SUPPORTED RUTHENIUM CARBONYLS AS CATALYSTS FOR THE HYDROGENATION OF CARBON MONOXIDE AND DIOXIDE

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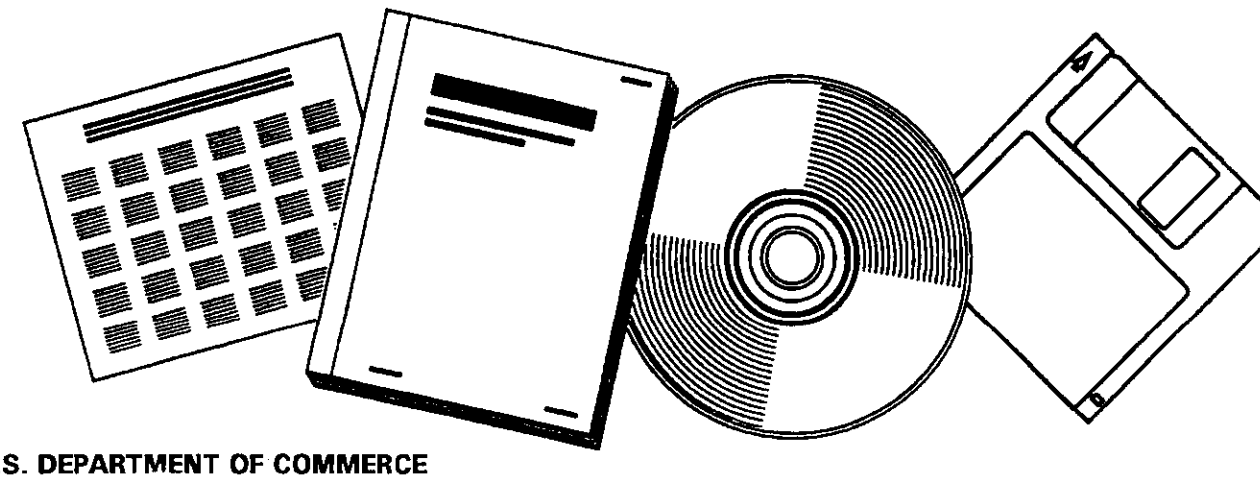

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by

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ABSTRACT

New supported ruthenium catalysts have been prepared (a) by diffusing $Ru(CO)_5$ into the pores of faujasitic zeolites, and (b) by sorbing ruthenium carbonyl cluster compounds onto oxide supports. After thermal activation, the supported ruthenium systems catalyse the hydrogenation of carbon monoxide to mixtures of paraffins and olefins, but the hydrogenation of carbon dioxide to paraffins only. Furthermore, while carbon monoxide hydrogenation results in typical Anderson-Schulz-Flory (A-S-F) product distributions, ie. low in C_2 and C_3 hydrocarbons, carbon dioxide hydrogenation gives a product distribution which is not depleted in C_2 and C_3 hydrocarbons. Possible reasons for the fundamentally different product distributions obtained for the two carbon oxides will be discussed. Use of promoters and variation of conditions to optimize olefin content and to induce shape selectivity will also be discussed.

INTRODUCTION

The hydrogenation of carbon monoxide (CO) using supported transition metal catalysts has long been recognized as providing potentially useful routes to both synthetic fuels and chemical feedstocks. Extensive reviews of results obtained and mechanistic implications suggested have appeared recently[1]. Prime concerns have been to optimize yields of C_2-C_4 olefins and to improve selectivity in terms of molecular weight distributions. The similarity between metal carbonyl clusters and the metal particles of heterogeneous catalyst surfaces, and the likelihood that such clusters when supported might give rise to very small aggregates of metal atoms, has stimulated research into the use of such clusters as precursors for Fischer-Tropsch catalysts. The phenomenon of "shape selectivity" observed when products are generated within the geometric restrictions of a zeolite has introduced an added incentive to develop such cluster catalysts within zeolite supports[2].

In contrast, although carbon dioxide (CO_2) is in principle a readily available, potentially inexpensive source of carbon, relatively little has been done in the field of its hydrogenation by similar means[3], and very little is known of the mechanism of CO_2 hydrogenation[3a-d].

