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CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION
QUARTERLY REPORT -- October 1, 1983 -
December 31, 1983

H. Heinemann

December 1983

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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QUARTERLY REPORT

October 1, 1983 - December 31, 1983

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

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This work was jointly supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, and the Assistant Secretary for Fossil Energy, Office of Coal Research, Liquefaction Division of the U. S. Department of Energy under Contract DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

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I. Technical Program for FY 1984

Task 1: SELECTIVE SYNTHESIS OF GASOLINE-RANGE COMPONENTS FROM SYNTHESIS GAS
A. T. Bell, Task Manager

It is planned to complete the objectives of the present project during FY 1984. The experimental results obtained for Fischer-Tropsch synthesis over α-FE, Fe_2O_3, and Fe_3C will be compared to establish patterns in catalytic activity and selectivity as a function of catalyst composition. X-ray diffraction patterns will be taken of the fresh and spent catalysts to determine whether bulk composition changes with time on stream. In particular it would be desirable to know whether these materials achieve a common bulk composition, catalytic activity, and selectivity after extended use.

Efforts will also be made to interpret the rate data obtained for α-Fe, Fe_2O_3, and Fe_3C in the light of mechanistic models of the reaction kinetics.

The work on supported Fe catalysts will be concluded by obtaining data on the performance of Fe/Al_2O_3, Fe/TiO_2, and Fe/MgO for comparison with the data already available for Fe/SiO_2 and zeolite-supported Fe. All catalysts will be examined both in a calcined and in a reduced state to determine the influence of pretreatment. Additional work will also be done with Fe/ZSM-5 to understand better why the zeolite appears to influence the product distribution so little at temperatures below 300°C. It is conceivable that for the zeolite to have an effect, the temperatures must exceed 300°C by a substantial margin.

Task 2: CATALYZED LOW TEMPERATURE REACTION OF CARBON AND WATER
G. A. Somorjai, Task Manager

Leads to make the production of higher hydrocarbons from carbon and water truly catalytic will be pursued. It appears possible to catalytically decompose phenolates formed, preventing stoichiometric limitations.

Attempts will be made to greatly increase rates and volume of hydrocarbon formation. This may be accomplished by operation at higher water partial pressure

and by catalytic promoters. Further, the addition of CO, resp. CO_2, to the reaction offers indications of producing liquid hydrocarbons.

Task 3: CHEMISTRY OF COAL SOLUBILIZATION AND LIQUEFACTION
R. H. Fish, Task Manager

The FY84 program will concentrate on the use of polymer-supported catalysts and their mechanistic implications in the selective catalytic hydrogenation of model coal compounds. This will include experiments with deuterium rates, and competitive reaction to better define potential catalyst poisoning as well as enhancement of rates of selected model coal compounds.

Catalytic cracking of partially hydrogenated nitrogen containing ring compounds will be investigated to determine the total savings of hydrogen in nitrogen removal over conventional hydrocracking.

In addition, we will attempt to define the important parameters in the catalytic transfer of hydrogen from saturated nitrogen heterocyclic compounds to other coal liquid constituents. This will include scope, rates and a perusal of polymer-supported catalysts capable of dehydrogenation-hydrogenation reactions.

II. Highlights

Task 1: SELECTIVE SYNTHESIS OF GASOLINE-RANGE COMPONENTS FROM SYNTHESIS GAS

Work with unsupported iron oxide (Fe_2O_3) catalysts has shown that prereduction in H_2 gives initial high activity, but gives rapid deactivation due to carbon and eventually graphite formation. Catalysts brought on stream with syngas and without prior reduction gradually increased in activity and reached a steady state activity lasting over extended periods of time.

A study of the effects of support composition for Fe_2O_3 catalysts on the composition of Fischer-Tropsch products has been completed. Synthesis activity decreases in the order $TiO_2 > SiO_2 > Al_2O_3 \simeq MgO$. Catalysts with the lowest dispersions (TiO_2 and MgO supported) showed the highest probability of chain growth. Olefin/paraffin ratio and water gas shift activity decrease in

the order $MgO > SiO_2 > Al_2O_3 > TiO_2$. Basic supports therefore seem to act like basic promoters.

Task 2: CATALYZED LOW TEMPERATURE REACTIONS OF CARBON AND WATER

It has previously been shown that the production of hydrocarbons from KOH impregnated graphite and water at 800K is stoichiometrically limited by the formation of a phenolate type compound. Recent work has shown that this compound is decomposed in the presence of Fe_2O_3 and that the production of hydrocarbons and hydrogen proceeds catalytically and for long periods of time. It has also been found that lithium hydroxide promoted the formation of hydrocarbons and hydrogen without the stoichiometric limitation observed with KOH, perhaps because of greater instability of lithium phenolate.

The adsorption and reactions of CO and CO_2 on graphite are being studied by spectroscopic methods.

Task 3: CHEMISTRY OF COAL SOLUBILIZATION AND LIQUEFACTION

A comparison between polymer-supported Wilkinson's catalyst, $\boxed{P}$ - $P\emptyset_2Rh(\emptyset_3P)_2Cl$, and its homogeneous analogue in the selective hydrogenation of polynuclear heteroaromatic compounds provides evidence for differences in initial rates and ability to exchange aromatic hydrogens for deuterium. Cross-linking of the polymer-supported catalyst also affected hydrogenation rates, but diffusion into the polymer bead was not rate limiting. High regioselectivity for reduction of the nitrogen heterocyclic ring was found in the hydrogenation of a model coal liquid with the polymer-supported catalyst.

III. Progress of Studies

Task 1: SELECTIVE SYNTHESIS OF GASOLINE RANGE COMPONENTS FROM SYNTHESIS GAS

Work during the past quarter has concentrated on characterizing the Fischer-Tropsch synthesis performance of unpromoted iron catalysts. Experiments with unsupported Fe_2O_3 were carried out in the stirred autoclave reactor. If the catalyst was first reduced in H_2 prior to introduction of the synthesis gas,

the synthesis activity slowly declined over several days. This loss of activity is believed to be due to the progressive accumulation of carbon on the catalyst.

If, on the other hand, the catalyst was brought on stream without reduction, the synthesis activity increased over several days eventually becoming comparable to that of the reduced catalyst. Quite significantly, it was observed that the activity of the catalyst without initial reduction could be maintained without any evidence of deactivation during the course of a week. These results suggest that excessive reduction of iron Fischer-Tropsch catalysts is detrimental, in that the high initial activity resulting from reduction is accompanied by a rapid deposition of carbon which is progressively converted to graphite.

