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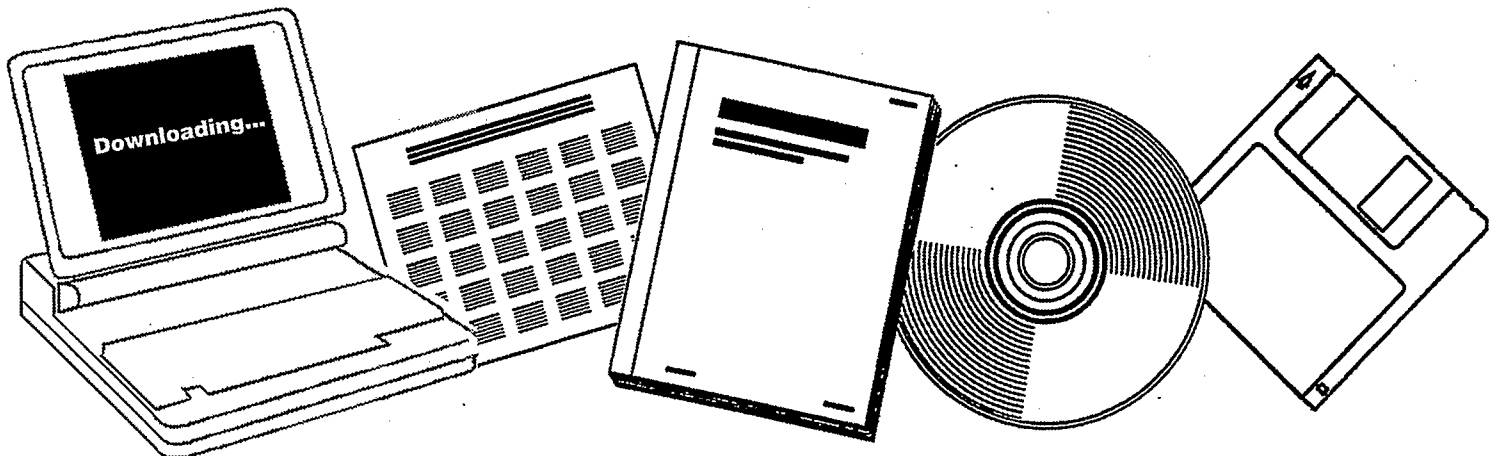
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**EFFECT OF CHEMICAL ADDITIVES ON THE
SYNTHESIS OF ETHANOL. TECHNICAL PROGRESS
REPORT 7, MARCH 16, 1989--JUNE 15, 1989**

**AKRON UNIV., OH. DEPT. OF CHEMICAL
ENGINEERING**

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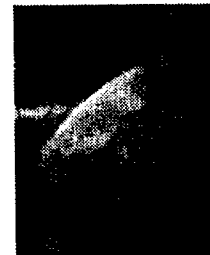
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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

Technical Progress Report 7
Grant No. DE-FG22-87PC79923

March 16, 1989 - June 15, 1989

by

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SUMMARY

The objective of this research is to elucidate the role of various chemical additives on ethanol synthesis over Rh- and Ni-based catalysts. Chemical additives used for this study will include S, P, Ag, Cu, Mn, and Na which have different electronegativities. The effect of additives on the surface state of the catalysts, heat of adsorption of reactant molecules, reaction intermediates, reaction pathways, reaction kinetics, and product distributions is/will be investigated by a series of experimental studies of NO adsorption, reactive probing, steady state rate measurement, and transient kinetic study.

A better understanding of the role of additive on the synthesis reaction may allow us to use chemical additives to manipulate the catalytic properties of Rh- and Ni-based catalysts for producing high yields of ethanol from syngas.

RESULTS TO DATE

During the second quarter of 1989, AgRh/SiO₂ was used as a model catalyst for studying the structure sensitivity of C₂ oxygenate synthesis. The results reveal that the C₂ oxygenate synthesis may be less structure-sensitive than the hydrocarbon synthesis during CO hydrogenation.

