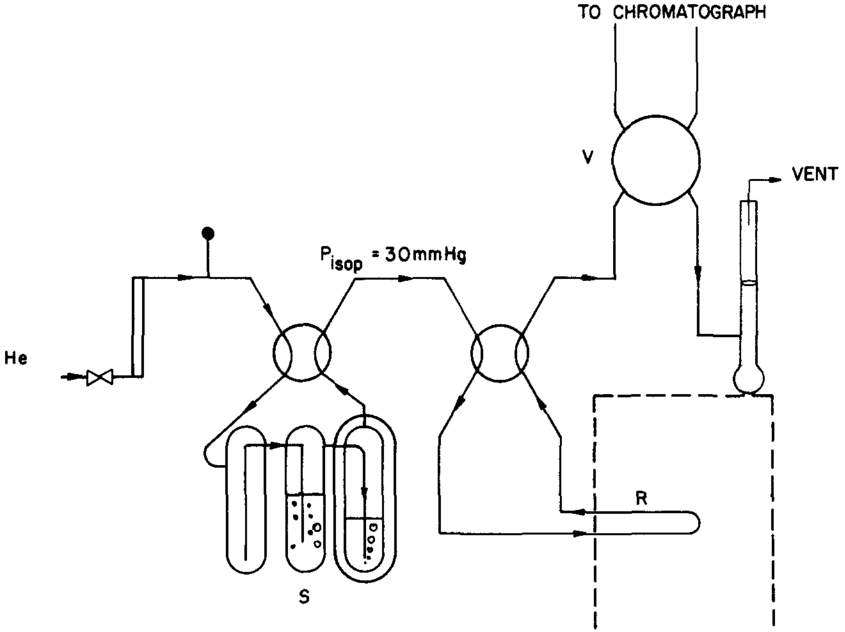


FIG. 1. Apparatus: S, T, isopropanol saturators; R, reactor; V, gas sampling valve.

15 min. Percent conversions were calculated with the following definitions:

To propene:

$$C_p = \frac{P_{\text{propene}}(\text{product})}{P_{\text{isopropanol}}(\text{feed})} \times 100$$

To acetone:

$$C_a = \frac{P_{\text{acetone}}(\text{product})}{P_{\text{isopropanol}}(\text{feed})} \times 100$$

Total conversion: $C = C_p + C_a$
Selectivity to propene:

$$S_p = P_{\text{propene}}/(P_{\text{propene}} + P_{\text{acetone}})$$

Total carbon balance:

$$CB = C_p + C_a + \frac{P_{\text{isopropanol}}(\text{product})}{P_{\text{isopropanol}}(\text{feed})} \times 100$$

The last variable, CB, was between 95 and 105% for all runs.

Prior to kinetic measurements of any sample, blank runs without mineral matter were performed in a reactor packed with quartz chips to fix the importance of homogeneous and (wall + quartz chip) surface reactions. At the maximum temperature of this study, 350°C, the minimum flow rate of 10 cm³/min, and the reference isopropanol pressure of 30 mm Hg, no propene was detectable in the product. A trace acetone peak represented 0.35% conversion. This latter conversion dropped rapidly with temperature diminution; it was negligible compared to all but the smallest conversions observed in the following experiments.

RESULTS

Activity

Reaction conditions were: $T = 350°C$, flow rate = 48 cm³/sec, and isopropanol pressure = 30 mg Hg. Figure 2 shows the activity versus time-on-stream for the six mineral samples of Table 1. In general, the activities appear to be stabilized after