The kinetics of hydrocarbon synthesis over initially unreduced Fe_2O_3 were explored. It was established that the dependencies of the synthesis rates on the partial pressures of H_2 and CO are poorly described by simple power-law expressions. The observed trends in synthesis rate and in particular the dependence of the rate on CO partial pressure can be rationalized readily in terms of a simple model of the synthesis process. This model also explains the inhibition of α to β-olefin conversion, and the hydrogenation of olefins to paraffins, at high CO partial pressures.

Experiments on the effects of support composition on the compositions of Fischer-Tropsch products formed over supported iron catalysts have been completed. For this work, SiO_2, Al_2O_3, TiO_2, and MgO were used as the supports. A summary of the characteristics for these catalysts is given in Table 1. It is observed that the synthesis activity decreases in the order $TiO_2 > SiO_2 > Al_2O_3 \approx MgO$. Quite surprisingly, the catalysts with the lowest dispersions (TiO_2 and MgO) exhibited the highest probabilities of chain growth, α. Experiments will be undertaken to further confirm the trend of decreasing α with increasing iron dispersion. Table I also demonstrates that the olefin to paraffin ratio and the water-gas-shift activity both decrease in the order $MgO > SiO_2 > Al_2O_3 > TiO_2$. These results suggest that basic supports act like basic promoters in that both suppress olefin hydrogenation and enhance the conversion of H_2O to CO_2.

Table I

Comparison of Performance Characteristics for Supported Iron Catalysts

Catalyst	$N_{CO}(S^{-1})$ (a)	α	$N_{C_4^=}/N_{C_4^-}$	N_{CO_2}/N_{CO} (b)
Fe/SiO_2	0.32	0.49	1.36	0.72
Fe/Al_2O_3	0.14	0.49	0.90	0.28
Fe/TiO_2	0.45	0.57	0.70	0.25
Fe/MgO	0.17	0.56	5.00	0.82

(a) The turnover frequency for CO conversion to hydrocarbons: T = 285; P = 10 atm; H_2/CO = 2.

(b) N_{CO_2}/N_{CO} is a measure of the water gas shift activity. The maximum value of this ratio is 1.0.

Task 2: CATALYZED LOW TEMPERATURE REACTIONS OF CARBON AND WATER

W. T. Tysoe, J. Carrazza, G. A. Somorjai

a) Introduction

Work has proceeded on two fronts. First, exploratory experiments have been performed using the flow reactor to discover a method of decomposing the rate limiting phenolate intermediate to allow low temperature coal gasification to proceed. Second, the interaction of CO and CO_2 with graphite was investigated using the high pressure/low pressure apparatus.

b) Flow Reactor Experiments

The gasification of graphite was studied using CO-deposited KOH as a catalyst. As was reported previously, the low temperature gasification of graphite was shown to be limited by the formation of potassium phenolate. In order to overcome this problem, mixtures of different oxides with KOH were prepared to try to decompose the phenolate. It had been found that char containing ash was gasified without being limited by potassium phenolate formation.

Low temperature catalytic gasification of graphite is obtained using these catalysts. The reactivity varies depending on the oxide co-catalyst. The results of Figure 1 show that the activity of the KOH/Fe_2O_3 catalyst is higher than for any of the other mixtures. However the activity at low temperature is still lower than in the case of KOH alone.

A plot of the graphite gasification activity of the KOH/FE_2O_3 additive against time proves that the reaction is catalytic. Figure 2 shows that the reaction proceeds even after a considerable number of turnovers, although there is a decrease in activity with time. A similar study with KOH shows the reaction steps after a half-turnover (i.e., a stoichiometric reaction).

Although this reaction is catalytic, the percentage of hydrocarbons decreases by a factor of 10, compared with KOH alone. (See Table 1). The same behavior is found when other oxide/KOH catalysts are used.

KOH and KOH/Fe_2O_3 have also been studied. Figure 3 shows that KOH does not show the stoichiometric limitation, although the activity at high temperature is similar to KOH. A Fe_2O_3/LiOH catalyst increases the rate of gas production compared with LiOH alone. However, as in the case of a KOH/Fe_2O_3 catalyst, the percentage of hydrocarbons decreases by a factor of 10.

Future Work

Other KOH/oxide systems will be studied, with emphasis on basic oxides such as ZnO or Al_2O_3. Also, mixtures of alkaline hydroxides and phosphates, and sulphates or sulfides of different metals will be examined.

Solid state NMR experiments of graphite samples after reaction will be performed to try to characterize reacton intermediates.

c) UHV/High Pressure Cell Reaction

Figure 4 shows two 28 amu (CO) and 44 amu (CO_2) TD spectra obtained from polycrystalline graphite exposed to $>10^8$ L of CO and CO_2. Peaks below 500K may be attributed to "physisorbed" gas [1] or support peaks. Both CO and CO_2 give rise to a CO_2 desorption at 730K and CO desorption at 1230K. This suggests that CO and CO_2 adsorption yield similar surface species. Figure 5(a) shows a MgKα XP spectrum of the edge plane of a sample of oriented graphite exposed to $>10^8$ L CO_2. New peaks are observed at chemical shifts from the graphite as peaks of 3.3 $\pm$ 0.2 ev and 4.4 $\pm$ 0.2 ev.

The peak shifted by 3.3 ev may be assigned to a carbonyl group, and the one shifted by 4.4 ev to a carboxyl group [2]. Upon heating to 850K (above the CO_2 desorption temperature) the spectrum changes to that shown in Figure 5b so that only a peak with a chemical shift of 3.0 ev (due to a carbonyl species) remains. This peak may be removed by heating to approximately 1400K corresponding to the desorption of CO. The 730K peak in thermal desorption is, then, due to the decomposition of a carboxyl species. Similarly, the 1230K peak is produced by carbonyl decomposition.

The reaction between CO or CO_2 and polycrystalline graphite was investigated

as a function of sample temperature in the high pressure reactor. The results for the reaction $CO_2 + C \rightleftharpoons 2CO$, using a gas pressure of 230 torr, are shown in Fig. 6. Measurement of the slope of this curve yields an activation energy for CO production of 67 ± 3 Kcal/mole. This is in good agreement with a value of 59 Kcal/mole obtained in a flow reactor [3].

Fig. 7 shows a similar plot for the reverse reaction ($2CO \simeq CO_2 + C$). An activation energy may be extracted from the linear region and yields a value of 24 + 2 Kcal/mole. The difference between these activation energies, i.e., the entropy for reaction, is 43 ± 5 Kcal/mole, which is in good agreement with the literature value (41.2 kcal/mole) [4].