In an effort to explore the relatively new field of CO_2 hydrogenation, we have investigated the catalytic behaviour of some ruthenium carbonyl clusters supported on both zeolitic and non-zeolitic supports. The results are compared and contrasted with similar hydrogenation reactions of CO, and differences in product distributions observed when the two oxides are hydrogenated with the same catalyst under identical conditions are discussed.

EXPERIMENTAL

NaY zeolites were purchased from Strem Chemicals, Inc. Zeolites and γ-alumina used in catalysis were dried at 10^{-2} mm Hg for 24 hours at 500 °C. Catalytic studies were carried out with 1/16" zeolite pellets and with alumina pieces (2-4 mm^3).

Triruthenium dodecacarbonyl[4] (I, $Ru_3(CO)_{12}$) was prepared from $RuCl_3 \cdot 3H_2O$ by the method of Johnson and Lewis[5]. Ruthenium pentacarbonyl (II, $Ru(CO)_5$) was generated from I in the presence of zeolites in a Superpressure Micro Series pressure reactor at 200 atm. CO and 160 °C[5]. The presence of II in the zeolite pores was confirmed by Fourier Transform IR spectroscopy (ν_{CO}(Nujol): 2167w, 2134w, 2105m, 2087m, 2067s,sh, 2058s, 2044vs, 2021m,sh, 2000s, 1944m cm^{-1})[6]. On exposure to nitrogen atmosphere, II reverts to I. The $Ru_3(CO)_{12}$-NaY catalyst thus prepared gives an IR spectrum which compares favourably with that reported by Zecchina[7] for the same catalyst prepared by another route (ν_{CO}(Nujol): 2167w, 2134w, 2105m,sh, 2077s,br, 2042m, 1974,sh cm^{-1}). For catalysts containing methyl iodide promoter, an appropriate amount (Ru/MeI 1:1) of methyl iodide was syringed into a flask containing stirred $Ru_3(CO)_{12}$-loaded zeolites.

All ruthenium carbonyl cluster compounds were prepared according to literature methods as indicated in Table II. Impregnation onto the γ-Al_2O_3 support was achieved by dissolving the clusters in pentane or methanol (for anionic clusters), filtering the solution into a flask containing the cooled support under nitrogen, and allowing the mixture to soak for about two hours with intermittent shaking. The solvent was then removed under vacuum and the catalyst dried *in vacuo* for several hours before activation.

Catalyst testing was performed under essentially differential conditions in a stainless steel fixed bed reactor (Chemical Data Systems 803 Micro Pilot Plant Reactor) with on-line gas chromatograph (Hewlett Packard 5800A, equipped with TC and FI detectors and n-octane porasil-C, SE-30 and Porapak Q columns). Catalysts were typically pretreated with flowing hydrogen (20 sccm) at 200 °C for 20 hours (exceptions are indicated in Tables I and II). Catalytic runs were performed at 320 psig pressure, and at gas hourly space velocity (GHSV) of 1000 h^{-1}. Ratios of H_2 to CO or CO_2 and temperatures of the various catalytic runs are as indicated in Tables I and II.

Steady state product distributions and CO and CO_2 conversions were normally achieved in 24 hours, and runs were normally of 4 to 5 days duration. In all A-S-F plots shown, total isomers at each carbon number are included, and all plots result from reproducible runs and a number of gc charts.

RESULTS AND DISCUSSION

(A) CO HYDROGENATION

Table I is representative of results obtained in CO and CO_2 hydrogenation studies performed using the $Ru_3(CO)_{12}$-zeolite catalysts, prepared by percolating $Ru(CO)_5$ into the pores of faujasitic zeolites. This method is considerably more efficient than reported methods[8] utilizing $Ru_3(CO)_{12}$, and it also has the advantage that the lower kinetic diameter of $Ru(CO)_5$ enables it to more easily penetrate into the pores and supercages of zeolites than does the trimer. Although our chief concern has been with CO_2 hydrogenation, for purposes of comparison the syn-gas activity of these catalysts have been investigated and it was anticipated that such catalysts might exhibit shape selectivity in the Fischer-Tropsch reaction.

The data for CO hydrogenation in Table I and as plotted in Figure 1a indicate that, disappointingly, shape selectivity was not observed. A typical A-S-F distriubtion is observed up to C_{20}, although the olefin/paraffin ratio was encouragingly high. $Ru_3(CO)_{12}$-NaY catalysts have been shown to exhibit non-A-S-F product distributions with sharp cut-off points at C_9-C_{10}[8,9]. The uniform conclusion of these authors is that this selectivity is more a function of the ruthenium particle size produced during activation than a geometric restriction shape-selectivity.