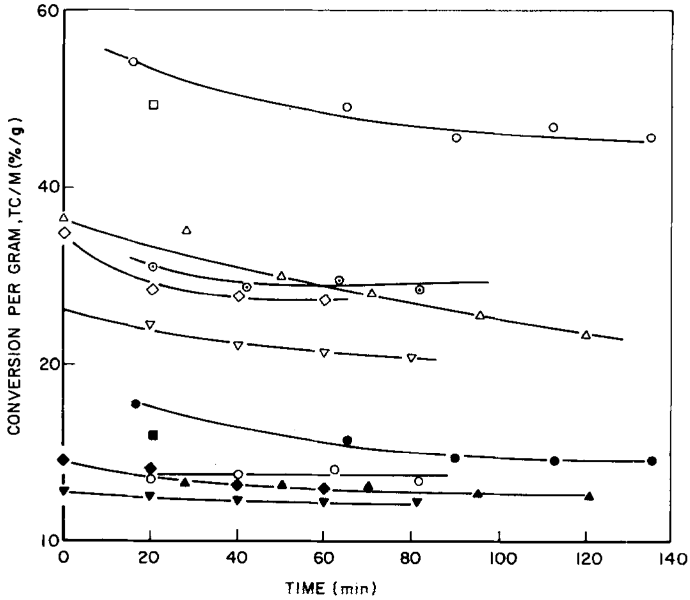


FIG. 2. Total conversion vs time, $T = 350°C$, $P_{(\text{isopropanol})} = 30$ mm Hg in feed, flow rate = 48 cm³/sec. Catalyst number [mass (g), C_1 (propene), C_2 (acetone)]: 83 (0.149, ▽, ▼), 52 (0.134, ⊙, ○), 70 (0.154, △, ▲), 89 (0.129, ○, ●), 67 (0.0914, □, ■), 62 (0.179, ◇, ◆).

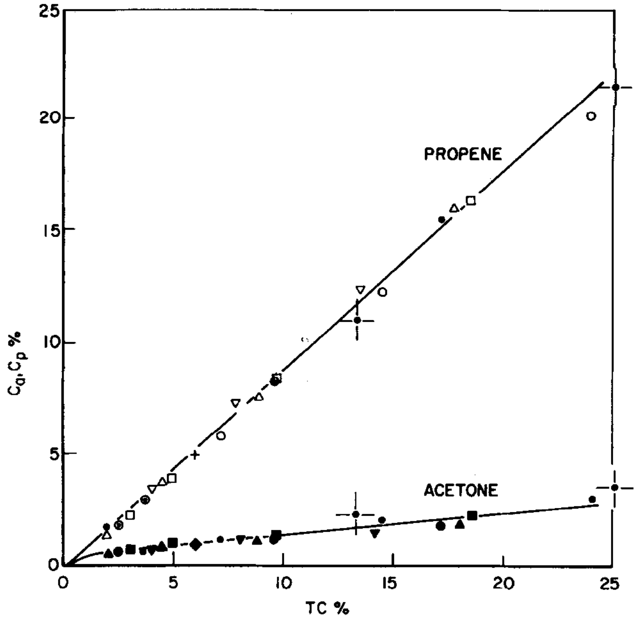


FIG. 3. Conversion to propene (C_1, open symbols) and acetone (C_2, closed symbols) vs total conversion (*TC*).

1 to 2 hr of operation. The following classification of activities is observed:

Sample: $89 \cong 67 > 70 \cong 52 \cong 62 > 83$.

Selectivity

The selectivity of a catalyst is usefully represented by plotting the variation of the respective conversions to particular products versus the total conversion. Such variations, which exclude time explicitly, permit easy comparison of catalysts with different surface areas or overall activities. Figure 3 presents the conversions *at 350°C*, after 2 hr of on-stream stabilization, to propene and acetone versus total conversion; the latter was changed by variation of the reactant flow rate at constant temperature. As all points lie near two straight lines for propene and acetone, respectively, the selectivity is almost independent of conversion *and of coal origin* for the six samples studied. For the entire collection, the selectivity to propene, S_p, is about 87% at 350°C for conversions of greater than 10%. At lower conversions, the selectivity diminishes due to the contribution by the acetone intercept.

Activation Energies

Activation energies were determined at the following reference conditions: 30 mm Hg isopropanol vapor, 48 cm³/min (25°C, 1 atm) by studying activity changes as the temperature was decreased. Apparent values were calculated from the slopes of semi-log plots of C_p/M and C_a/M (M = catalyst mass) vs reciprocal temperature.

Figure 4 presents the Arrhenius plot for sample #67; two distinct straight lines through the data for propene and acetone have slopes corresponding to 18 and 6 kcal/mol, respectively. The difference in activation energies reflects the observed sharp decrease in selectivity to propene as the temperature was diminished. Table 2 summarizes the activation energies measured for the samples of Table 1. The apparent activation energy for each re-