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2. D. T. Clark and H. R. Thomas, J. Polymer Science (Polymer Chem. Ed.) 16 791 (1978).

3. S. Ergun, J. Phys. Chem., 60 480 (1956).

4. Handbook of Chemistry and Physics, 61st ed., Editor R. C. Weast (CRC Press, 1980 - 1981).

Figures and Tables

Figure 1: Plot of the temperature dependence of the gas production rate during a temperature programmed reaction at a heating rate of 5 K $min.^{-1}$ for various KOH/oxide catalysts. The ratio KOH/oxide is 1 and the ratio K/C is 0.04 in all the cases.

Figure 2: Plot of the H_2 production rate per potassium atom deposited on the surface (i.e., turnover frequency) as a function of the total amount of H_2 produced per potassium (i.e., turnover number); for the KOH and KOH/Fe_2O_3 catalysts at 850K. The ratio K/C is equal to 0.043 for the KOH catalyst and 0.015 for the KOH/Fe_2O_3 catalyst. The ratio Fe/K is equal to 1.

Figure 3: Plot of the temperature dependence of the gas production rate during a temperature programmed reaction at a heating rate of 5 K $min.^{-1}$ for LiOH, $LiOH/Fe_2O_3$ and KOH catalysts. The ratio $LiOH/Fe_2O_3$ is equal to 1, and the ratio Li/C and K/C is equal to 0.04 in all the cases.

Table 1: Activation energy and percentage of CH_4 in the gas products for all the systems studied.

Figure 4: 28 and 44 amu spectra obtained after (a) 5×10^8L exposure of CO and (b) 5×10^8L exposure of CO_2 onto polycrystalline graphite.

Figure 5: (a) A spectrum of the graphite edge plane exposed to 10^9 L CO_2 at room temperature. The spectrum of a clean surface is shown as a line. (b) Spectrum after flashing to approximately 850K.

Figure 6: Arrhenius plot for the reaction $CO_2 + C \simeq 2CO$.

Figure 7: Arrhenius plot for the reaction $2\ CO \simeq CO_2 + C$.

Table 1

Catalyst	Activation Energy (Kcal/mol)	% CH_4 at 800K ($N\ CH_4/N$ gas) x 100
KOH	35.1	0.20
KOH/Fe_2O_3	35.9	0.03
KOH/Cr_xO_y	42.3	n/a
KOH/V_xO_y	50.2	0.03
KOH/Mo_xO_y	38.8	0.02
LiOH	(29.8 - 37.6)	0.40
$LiOH/Fe_2O_3$	42.7	0.08