It may be that the activation conditions we have employed have been conducive to the formation of large Ru particles, and that a slower rate of heating[8a], and higher temperatures of activation will lead to the observation of a similar molecular weight selectivity. Conversely, it may be that milder activation conditions are required to prevent movement of ruthenium out of the pores and onto the surface of the zeolites, and that this might result in the observation of true geometric shape-selectivity.

As indicated in Figure 1b, the addition of methyl iodide to the $Ru_3(CO)_{12}$-NaY catalyst does result in the observation of shape-selectivity. The quantity of hydrocarbon produced plummets at C_8, C_9, and in fact no hydrocarbons above C_{10} are detected at all. A possible explanation for this is that the methyl iodide is poisoning the surface of the catalyst, thus ensuring that all catalysis occurs within the zeolite structure. Alternatively, methyl iodide may be blocking the zeolite pores and preventing movement of encaged Ru particles onto the surface during activation. It is notable, however, that no pretreatment was applied to this catalyst, and the occurrence of shape selectivity may be due to this (see comments above) rather than to the presence of methyl iodide. The methyl iodide promoter significantly enhances the amount of C_2 produced with respect to the unpromoted $Ru_3(CO)_{12}$-NaY catalyst, and this is in agreement with the findings of Tatsumi *et al*[8c]. It is also interesting to observe the absence of olefins, and the significant degree of reverse water gas shift catalysis which results from methyl iodide promotion.

Jacobs *et al*[9] have reported the use of a lanthanide-exchanged Y zeolite to reduce Ru particle size in the supercages, and so to enable enhancement of the olefin fraction and a cut-off at C_5. Results of CO hydrogenation with our $Ru_3(CO)_{12}$-LaY catalyst, as indicated in Table I, did show enhanced total olefin formation, but shape selectivity was again absent. This may again be due to activation procedures, and studies in which these are varied are in progress. The higher methane, lower olefin production observed with this catalyst with higher H_2/CO ratio is somewhat typical of these catalysts.

The $Ru_3(CO)_{12}$-NaY catalyst prepared via $Ru(CO)_5$, does show promising Fischer-Tropsch activity, with an encouragingly large olefin fraction. By experimenting with activation conditions, we believe that we will observe true

shape selectivity.

(b) CO_2 HYDROGENATION

In a previous publication[3e], we noted the promising activity of ruthenium catalysts for CO_2 hydrogenation at 1 atmosphere pressure. As indicated in Table I, the $Ru_3(CO)_{12}$-NaY catalyst is a superb CO_2 methanation catalyst, and under the conditions indicated in the first column (optimized towards methanation), this catalyst shows 100% conversion of CO_2 into methane of high purity (99.8%). This high conversion is not greatly sensitive to pressure, as runs at 1 atm., 8 atm. and 22 atm. all show similar conversions at 320°C (H_2/CO_2 = 4:1). This is in agreement with the relatively small pressure dependencies observed by other workers for CO_2 hydrogenation on Ru[3f] and other metals[3f,13,14]. The degree of conversion is temperature-dependent, and increases from about 10% at 150°C to 100% at 320°C (H_2/CO_2 = 4:1 on $Ru_3(CO)_{12}$-NaY, 2% Ru). The activity data for CO_2 hydrogenation over a $Ru_3(CO)_{12}$-LINDE 5A catalyst are indicated in Table III, and an Arrhenius plot to obtain an activation energy is shown in Figure 2. The value obtained of 29.8 kJ/mole is of similar magnitude to that obtained by Gupta *et al*[3d] for a Ru-molecular sieve catalyst (30.5 to 57.7 kJ/mol), and significantly lower than that reported by Lunde and Kester[19] (70.3 kJ/mol) for the Ru/Al_2O_3, and Weatherbee and Bartholomew[3f] (72 to 103 kJ/mol) for Ru/SiO_2 catalysts.