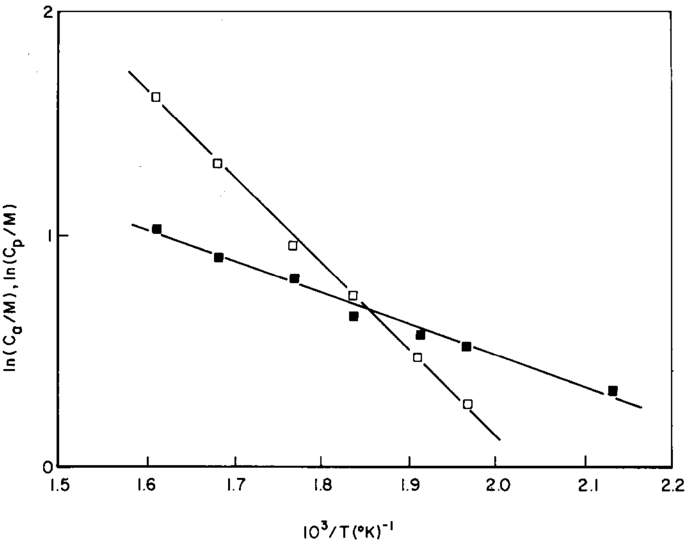


FIG. 4. Conversion vs reciprocal temperature, sample 67 (see caption Fig. 1 and Table 1). Propene (□); acetone (■).

action product appearance over all samples is similar, especially for propene.

As iron sulfides are frequently suspected of a possible catalytic role in coal hydrogenation liquefaction, we examined the properties of pure pyrite samples for the same reaction. While isopropanol decompositions have been widely studied, and many sulfides are reported in the earlier literature (*5*), we find no mention of isopropanol decompositions over pyrites or other iron sulfides. Pure pyrite mineral exhibited catalytic activity which was of the same order of magnitude (rate/mass basis) as the mineral samples; these results for modest conversions are shown as (-|-) in Fig. 3. This similarity is reinforced by Fig. 5 which compares the selectivities of pyrities and of sample #67 (representative of all those in Fig. 3); the entire propene and acetone conversions versus total conversion curves appear to lie on the same lines.

Arrhenius plots for the products resulting from pyrite catalysts are presented in Fig. 6; the calculated apparent activation energies are 22 and 10 kcal/mol for propene and acetone formation, respectively (Table 2).

Catalytic activity of coal-derived samples was increased by pretreatment with flowing H_2S. In Fig. 7, the activity enhancement of the mineral phases and the deactivation curve is presented for sample 67 and pyrite. While presulfiding sample 67 altered the activity, the *selectivity* of the resulting catalyst was unchanged from the original at all times.

X-ray diffraction studies indicated the presence of kaolinite, quartz, and iron sulfides near FeS. No reflections attribu-

TABLE 2

Activation Energies for Isopropanol Conversions

Sample	Dehydration E1	Dehydrogenation E2
83	17	7
67	18	6
52	21	6
70	18	10
89	18	10
62	18	10
Pyrite	22	10

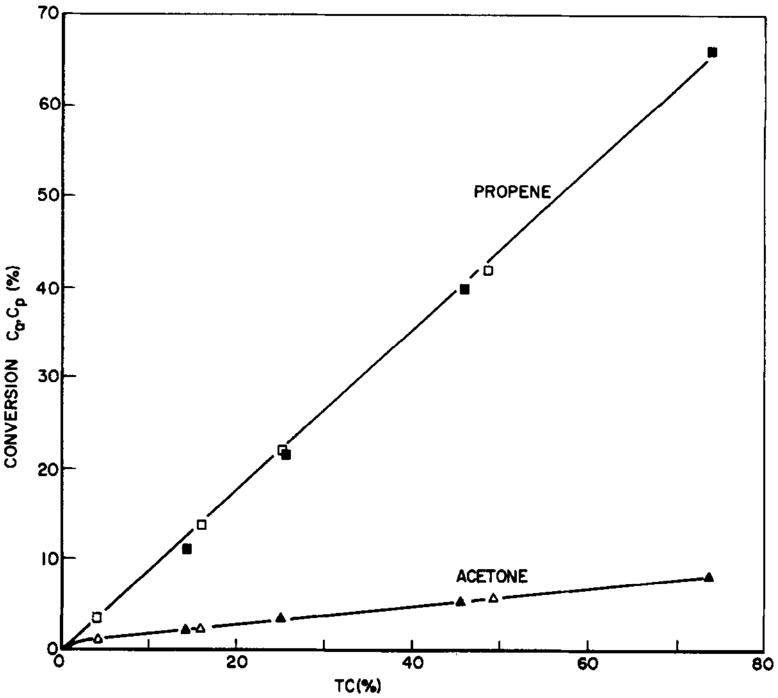


FIG. 5. Conversion to propene (squares) and acetone (triangles) for pure pyrite mineral (filled symbols), and sample #67 (open symbols, West Kentucky origin).