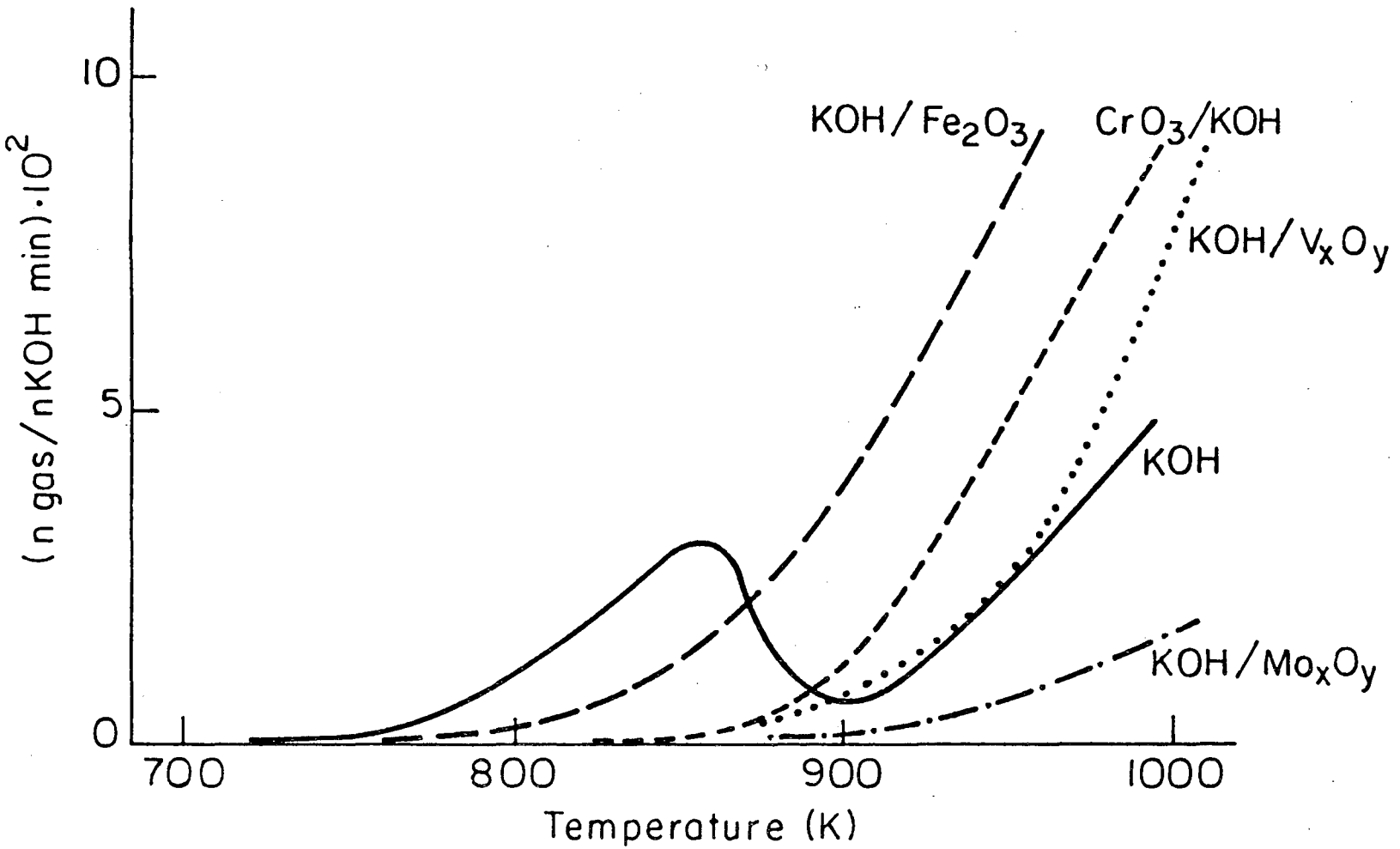

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Figure 1

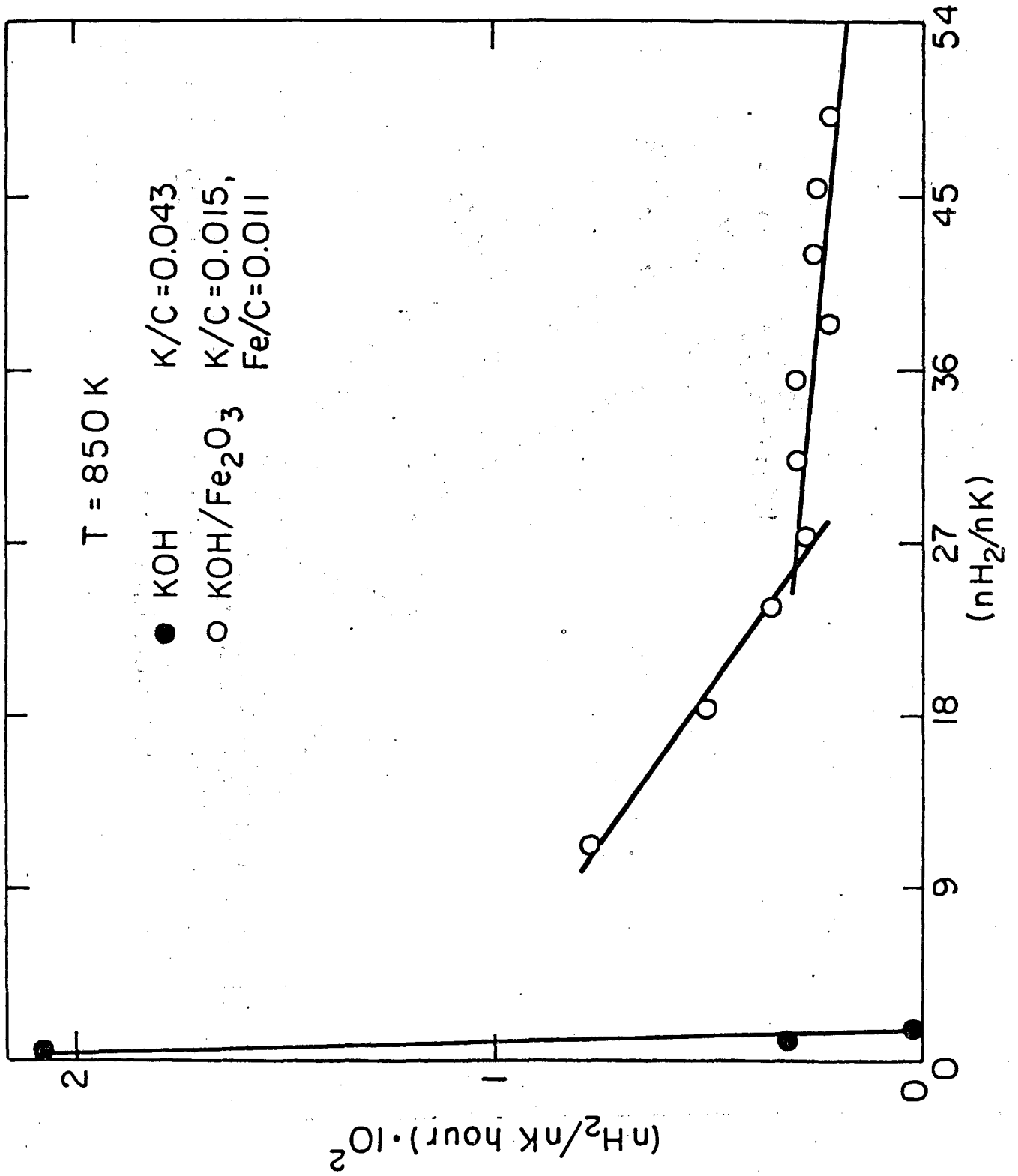

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Figure 2

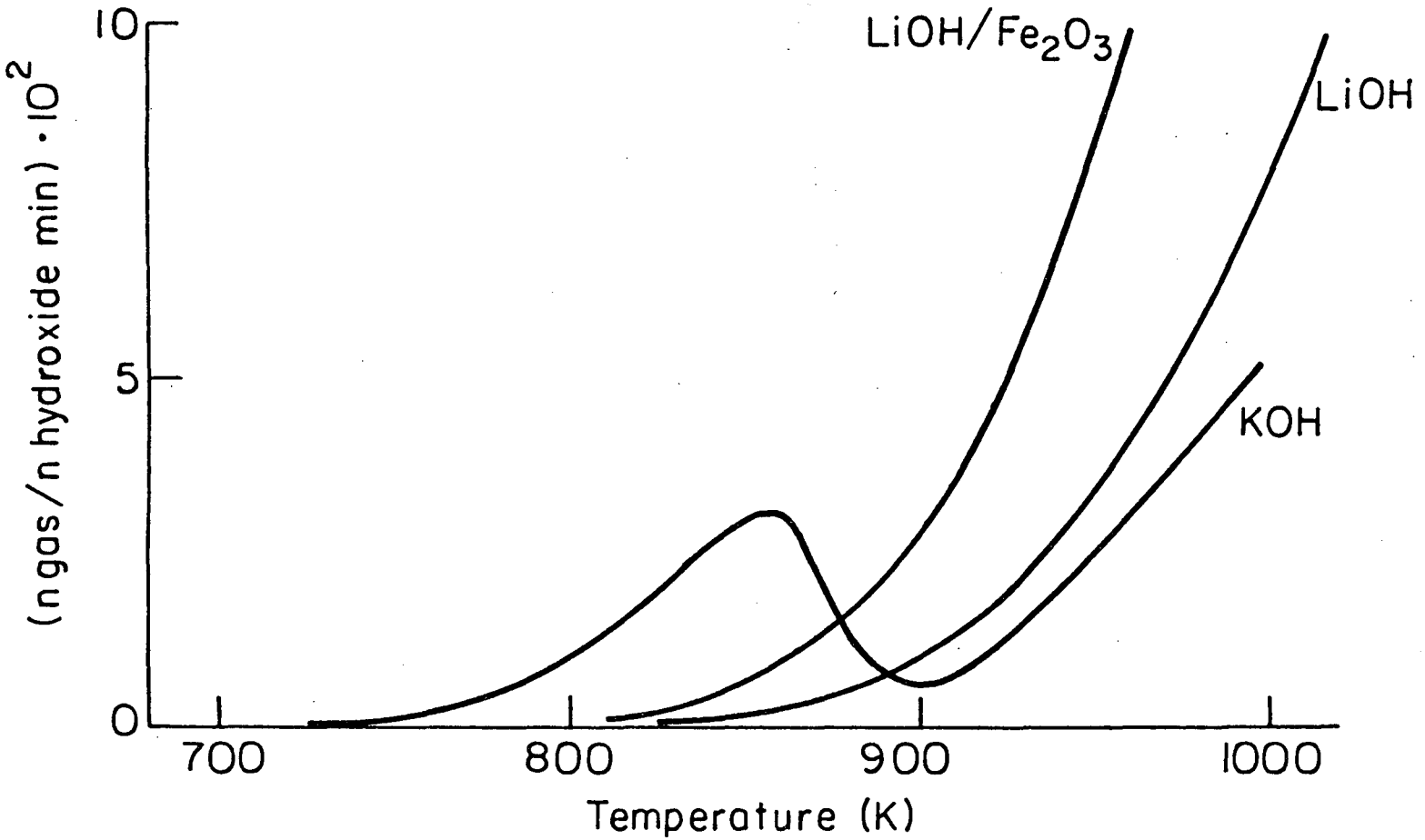