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ABSTRACT

The effect of Ag on CO hydrogenation over Rh/SiO₂ has been studied. Ag is found to decrease the rates of formation for CH₄ and C₂₊ hydrocarbons more than those for C₂ oxygenates resulting in a marked increase in C₂ oxygenate selectivity. Infrared spectroscopic studies reveal that Ag blocks the bridge-CO sites. Ethylene addition studies show that Ag promotes CO insertion and suppresses hydrogenation. The results suggest that the number of Rh atoms required for CO insertion may be less than that for hydrogenation and methanation.

INTRODUCTION

Approaches to the synthesis of higher alcohols from syngas have included the use of catalysts based on (i) supported metal catalysts, such as supported Rh, Ru, Co, Fe, and Mo [1-5] and (ii) Cu/ZnO-based catalysts, such as alkali-promoted Cu/ZnO and Co-Cu/ZnO/Al₂O₃ catalysts [6-8]. The synthesis over Cu/ZnO-based catalysts which requires the use of high pressure (at least 5 MPa) produces methanol as a major product and higher alcohols as minor products. In contrast, supported Rh catalysts have been found to be highly active and selective for the production of C₂ oxygenates including acetaldehyde, ethanol, and acetic acid at low pressure conditions [1,9-14].

The unique activity of the rhodium-based catalysts for C₂ oxygenate synthesis lies in their moderate CO dissociation and strong CO insertion capabilities. Additives, including Zn, Ti, Zr, V and La oxides, have been demonstrated to enhance CO

insertion activity of Rh/SiO₂ catalysts [10,11]. The additives such as Mn and Mo resulted in increases in the rate of both CO dissociation and CO insertion leading to increases in the activity for the formation of C₂ oxygenates [12,13]. In contrast to the promoting effect of transition metal oxides, a selective inhibition effect of alkali additives on hydrogenation led to enhancement of C₂ oxygenate selectivity on Rh catalysts [14]. The modification of catalytic behavior by these various additives has been attributed to either the electronic effect of additives or the chemical interaction of additives with reactant molecules.

Ag, for which electronegativity is similar to that of Rh metal, is an inactive component for a number of reactions including CO hydrogenation, olefin hydrogenation, and alkane hydrogenolysis [15,16]. Depending on the structure sensitivity of the reactions and distribution of inert additives on the surface of an active metal, the addition of the inactive component such as Ag may not only modify the overall activity but also change the selectivity of the reaction. This paper reports results of the CO hydrogenation study on AgRh/SiO₂ catalysts. Emphasis was placed on the effect of temperature and the concentration of Ag on the C₂ oxygenate selectivity. Ethylene addition was used to determine the effect of Ag on the activity of Rh/SiO₂ for CO insertion and hydrogenation. Infrared spectroscopic studies of CO adsorption were employed to probe the structure of the surface of AgRh/SiO₂ catalysts.

EXPERIMENTAL

Catalyst Preparation

Three wt. % Rh/SiO₂ was prepared by impregnation of SiO₂ (Strem Chemicals) using Rh nitrate (Alfa Chemicals). AgRh/SiO₂ was prepared by coimpregnation using both Rh and Ag nitrates. The percentage of Rh was the same in all of the Rh/SiO₂ and AgRh/SiO₂ catalysts. The molar ratios of Ag to Rh are 0.25, 0.5, and 1. After impregnation, the samples were dried overnight in air at 313 K, then reduced in flowing hydrogen at 673 K for 16 hr. The crystallite sizes of the Rh and Ag metals was determined by X-ray diffraction line-broadening technique. Effect of Ag on the hydrogen chemisorption was determined by the flow chemisorption method.