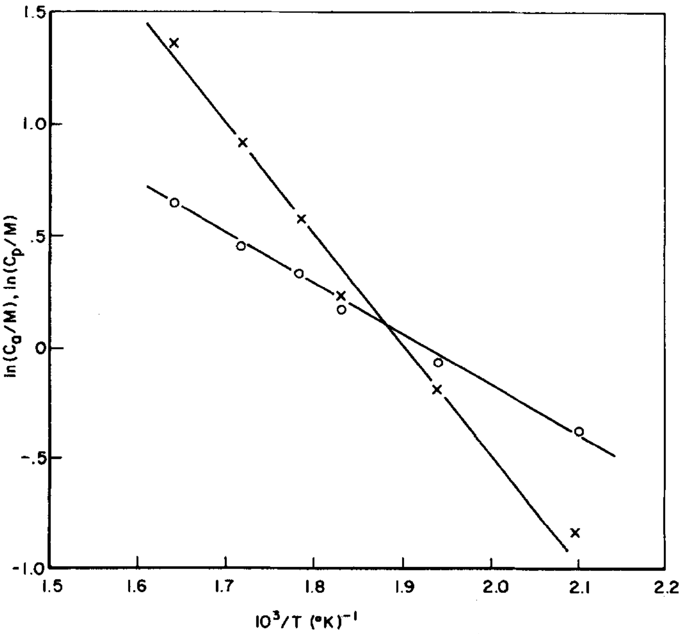


FIG. 6. Activity for propene (×) and acetone (○) conversions vs $1/T$. Ground pyrite minerals, 30 mm Hg isopropanol in feed gas.

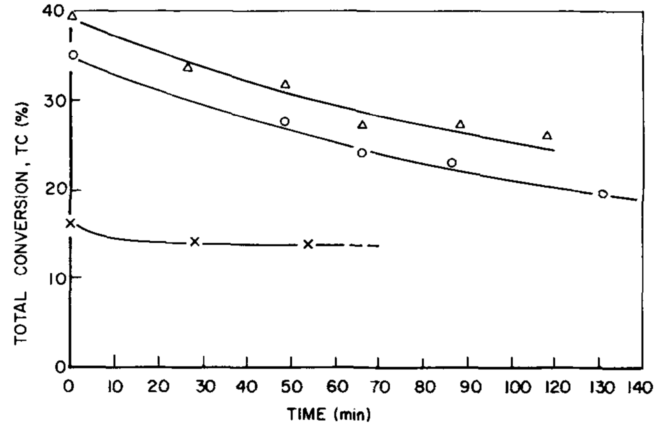


FIG. 7. Deactivation study: total conversion vs time. Sample 67 (0.207 g) pretreatments: 2 hr He at 350°C, 40 cm^3/min (×); same sample followed by 1 hr H_2S at 350°C, 40 cm^3/min (○). Pyrite (0.554 g) pretreatment: 0.25 hr He, at 350°C, 48 cm^3/min (△). Selectivity = constant (86%). $T_{(reaction)}$ = 350°C (all samples).

table to pure pyrite (FeS_2) were observed in any coal mineral sample extracted from the liquefaction residue, consistent with the theme that such processing conditions convert pyrites to lower sulfides. The most active extraction sample, #89, shows only one reflection, indicating little crystallinity above 100 Å diameter- and/or highly dispersed crystallites.

For a reaction of any kinetic order, in a plug flow reactor,

$$(\text{rate/vol}) \times dV = F dX(1 + \epsilon),$$

where ϵ = molar expansion or contraction on complete conversion of isopropanol = 30 mm/760 mm = 0.04. With zero order reaction, (rate/vol) = constant = k_v. Integrating and replacing k_v by $k_0 S_c \rho_b$ and V by (M_c/ρ_b) [k_0 = zero order specific rate (rate/m^2), S_c = m^2/g, ρ_b = g catalyst/cm^3 reactor volume, M_c = catalyst mass],

$$X = \frac{(k_0 \cdot S_c \cdot \rho_b)}{(1+\epsilon)} \left(\frac{M_c}{\rho_b}\right) \cdot \left(\frac{1}{F}\right)$$