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Figure 3

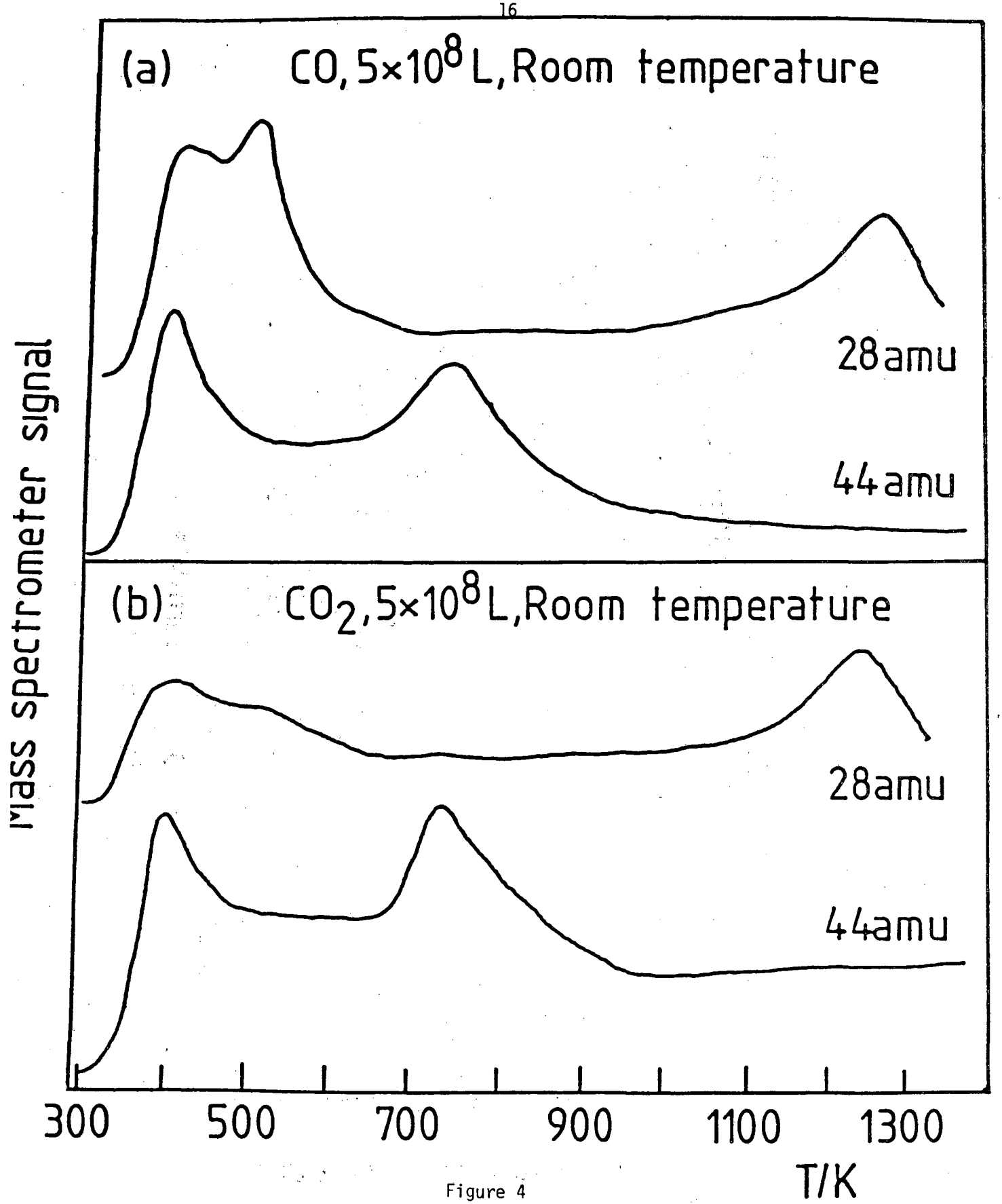

(a) CO, 5×10^8 L, Room temperature
28amu
44amu
(b) CO2, 5×10^8 L, Room temperature
28amu
44amu
Mass spectrometer signal
300
500
700
900
1100
1300
T/K