The activation energy for CO_2 hydrogenation is significantly lower than for CO hydrogenation, as observed by comparison of conversion over the same catalyst at 200°C. This too is in agreement with observations by other workers[3]. Comparison of conversions at H_2/CO_2 ratios of 4:1 and 1:1 (for example, the Ru-LaY (5% Ru) catalyst shows conversion of 41% when the ratio is 1:1 at 280°C, and 97% when ratio is 4:1 at the same temperature) indicate that activity is sensitive to this ratio.

Attempts to minimize the selectivity to methane and to enhance C_{2+} hydrocarbon production have been made in three ways. These entailed (i) lowering the H_2/CO_2 ratio to 1:1 using the unpromoted $Ru_3(CO)_{12}$-NaY catalyst; (ii) use of methyl iodide promoter[8c]; and (iii) use of a lanthanide-exchanged zeolite[9]. These attempts have met with limited success, but we note early reports[16,17] that production of hydrocarbons other than methane from CO_2 does not occur, and it is only recently that Somorjai[18] (small fraction of C_2 with Fe catalyst) and Bartholomew[3f] (small amounts of C_2, C_3 over Ru, C_2-C_5 our Fe) have observed other hydrocarbons. Thus although the quantities of heavier hydrocarbons which we have observed are small, the formation of hydrocarbons up to C_{16} over a Ru catalyst is, we feel, significant. Lowering the H_2/CO_2 ratio did result in the formation of alkanes up to C_{16}, but the relative molar amount of C_2-C_{16} was only 3%.

Use of methyl iodide increased the fraction of heavier hydrocarbons to 16% of total hydrocarbons, but the amount of CO generated as opposed to hydrocarbons (19:1) served to negate this advantage. Employing the LaY-zeolite served only to increase the activity slightly and selectivity for methane was in fact enhanced. Use of NaX and Linde 5A zeolites showed similar activity and selectivity for methane.

Attempts to generate products other than methane from CO_2 hydrogenation over ruthenium clusters on γ-Al_2O_3 have also proved to be qualitatively successful, as noted from Table II. However, none of these clusters is as active as $Ru_3(CO)_{12}$ on NaY towards CO_2 hydrogenation, and amounts of C_{2+} hydrocarbons

produced at 200°C, H_2/CO = 1:1 are no better.

The rationale behind the use of individual clusters arose from reported trends in CO hydrogenation[10-12], and it was hoped there would be some analogy in CO_2 hydrogenation. For example, Na is known to be a catalytic promoter of chain growth, and increases the olefin content in CO hydrogenation experiments[10]. It was hoped that $NaHRu_3(CO)_{11}$ might therefore provide a CO_2 hydrogenation catalyst with these qualities. $H_4Ru_4(CO)_{12}$ has also been shown to exhibit unusual product distributions in CO hydrogenation experiments[11]. Further, Cu as a co-catalyst with Ru in the Ru-Cu clusters was employed in the hope that the increased olefin/paraffin ratio observed for CO hydrogenation of Ru-Cu mixtures on alumina[12] might also be observed in CO_2 hydrogenation. To date, none of these approaches has proved greatly successful, and it is clear that one cannot extrapolate trends from the hydrogen of CO to that of CO_2.

These observations suggest that the mechanisms for hydrogenation of the two carbon oxides over supported ruthenium are different and it seems likely that CO_2 and CO hydrogenation do not involve common CO-containing intermediates. This suggestion is further borne out by comparison of the product distributions obtained when the hydrogenations of the two oxides are carried out over the same catalyst under identical conditions. Catalytic runs in which the feed gas was changed from CO and H_2 to CO_2 and H_2, and then back to CO and H_2 clearly demonstrated this difference, as shown in Figure 1a. On reverting to CO and H_2 the second time, the original product distribution was repeated. The CO_2 product distributions were no different to those obtained in experiments when CO had not previously been passed over the catalyst. The pattern illustrated in Figure 1 was observed for the $Ru_3(CO)_{12}$-NaY, $Ru_3(CO)_{12}$-LaY, and in the $Ru_3(CO)_{12}$-Al_2O_3 and $NaHRu_3(CO)_{11}$-Al_2O_3 systems as indicated in Table II.

Current views are that CO_2 hydrogenation follows a similar path to that of CO hydrogenation. Falconer and Zagli[3c] present this view based on evidence that adsorbed CO_2 and CO are hydrogenated on Ni and Ru catalysts at the same temperature. Kinetic studies by Dalmon and Martin[15], Weatherbee and Bartholomew[3f] and Peebles et al[14] are indicated to strongly suggest that CO_2 hydrogenation in fact proceeds via CO hydrogenation. The similarity of the orders of magnitude of catalyst activity for CO and CO_2 hydrogenation are also quoted by Bartholomew[3f] as evidence for this.