$$= \frac{k_0 \cdot S_c \cdot M_c}{(1+\epsilon)} \cdot \frac{1}{F}.$$

Thus, for a zero order reaction, a plot of X vs $(1/F)$ is linear, and it passes through the origin with a slope $X/(1/F) = k_0 S_c M_c/(1 + \epsilon)$ from which k_0, the specific activity, may be calculated. Total conversion (X) vs reciprocal flow rate [$1/F$, $(\text{ml/min})^{-1}$] is shown in Fig. 8. The specific activities calculated from these slopes are presented in Table 3. The pyrite powders possess a very low unknown surface area; for illustrative purpose, it is assumed that the pyrite particle "diameter" is 10^{-2} cm.

The simultaneous occurrence of acetone and propene over all catalysts suggested the possibility of a direct interconversion pathway:

$$\text{acetone} + \text{hydrogen} \rightleftarrows \text{propene} + \text{water}$$

This reaction has an equilibrium constant near 60 at 350 K (see Discussion). As pyrite samples exhibited the highest specific activity for isopropanol conversions (Table 3), the following experiments to test the existence of a direct pathway were performed [catalysts: pyrite and #67 (*8*)]:

(a) Two hours H_2 pretreatment, feed: 57 mm Hg acetone and 117 mm Hg hydrogen, T varied from 473 to 623 K.

(b) Same as (a), with additional 1 hr pretreatment flowing in H_2S (atm).

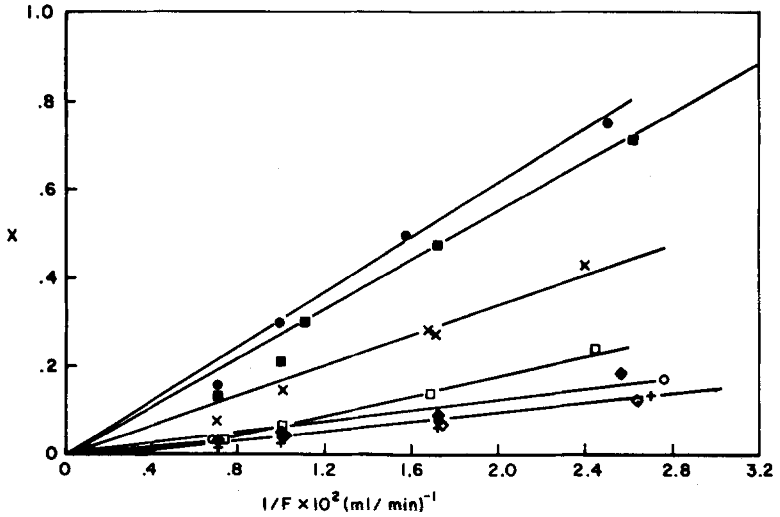


FIG. 8. Total conversion (X) vs reciprocal flow rate ($1/F$). Catalyst pretreatment: 2 hr in flowing H_2, additional as noted: sample (run #)—(symbol): 52 (33)—(○); 67 (29)—(■); 67 (30) (+15 min in He)—(◆); 70 (32)—(+); 83 (34)—(◇); 87 (31)—(□); pyrite (26)—(×); pyrite (28) (10% O_2/He)—(●).

(c) Two hydrogen pretreatment, T = 350°K, feed: 4 mm Hg acetone + 756 mm Hg hydrogen.

(d) Two hours hydrogen pretreatment (a) T = 350 K, then reaction at 673 K, feed = 33 mm isopropanol and balance = inert. Analysis of exit streams from experiments a, b, and c above indicated no isopropanol or propene. The exit selectivities for repeated runs (*6*) under conditions (d) have a mean value of 90.5% and a standard deviation of 1.4%.