Figure 4

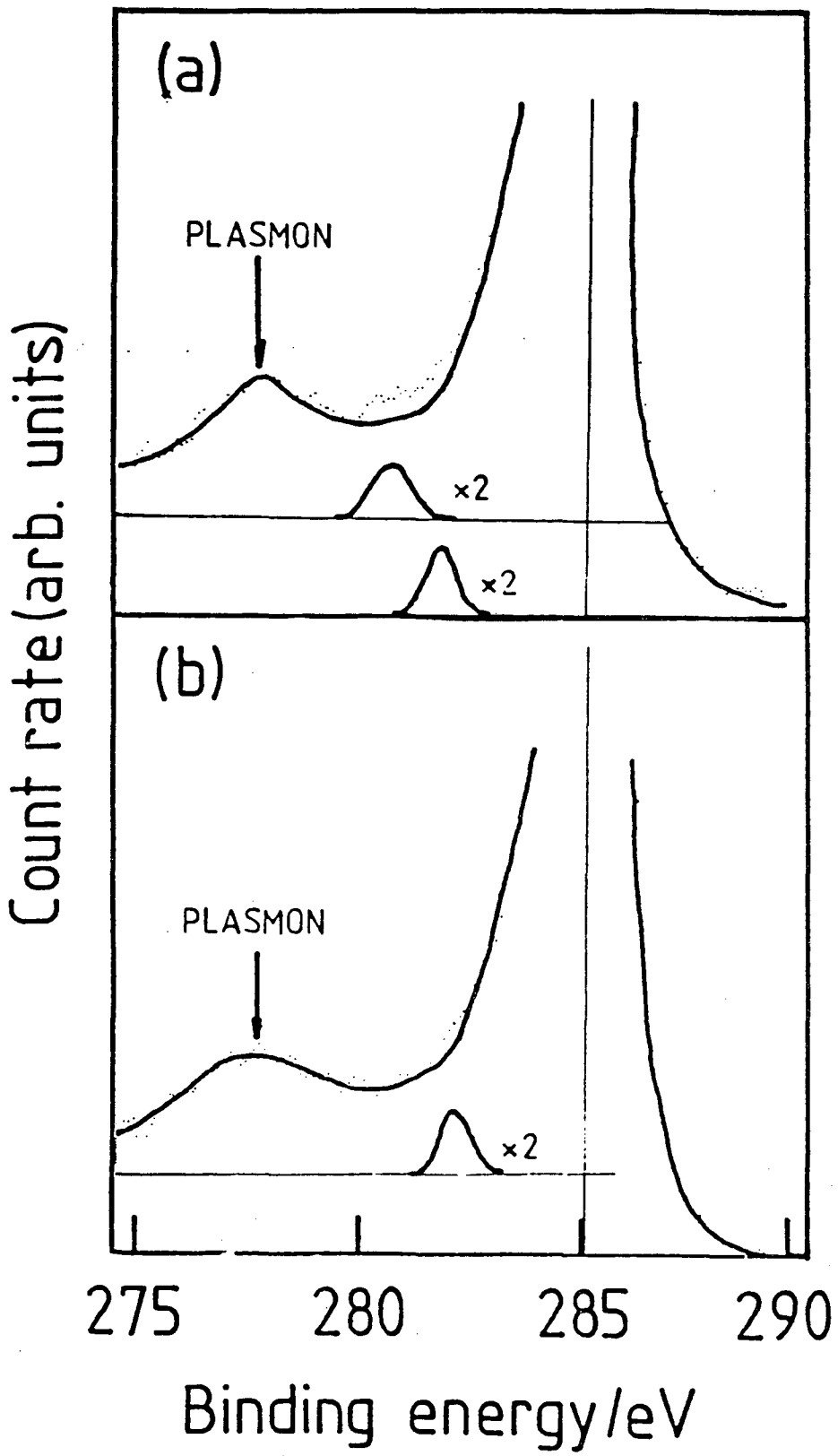

(a)
PLASMON
×2
×2
(b)
PLASMON
×2
Count rate (arb. units)
275
280
285
290
Binding energy/eV

Figure 5

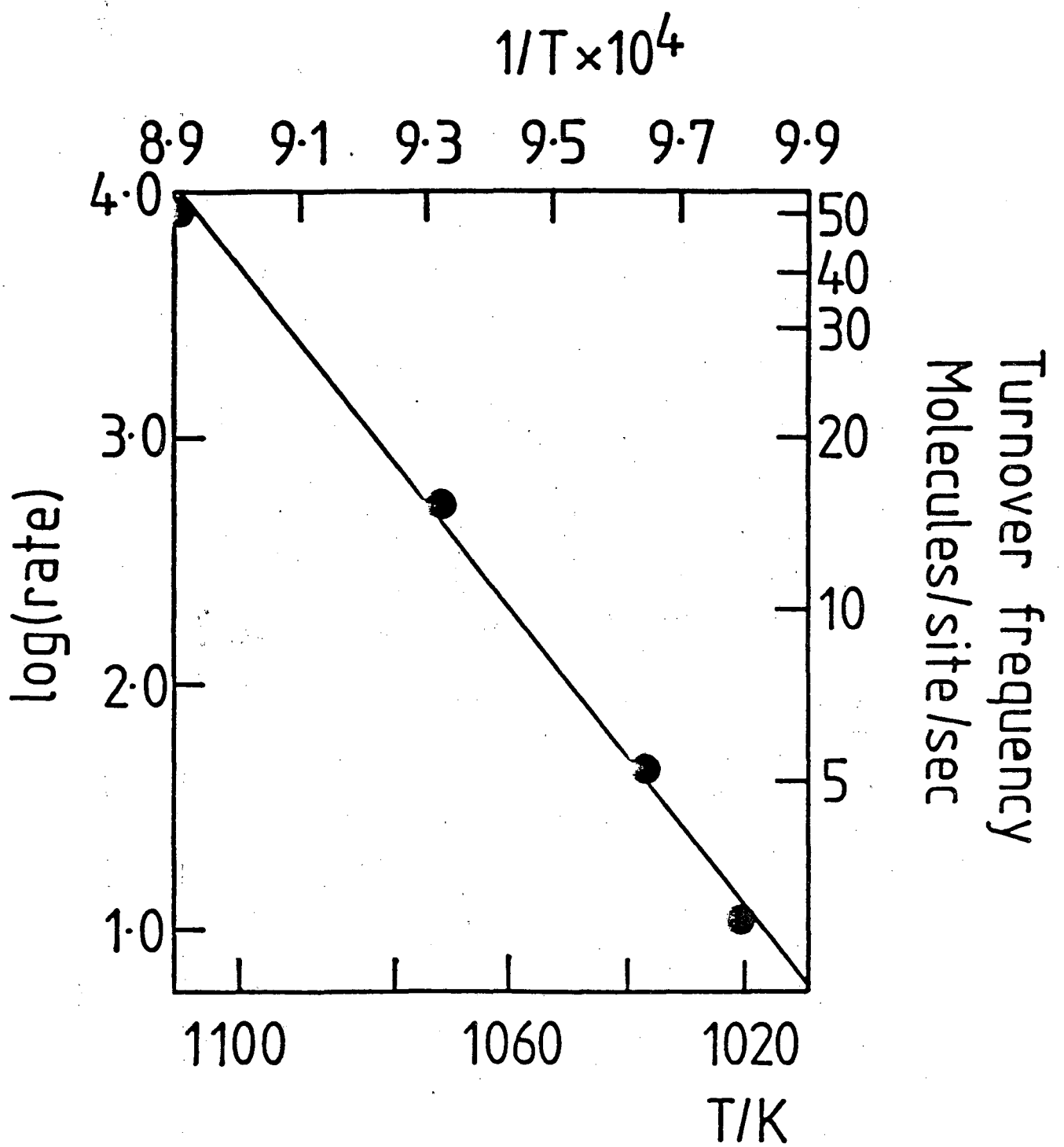

Turnover frequency
Molecules/site/sec
50
40
30
20
10
5
1/T×10^4
8·9
9·1
9·3
9·5
9·7
9·9
log(rate)
4·0
3·0
2·0
1·0
1100
1060
1020
T/K