Reaction Studies

CO hydrogenation (CO/H₂ = 1) was performed over the catalysts in a differential reactor system under 393 - 573 K and 1.01 MPa. Space velocities of 1,100 to 11,000 hr⁻¹ were used to keep CO conversion below 5% in order to minimize heat and mass transfer effects and secondary reactions. Product distribution was determined by an HP-5890A gas chromatograph (GC) with a 6 ft Porapak PS in series with a 6 ft Porapak Q column. The combination of these two GC columns permits a good on-line separation of methane and C₂~C₆ paraffins and olefins as well as C₁~C₄ alcohols and aldehydes.

A small amount of ethylene (2 mole % of the reactant mixture) was added to the syngas stream to initiate the reaction of ethylene with syngas (ethylene hydroformylation) at 573 K and

1.01 MPa. The addition of ethylene led to a significant increase in the rate of formation of ethane and propionaldehyde while the addition hardly affected the rate of formation of other CO hydrogenation products (14). The rate of ethane and propionaldehyde formation during ethylene addition on the various AgRh/SiO₂ was used to determine the effect of Ag on hydrogenation and CO insertion activities of Rh catalysts.

Infrared Spectroscopic (IR) Studies

Adsorption of CO on the Rh/SiO₂ and AgRh/SiO₂ was studied in an IR cell at 510 K and 1.01 MPa. The IR cell is made of stainless steel with CaF₂ windows using Grafoil O-rings (Union Carbide). The catalysts for the study were ground to a fine powder and pressed into a disk (approx. 10 mm in diameter and 1 mm in thickness with 25 mg). IR spectra of adsorbed species were recorded by a Nicolet 5SXC FTIR spectrometer with a DTGS detector at a resolution of 4 cm⁻¹. Gas phase CO bands were eliminated by subtracting the absorbance of gas phase CO with a SiO₂ disk in the cell from the spectra of adsorbed species on the Rh/SiO₂ and AgRh/SiO₂ catalysts.

RESULTS AND DISCUSSION

Table 1 lists results of hydrogen chemisorption and X-ray diffraction studies. The small variation of hydrogenation chemisorption to Ag/Rh ratio and the observation of large Ag crystallites indicates that only a small amount of Ag covers the surface of the Rh particles and that most of the Ag atoms gather together to form aggregates. Temperature programmed desorption

studies of hydrogen showed that Ag does not affect the sites for hydrogen chemisorption [17]. Figure 1 shows infrared spectra of CO adsorption at 513 K. Two major bands were observed on Rh/SiO₂ and AgRh/SiO₂: linear CO band around 2041-2064 cm⁻¹ and bridge-CO band around 1854-1876 cm⁻¹. For Ag/Rh= 0.5, the intensity of linear CO band was slightly increased while the intensity of bridge-CO band was decreased. As the ratio of Ag to Rh increased to 1, Ag additives decreased the intensity of bridge-CO band more than that of linear CO. In general, the increases in Ag content on the catalyst led to an increase in the ratio of linear CO intensity to bridge-CO intensity and a slight variation of both linear and bridge-CO wave number.

The small change in the wave number of adsorbed CO may be attributed to the dilution of Rh by Ag rather than the ligand (electronic) effect of Ag. Ponec and coworkers [18] have suggested that a downward shift of 15~30 cm⁻¹ for adsorbed CO upon alloying of metals, such as Ni-Cu, Pd-Ag, Pd-Au, and Pt-Cu, should be ascribed to the geometric effect of group IB metals. The reduction of bridge-CO intensity brought about by Ag indicates that the major effect of Ag is to block bridge-CO sites. Such a blockage effect of Ag on the bridge-CO site on Rh has been reported by Kochetkova and Sokolova [19]. The blockage of bridge-CO site on Group VIII metals by IB and IIB metals has also been observed for Ag-Pd, Cu-Rh, and Zn-Rh systems [20-22]. These results suggest that Ag may be interdispersed on the surface of Rh particle. However, results of an ethane

hydrogenolysis study on AgRh/SiO₂ suggest that Ag may form patches or islands on the surface of Rh catalysts [23]. Further investigation of these catalysts using the model reaction is required for verifying how Ag distributes on the Rh surface.