DISCUSSION

From Fig. 3 and Table 2, both the selectivity at reference conditions and the activation energies are very similar for all coal-derived samples. This behavior would

TABLE 3

Specific Activity of Catalysts

Sample (Run No.)	Mass, M_c (g)	Specific surface, S_c (m^2/g)	$X/(1/F)$ (ml/min)	$k_0 = \frac{X(1+\epsilon)F}{M_c \cdot S_c}$ [molecules/(cm²-sec)]
52 (33)	0.135	9.9	6.0	21×10^{13}
67 (29)	0.207	37.1	27.6	16×10^{13}
67[a] (30)	0.091	37.1	6.8	9.4×10^{13}
70 (32)	0.154	11.9	5.0	8.2×10^{13}
83 (34)	0.149	13.9	4.8	11×10^{13}
89 (31)	0.129	9.2	9.2	36×10^{13}
Pyrite (26)	0.554	(6×10^{-2})[c]	16	2.3×10^{16}
Pyrite[b] (28)	0.217	(6×10^{-2})[c]	31	9.6×10^{16}

Note. Except as noted below, catalyst heated 2 hr in H_2 at 350°C prior to run.

[a] One-fourth hour in He (after 2 hr in H_2).

[b] Two hours in 10% O_2 in He (after 2 hr in H_2).

[c] *Assumed* "diameter" of nonporous particles: $\sim 10^{-2}$ cm; $S_c = 6/d = 600$ cm²/cm³.

arise if a single predominant phase is responsible for the observed catalytic activity. The kinetic similarity between the processed coal minerals and the pyrite samples are very suggestive in this regard.

It appeared, however, that the correct explanation of the above results lay in the following equilibrium argument. The isopropanol was presumed to undergo either or both of the reactions below:

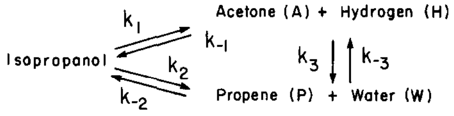
(i) $CH_3CHOHCH_3 \rightarrow$
$CH_3COCH_3 + H_2$ (dehydrogenation)

(ii) $CH_3CHOHCH_3 \rightarrow$
$CH_3CHCH_2 + H_2O$ (dehydration)

A constant selectivity value could arise if all catalysts equilibrated the reactions (iii):

(iii) $CH_3COCH_3 + H_2 \rightleftarrows$
$CH_3CHCH_2 + H_2O$
(olefin partial oxidation with water)

Under this hypothesis, the full reaction network could be written as follows:



Provided $(k_1, k_{-1}, k_2, k_{-2}) < (k_3, k_{-3})$, any conversion of isopropanol to acetone or propene would produce an equilibrated acetone/propene ratio at every conversion value of isopropanol, as observed in the data of Fig. 3.

The equilibrium constant of reaction (iii) at 350°C (623°K) is calculable from the free energies of formation:

$$K_e(623\ \mathrm{K}) = e^{-\Delta G^0{}_{\mathrm{rXn}}/RT}$$

where

$$\Delta G^0{}_{\mathrm{rXn}} = \Delta G^0{}_f(W) + \Delta G^0{}_f(P) - \Delta G^0{}_f(H) - \Delta G^0{}_f(A)$$

From Stull *et al.* (7), the free energies of formation are obtained. The resulting calculated free energy change is −4.43, −5.05, and −5.63 kcal/mol at 500, 600, and 700 K, respectively. Interpolation yields $K_e(623°\mathrm{K}) = 66$.

From the stoichiometry of the full reaction network above, let

TC = total conversion of isopropanol
x = conversion to acetone.

Then at any conversion,

$$A, H = x$$
$$P, W = TC - x.$$

The equilibrium for reaction (iii) is $K_e = P_eW_e/(H_eA_e)$. The value of x which satisfies the equilibrium at any TC is given by $K_e = (TC - x_e)^2/x_e^2$. Then the ratio

$$\frac{\text{propene}}{\text{acetone}} = \frac{TC - x_e}{x_e} = (K_e)^{\frac{1}{2}}$$
$$= (66)^{\frac{1}{2}} = 8.12$$

corresponding to a selectivity of

$$\frac{\text{propene}}{\text{propene} + \text{acetone}} = \frac{8.12}{9.12} \cong 89\%,$$

in agreement with the experimental value of 87% found in Fig. 3.

Examination of our selectivity data shows that all results for coal- or pyrite-derived samples lie near or below the value corresponding to propene–acetone equilibration. A sampling of catalysts pretreated in He, H_2, or H_2S are shown in Fig. 8 to illustrate this feature. Note that a γ-Al_2O_3 test, as a reference point, produced 100% selectivity to propene as expected.