Figure 6

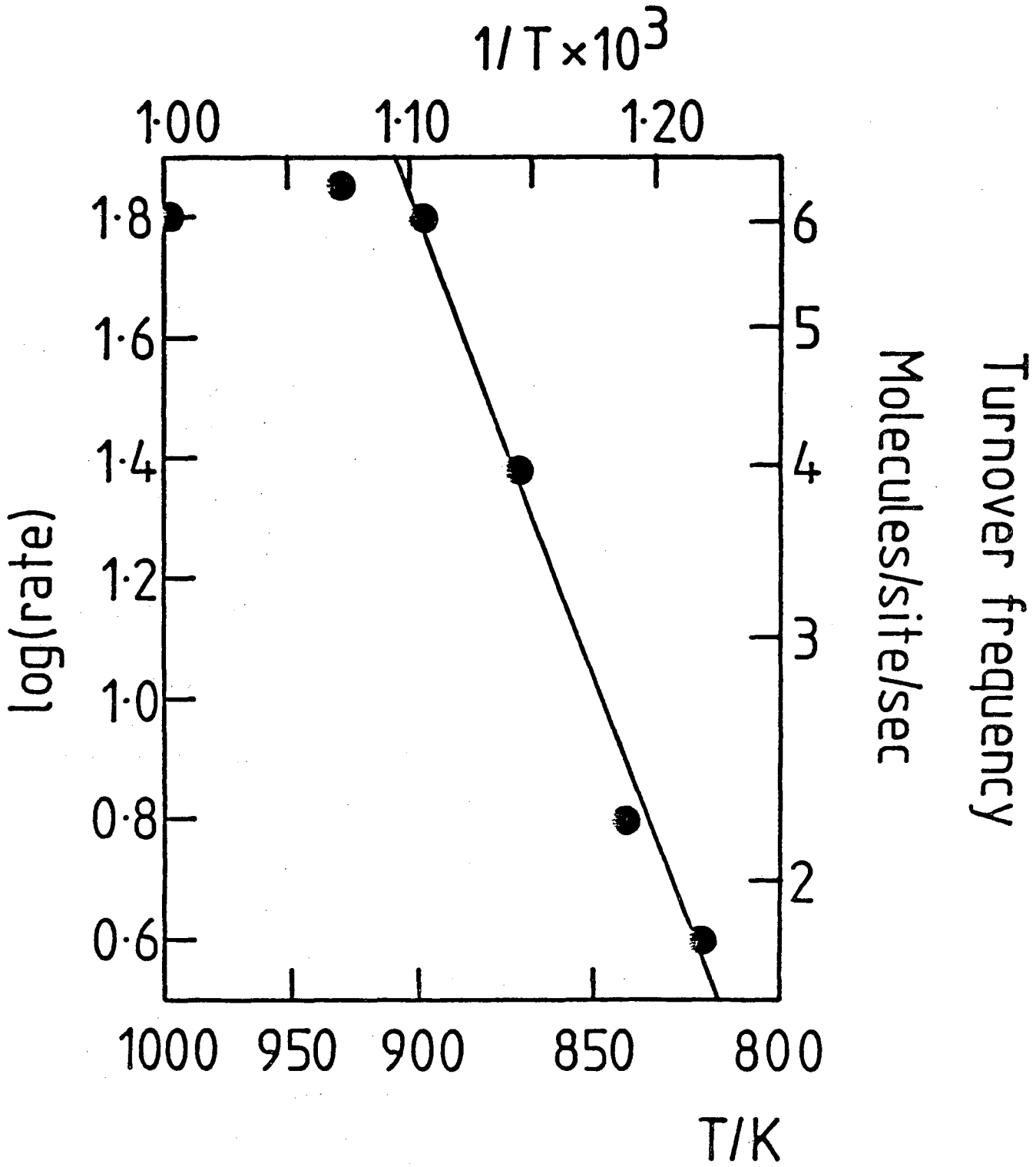

Turnover frequency
Molecules/site/sec
6
5
4
3
2
1·00
1·10
1·20
1/T×10^3
1000
950
900
850
800
T/K
1·8
1·6
1·4
1·2
1·0
0·8
0·6
log(rate)

Figure 7

Task 3: CHEMISTRY OF COAL SOLUBILIZATION AND LIQUEFACTION

R. H. Fish, A. Thormodsen and M. Simmons

In this quarterly report, we wish to report on our initial results of a comparison of polymer-supported Wilkinson's catalyst on 2% cross-linked phosphinated polystyrene-divinylbenzene (PS-DVB) with results obtained with the homogeneous analogue for the selective reduction of polynuclear heteroaromatic nitrogen and sulfur compounds

Initial and Relative Rates

The initial and relative rates of reduction of the substrates were obtained using a Parr kinetic apparatus. Table 1 (parts of which were also shown in the Sept. 30 report) indicates the results of this comparison, with substrate to metal ratio, temperature, and partial pressure of hydrogen being equivalent for both forms of Wilkinson's catalyst. The polymer-supported catalysts results in Table 1 were carried out with the same batch of 2% PS-DVB beads with excellent reproducibility upon repetition of each experiment.

Several important observations become apparent from these results; namely, the initial rates of hydrogenation of the nitrogen heterocyclic compounds studied with polymer-supported Wilkinson's catalyst are 10-to-20 times faster than the homogeneous equivalent. This unusual enhancement is extremely relevant for practical applications and has not been observed with many polymer-supported catalysts in other reduction reactions.

Several reasons for the rate enhancement of the polymer-supported over the homogeneous catalyst can be formulated. One important consideration may be found in the fact that the substrates are themselves suitable ligands. Also, a higher concentration or enrichment of substrate around the polymer-supported metal center, with concomitant loss of triphenylphosphine, may be of consequence in these rate enhancements. Other factors such as steric and electronic effects are also probably involved in these rate enhancements. For example, the relative rate differences between the compounds studied for both forms of Wilkinson's catalyst may involve steric effects as accentuated by the 5,6 and 7,8-benzoquinoline rate ratio 2/3 = 6.0 as well as quinoline-benzoquinoline rate

ratios of 2 and 13 respectively. It is interesting to note that only in the case of the sulfur heterocyclic compound is the initial rate larger for the homogeneous catalyst, while overall relative rates are similar for the nitrogen compounds within each set of catalyst results.