However, we find it difficult to account for the different product distributions from the hydrogenation of the two oxides if these views are correct. The distinctive features of the product distribution in CO_2 hydrogenation relate to the predominant methane production, the total absence of olefins, and the absence of a C_2 depletion. It is widely accepted that the low C_2 concentrations arise in CO hydrogenation because of the incorporation of ethylene units into the growing hydrocarbons chains[1]. The failure to observe such a depletion points to the possibility that chain growth in CO_2 hydrogenation does not occur by this mechanism. The failure to observe olefins seems to corroborate this. The lack of availability of ethylene units may necessitate the operation of a different chain-growth mechanism, possibly methylene polymerisation[1], which may be less efficient, and results in a high C_1 and C_{2+} ratio.

It is apparent therefore, that much work remains to be done in clarification of the kinetics and mechanism of CO_2 hydrogenation.

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TABLE I

CO AND CO_2 HYDROGENATION OVER I - ZEOLITE CATALYSTS

(catalysts 2% Ru by wt.)

CATALYST	I-NaY	I-NaY			I-MeI-NaY			I-LaY		
REACTANT	CO_2	CO_2	CO	CO	CO_2	CO	CO	CO_2	CO	CO
H_2/CO or CO_2	4:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1	1:1
TEMPERATURE (°C)	320	200	200	260	200	200	260	200	240	240
% CONVERSION (CO OR CO_2)										
TOTAL	95+	25	3.5	11	20	3	3	29	5	36
Into H/C's	95+	25	3.0	10	1	1	1	29	5	36
Into CO or CO_2	0	0	0.5	1	19	2	2	0	0	0
REL. MOLAR %										
C_1	99.8	97	67.4	50.1	84	69.6	63.5	99.6	26	68
C_2	0.2	1.8	5.1	6.4	7	12.5	10.1	0.37	4	5.5
C_3+	-	1.2	27.5	43.5	9	17.9	26.4	0.03	70	26.5
C_{max}	C_2	C_{16}	C_{20}	C_{26}	C_{11}	C_9	C_9	C_3	C_{16}	C_{25}
$C_{2=}/C_2$	0	0	0.47	0.28	0	0	0	0	0.6	0.3
$C_{3=}/C_3$	0	0	0.74	0.70	0	0	0	0	0.6	0.3
C_4 n/iso	-	-	-	5	10	2.2	-	-	-	-

TABLE II

CO AND CO_2 HYDROGENATION OVER RUTHENIUM CARBONYL CLUSTER/γ-Al_2O_3 CATALYSTS

(activation at 350°C for 12 hours under hydrogen flow, unless otherwise stated;

GHSV = 1700 h^{-1}; catalysts 1-2% Ru)

CATALYST	$Ru_3(CO)_{12}$/Al_2O_3		$NaHRu_3(CO)_{11}$[a]/Al_2O_3		$(PPN)HRu_3(CO)_{11}$[a]/Al_2O_3	$H_4Ru_4(CO)_{12}$[b]/Al_2O_3	$Ru_6(CO)_{18}Cu_2(tol)_2$[c]/Al_2O_3 (activated at 200°C)
REACTANT	CO_2	CO	CO_2	CO	CO_2	CO_2	CO_2 (GHSV = 1000 h^{-1})
H_2/CO or CO_2	1:1	1:1	1:1	1:1	1:1	1:1	1:1
TEMP (°C)	220	220	220	220	220	220	242
% CONVERSION (CO_2 or CO)	9	4	9	4	2	9	23
REL.MOLAR %							
C_1	97.2	64.6	96.4	65.0	96	97.9	97
C_2	2.5	7.0	2.6	8.2	3.5	1.7	2.5
C_3	0.3	28.4	1.0	26.8	0.2	0.4	0.5
C_{max}	C_{15}	C_{22}	C_{10}	C_{21}	C_3	C_{16}	C_{15}
TOTAL % OLEFINS	0	20	0	20	0	0	0

a. Prepared by method of B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Suss, J.C.S. Dalton Trans. 1979, 1356

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TABLE III

ACTIVITY DATA FOR $Ru_3(CO)_{12}$-LINDE 5A CO_2 HYDROGENATION

(2% Ru on LINDE 5A, 1.26 g catalyst used per run; P = 240 psig, GHSV = 812 h^{-1}, H_2/CO_2 = 4:1. Activation under 20 sccm H_2 Flow for 20 h at 130°C).