The product distribution from CO hydrogenation on Rh/SiO₂ is shown in Table 2. Methane, C₂₊ hydrocarbons, and C₂ oxygenates are the major products while methanol constitutes the minor product. The turnover frequency for CO conversion in the present study for Rh/SiO₂ is in the same range as those reported for Rh/SiO₂ [11], although reaction conditions for these two studies are not exactly the same. The selectivity for methane decreased slightly from 473 to 503 K and increased with further increase in temperature while the C₂ oxygenates selectivity increased from 473 to 503 K and decreased with further increase in temperature. The maximum C₂ oxygenate selectivity appears to occur around 503 K. A similar variation of C₂ oxygenate selectivity versus temperature has also been observed on Ag/Rh= 0.25 and Ag/Rh= 0.5 catalysts as shown in Figure 2. The temperature (T_m) for maximum C₂ oxygenate selectivity depends on the Ag/Rh ratio.

Extensive research on CO hydrogenation on the Rh-based catalysts has shown that C₂ oxygenates are formed via the formal insertion of CO into CH_x which is produced from CO dissociation followed by hydrogenation [1,9-14]. The reaction scheme is shown in Figure 3. Since the formation of C₂ oxygenates, CH₄, and C₂₊ hydrocarbons involves a common intermediate, CH_x, the selectivity and rate for C₂ oxygenate formation should depend on the relative concentration of adsorbed species, such as *CO, *CH_x and *H as

well as the rate of these specific reaction steps. The presence of both dissociative and nondissociative CO on the catalyst surface is essential for the formation of C₂ oxygenate since the dissociative CO is the precursor for the formation of CH_x and the nondissociative CO is the precursor for the CO insertion.

The variation of C₂ oxygenate selectivity with temperature reflects the difference in the dependence of these various specific reactions (shown in Figure 3) on temperature. Watson and Somorjai [24] suggested that CO insertion competes favorably with hydrogenation in the intermediate temperature range (498-598 K) on the RhLaO₃ catalyst which exhibits a maximum C₂ oxygenate selectivity around 573 K. In the high temperature range (above 598 K), CO dissociation and hydrogenation of CH_x generally predominate over CO insertion resulting in the formation of methane as a major product. The similar variation of C₂ oxygenate selectivity with temperature among Ag/Rh=0, Ag/Rh=0.25, and Ag/Rh=0.5 catalysts indicates that Ag does not modify the dependence of the specific reaction rates on the temperature. However, Ag does promote the CO insertion as indicated by the higher C₂ oxygenate selectivities on AgRh/SiO₂ catalysts compared with that on Rh/SiO₂. Further increase in Ag/Rh from 0.5 to 1 led to the shift of the T_m to higher temperature rather than increases in the C₂ oxygenate selectivity. This observation suggests there may be an upper limit of Ag promotion on the C₂ oxygenate selectivity.

Rates of formation for CH_4 and C_2 oxygenates versus Ag/Rh ratio at different temperatures are shown in the Figures 4 and 5. The most obvious effect of Ag is to decrease the activity for the product formation. The suppression of the rate of product formation by Ag suggests that Ag may inhibit both CO dissociation and hydrogenation resulting in decreases in the rate of formation of CH_x for further reactions toward products. The inhibition effect of Ag on the product formation rate is more pronounced at high temperature than at low temperature. As Ag/Rh ratio varied from 0 to 1 at 573°K , the rate of formation of methane decreased by a factor of 10 while the rate of formation of C_2 oxygenates only decreased by a factor of 2 to 3. The less inhibition effect of Ag on C_2 oxygenate formation compared with that of methane formation led to increases in C_2 oxygenate selectivity.