Selectivity

The high regioselectivity for the heteroaromatic ring, with both forms of the catalyst, is evident (Table 11). In one case (acridine), the polymer-supported catalyst gave only 9,10-dihydroacridine with no 1,2,3,4-tetrahydroacridine apparent. In contrast, the homogeneous analogue gave substantial amounts of the outer ring product (approx. 50%) and this difference may result from the more pronounced steric requirements surrounding the active metal sites on the polystyrene-divinylbenzene supported catalyst.

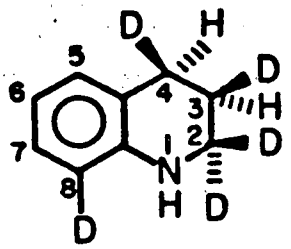
Parameters that Affect Rate

Several other parameters that were critical to study included the effect of cross-linking and diffuson rates of substrate into the PS-DVB beads. In experiments to clarify these points, the 2% cross-linked polystyrene-divinylbenzene beads with Wilkinson's catalyst were compared to the 20% cross-linked beads for reduction of quinoline and the initial rate ratio for both (2%/20%) was found to be approximately 3. We also ground the 2% beads and hydrogenated quinoline using similar reaction conditions to show that diffusion of substrate into the bead was not rate limiting, i.e., both ground and whole (approx. 30 μ) 2% cross-linked beads gave the same initial rates within experimental error.

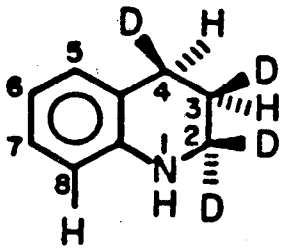
Mechanism of Hydrogenation of Quinoline with Polymer-Supported Wilkinson's Catalyst

The mechanism of reduction of quinoline with deuterium gas was recently elucidated with homogeneous Wilkinson's catalyst. In that study, we found the following pattern of deuterium incorporation as shown, 6.

In contrast, compound 7 shows the deuterium pattern (nmr and ms) obtained with 2% cross-linked PS-DVB Wilkinson's catalyst. The pertinent diference is the



6



7

lack of aromatic C-H exchange (C_8) for the polymer-supported catalyst, while stereochemistry at the 3,4-double bond (cis) and reversible dehydrogenation of the reduced carbon-nitrogen bond (positions 1 and 2) to provide 1.6D at the 2-position, via quinoline-2-d, is similar for both forms of the catalyst. Moreover, reaction of the product, 1,2,3,4-tetrahydroquinoline, with PS-DVB Wilkinson's catalyst under similar deuteration conditions also shows, by nmr and ms analysis, no exchange of the aromatic hydrogen at position 8 (6.42 ppm), and is in contrast to the homogeneous catalyst result. Again, steric requirements surrounding the polymer-supported catalyst active metal center may be responsible for the lack of aromatic C-H exchange.

Reduction of Quinoline in the Presence of Model Coal Liquid Constituents

Since the compounds shown in the Table 1 are prevalent in synthetic fuel products such as coal liquids, we wanted to determine whether the selectivity for the nitrogen heterocyclic ring (with quinoline as the example) would prevail in the presence of other coal liquid constituents. The model coal liquid, dissolved in benzene and containing (wt%) 30% pyrene, 5% tetralin, 38% methylnaphthalene, 17% m-cresol, 7.5% quinoline and 2.5% 2-methylpyridine, was hydrogenated with the 2% PS-DVB Wilkinson's beads (similar conditions as shown in Table 1) to provide 1,2,3,4-tetrahydroquinoline as the only reduction product (initial rate 0.42%/min). Removal of 2-methylpyridine had no effect on the initial rate in contrast to the competitive inhibition on quinoline by the pyridine derivative in the homogeneous reaction. Interestingly, reduction of quinoline alone, at a similar substrate-to-metal ratio as in the model coal liquid, provided an initial rate (0.18%/min) that was approximately 2.2 times slower than the rate

of quinoline in the presence of the model coal liquid constituents.

This result emphasizes the highly selective reaction taking place in the presence of other functionalities i.e., regiospecific reduction of the nitrogen heterocyclic ring as well as the rate enhancement phenomena, and provides dramatic evidence for the potential usefulness of polymer-supported catalysts in synthetic fuel (hydroprocessing) applications.

Denitrification of Partially Hydrogenated Nitrogen Containing Aromatics

Equipment has been set up and work started on catalytic cracking of compounds such as tetrahydroquinoline dihydroacridine in admixture with paraffins like hexadecane. If nitrogen can be split out, this would offer a route for hydrocarbon denitrificatin requiring much less hydrogen consumption than conventional routes.

Table 1

Comparison of Initial and Relative Rates of Hydrogenation of Substates 1-5 Using Both Polymer-Supported and Homogeneous Wilkinson's Catalysis[a]

Substrate	Product[b]	Polymer-Supported Rates[c] Initial (%/min)	Polymer-Supported Rates[c] Relative	Homogeneous Rates Initial (%/min)	Homogeneous Rates Relative	PS/H Rate Ratio
Quinoline	1,2,3,4 Tetrahydro-	.29	1	.013	1	22
5,6 Benzoquinoline	1,2,3,4 Tetrahydro-	.14	.48	.0065	.5	22
7,8 Benzoquinoline	1,2,3,4 Tetrahydro-	.024	.08	.0012	.09	20
Acridine	9,10 dihydro-	~.4	~1.4	~.04	~3	10
Acridine	1,2,3,4 Tetrahydro-	0	0	.047	3.6	0
Benzothiophene	2,3 Dihydro	~.03	~.1	.044	3.4	.7

a) Reaction conditions were as follows: P_{H2}=310 psi, T=85°C, sub./Cat.=91/1, Benzene (20 ml), 1 mmole substrate in each case, with either 10.2 mg of homogeneous $RhCl(PPh_3)_3$ or 52 mg of polymer-supported Wilkinson's catalyst [2% cross-linked, 2.19% Rh, initial P/Rh=2.9 (Strem Chemical Co.), P/Rh after reaction with substrate 1-5 ~3.3] contained in a wire basket attached to the end of the dip-tube of the kinetic apparatus.

b) Analysis by gas chromatography.

c) Plots of % conversion vs. time provided initial (pseudo zero order) rates. Rates are relative to quinoline (1.0). Substrates, 1-5, were reacted with the same beads for all initial rates reported.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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