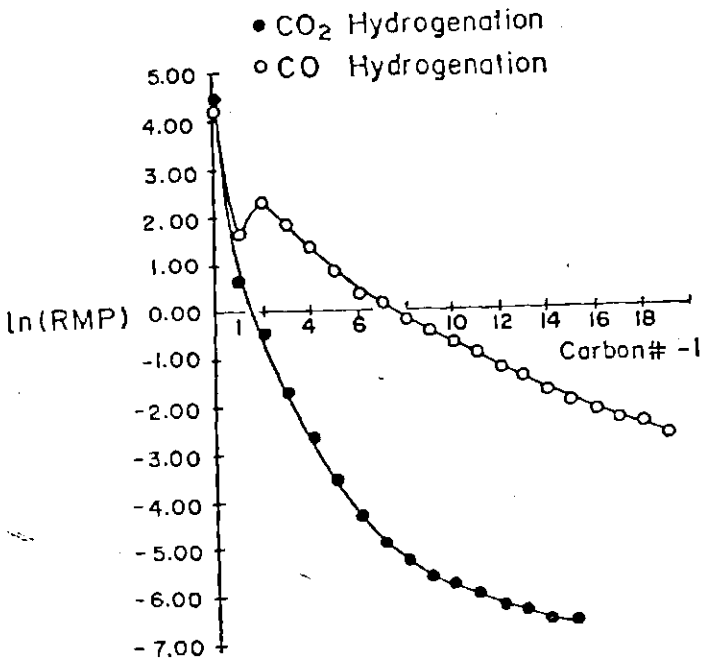
TEMPERATURE		1/T (K^{-1})	% CO_2	N_{CO_2} [a]	N_{CH_4} [b]	$\ln(N_{CH_4} \times 10^3)$
°C	K	($\times 10^3$)	CONVERTED	($\times 10^3$)	($\times 10^3$)	
150	423	2.36	12	24.9	24.8	3.215
200	473	2.11	30	55.8	55.5	4.022
240	513	1.95	64	109.7	109.5	4.698
320	593	1.69	93	137.9	137.1	4.927

a molecules of CO_2 reacted per atom Ru per second

b molecules of CH_4 produced per atom Ru per second

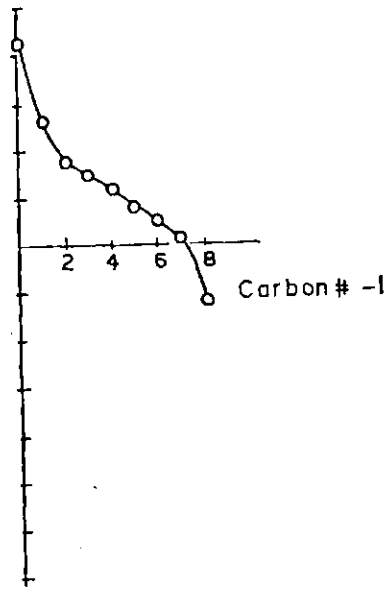
Figure 1.

1(a) Anderson - Schulz - Flory Plots of CO and CO_2 Hydrogenation on $Ru_3(CO)_{12}$ - NaY



GHSV = 1000h^{-1}., H_2: CO or CO_2 = 1:1.,
T = 200°C., P = 320psig.
2 % Ru. Activated with flowing H_2 for 20h at 200°C.

1(b) Anderson - Schulz - Flory Plot of CO Hydrogenation on $Ru_3(CO)_{12}$ - MeI - NaY



GHSV = 1000h^{-1}., H_2: CO = 1:1.,
T = 200°C., P = 320psig.
2% Ru, Ru : MeI = 1:1
NO PRETREATMENT

Figure 2.

ARRHENIUS Plot of Methane Turnover Frequencies in CO_2 Hydrogenation on $Ru_3(CO)_{12}$-Linde 5A (2% Ru., 1·26g catalyst; $H_2/CO_2 = 4:1$ p = 240 psig)