Table 3 lists the apparent activation energy for the formation of methane, C_2+ hydrocarbons, acetaldehyde, and ethanol. The activation energies obtained from this study are in the range 16-30 Kcal/mole indicating that the reaction was operated in the kinetic regime. Ag has little effect on the apparent activation energy for methane formation. This is in agreement with a number of CO hydrogenation studies on the bimetallic catalysts indicating that the mechanism for the formation of methane is virtually unchanged [25,26]. For Ag/Rh = 1, the apparent activation energy for the formation of C_2+ hydrocarbons is lower than that for other Ag/Rh ratios while the apparent activation energy for the formation of acetaldehyde is

higher than that for other Ag/Rh ratios. The high activation energy for acetaldehyde formation for Ag/Rh = 1 indicates that the formation of acetaldehyde is favored at high temperature on this catalyst. Comparison of the activation energy for the product formation in Table 3 reveals that activation energies for methane formation are generally higher than those for acetaldehyde formation. This is another indication that hydrogenation competes favorably with CO insertion at high temperature on AgRh/SiO₂.

In order to gain a better understanding of the Ag effect on hydrogenation and CO insertion activities of Rh catalysts, a small amount of ethylene was added to the CO/H₂ mixture. The rate of product formation from reaction of ethylene with syngas (C₂H₄/CO/H₂) on Rh/SiO₂ is shown in Table 4. The observation of CH₄, C₃₊ hydrocarbons (HC), C₂ oxygenates, ethane, and propionaldehyde indicates that CO hydrogenation, ethylene hydrogenation, and ethylene hydroformylation take place at the same time. Higher rates of formation for ethane and propionaldehyde compared with those for methane suggest that ethylene hydrogenation and hydroformylation are the dominant reactions during ethylene addition. The proposed reaction scheme for the formation of ethane and propionaldehyde from ethylene are shown in Figure 6. It is important to note that the CO insertion step in CO hydrogenation (in Figure 3) has been considered to closely resemble that in ethylene hydroformylation [24,27].

As shown in Table 4, the most obvious effects of Ag on the reaction of ethylene with syngas are (i) the suppression of

hydrogenation and (ii) a slight enhancement of CO insertion (hydroformylation) at 573 K and 1.01 MPa. These observations suggest that the size of active site for CO insertion may be smaller than that for hydrogenation since the reactions catalyzed by large ensembles are generally more sensitive to alloying than those catalyzed by small ensembles [16,18]. A recent study by Arakawa et. al. [28] have shown that the CO insertion competes favorably with hydrogenation on Rh/SiO₂ for Rh particle sizes below 30 Å.

The results of Ag effect on the CO adsorption and syngas reaction are, to some extent, similar to those reported for Zn and S-Rh/SiO₂ [22,29,30]. The addition of these additives on Rh/SiO₂ led to (i) blockage of bridge-CO sites, (ii) decrease in methanation, (iii) reduction in hydrogenation, and (iv) increase in CO insertion. The blockage of bridge-CO sites and promotion of CO insertion brought about by these additives suggest that a CO insertion site may be a single atom site. Comparison of the results of this study with those reported for S-Rh and Zn-Rh catalysts shows that sulfur (S) has a greater inhibition effect on hydrogenation and methanation than Ag and Zn while Zn has a greater enhancement effect on CO insertion than S and Ag. Goodman and coworkers [15,25] have shown that Ag serves as a diluent of Rh to block sites for methanation on the one-to-one basis. In contrast, adsorbed S on the Rh surface caused a marked decrease in the methanation activity through modification of the surface electronic structure. The CO insertion site appears to

be less sensitive to additives (such as alkali, Ag and S) with various electronegativities than the methanation site.

SUMMARY

The effect of Ag on Rh/SiO₂ can be summarized as follows:

- (1) Ag blocks the bridge-CO site on Rh/SiO₂.
- (2) The selectivity for hydrocarbon decreases with increased Ag while the selectivity for C₂ oxygenates increases with increased Ag during CO hydrogenation.
- (3) Ethylene addition studies show that Ag promotes CO insertion and suppresses hydrogenation.

Although results of this study do not permit identification of the state of active site for CO insertion, the above observations indicate that CO insertion may be less structure sensitive than hydrogenation; C₂ oxygenate synthesis reaction may be less structure-sensitive than the hydrocarbon synthesis reaction.