As the direct pathway (iii) tests with our catalysts all failed to produce any products when the feed stream consisted of acetone and hydrogen, we conclude that such a pathway cannot make an appreciable contribution to our observed kinetics with isopropanol. Accordingly, mechanistic possibilities remaining include: (a) isopropanol conversions on two (or more) types of sites, with separate dehydrogena-

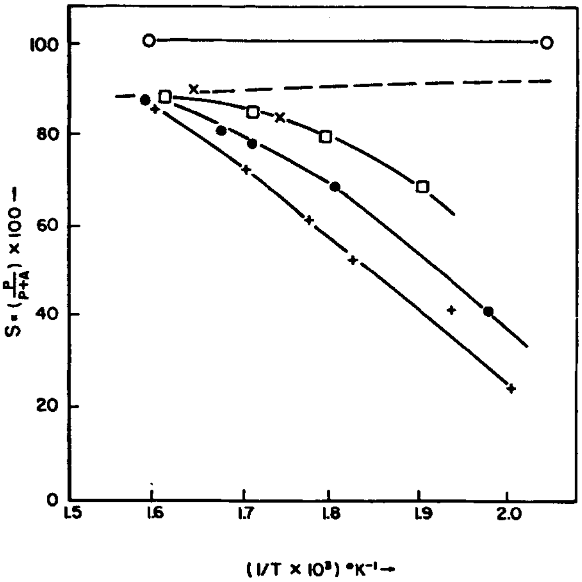


FIG. 9. Selectivity [= 100 × $P/(P + A)$] vs $1/T$. Samples: γ-Al_2O_3 (○), #67 [H_2 pretreatment (+), H_2S pretreatment (×)]; #62 [He pretreatment (□)]; pyrite (●). Propene–acetone equilibrium locus (– – – –).

tion and dehydration sites. (b) Isopropanol conversions through a common single site, with subsequent kinetic selectivity determining the relative amounts of acetone and propene generated. Here the step to acetone and hydrogen must be irreversible to account for our pyrite experiments. (c) Isopropanol serial conversion through *two* intermediates, one giving acetone (by an irreversible step) and another giving propene.

From the observation that "monosulfide" phases exist in (at least) all but one processed mineral sample, it appears reasonable to suggest that the active catalyst for isopropanol conversion is an iron-containing phase, probably one or more, of the iron "monosulfides." (The pyrite surface itself probably undergoes conversion to a lower iron–sulfur phase at the temperature of 350°C.)

Figure 9 indicates that appreciable acidity (see γ-Al_2O_3 sample data) should lead to a higher (olefin/ketone) equilibrium ratio at lower temperature. Higher temperature pretreatment of the pyridine-extracted samples is now being explored to see if pyridine desorption releases any pyridine-poisoned acidity.

The linearity of the plots through the origin in Fig. 8 indicates that a zero order reaction provides a reasonable description for isopropanol conversion over all catalysts but sample 89. At highest flow rates, some deviations from linearity appear, possibly due to loss from the reactor of some powdered catalyst. The high specific activity of pyrite for isopropanol conversion (Table 3) is evident. Thus, if small amounts of any phase as active as the pyrite-derived samples are found in the extracted coal samples, these would suffice to explain the observed specific activities.

ACKNOWLEDGMENTS

We thank Mobil Research and Development Laboratories for the coal liquefaction pyridine-extracted samples and Professor David Crerar of Princeton's Geology department for the pyrite crystals. Dr. J. P. Joly is pleased to thank the Universite Claude Bernard de Lyon and NATO for financial assistance during this study. Presented at Pennsylvania State University, September 1977.

REFERENCES

1. Wright, C. H., and Severson, D. E., *Preprints, Div. of Fuel Chem. A.C.S.* **16**, 68 (1972).
2. Mukherjee, D. K., and Chowdhury, P. B., *Fuel* **55**, 4 (1976).
3. Hodek, W., and Kühn, L., *Endöl und Kohle, Erdgas, Petrochem.* **30**, 85 (1977).
4. Morooka, S., and Hamrin, C. E., Jr., *Chem. Eng. Sci.* **32**, 125 (1977).
5. Krylov, O. V., "Catalysis by Non-metals." Academic Press, New York, 1970.
6. de Mourgues, L., *in* "La catalyse au laboratoire et dans l'Industrie" (B. Claude, Ed.). Masson, 1965.
7. Stull, D. R., Westrum, E. F., Jr., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds." J. Wiley, New York, 1969.
8. Jacobs, E., Ph.D. thesis, Princeton University (1979).