ACKNOWLEDGEMENTS

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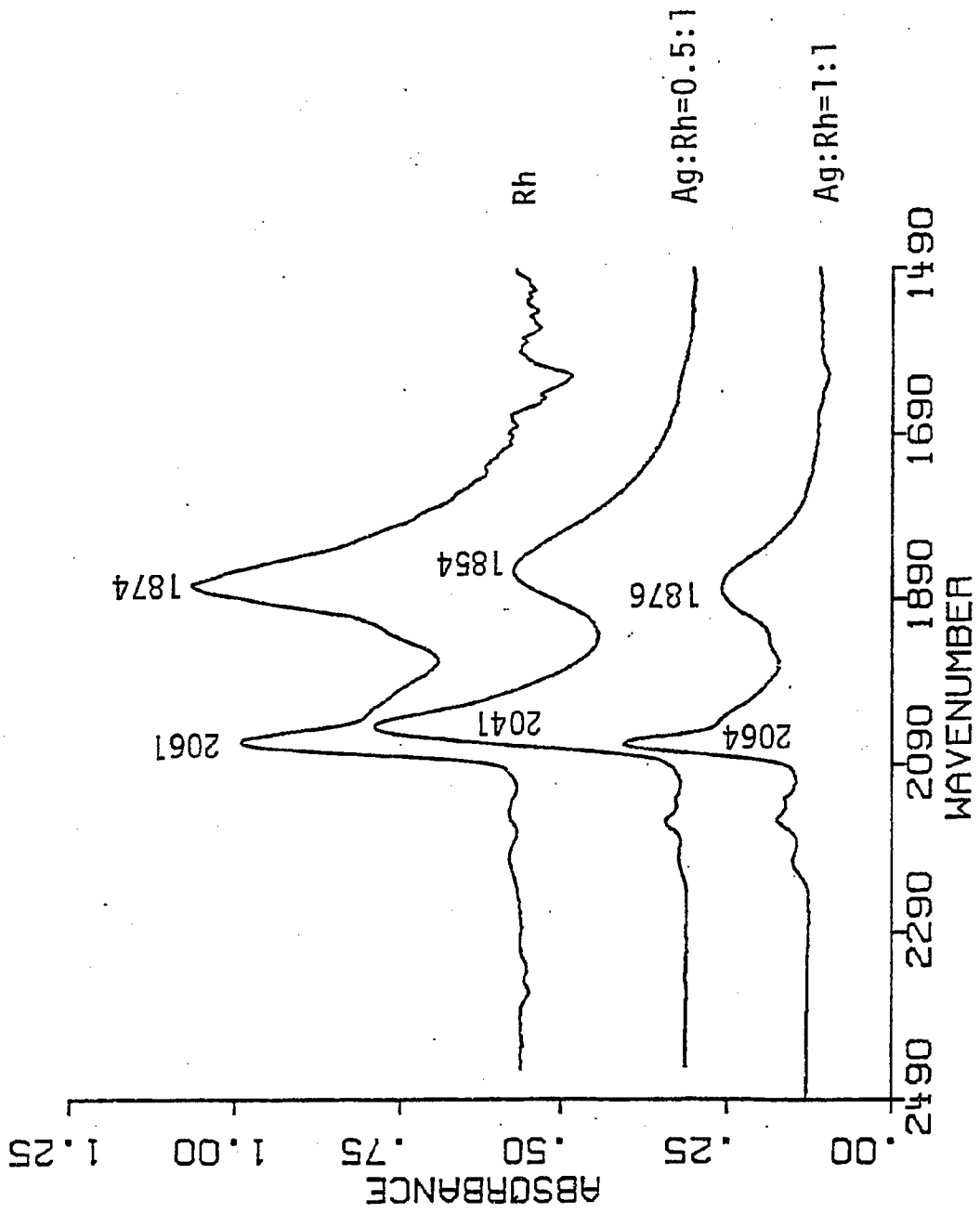
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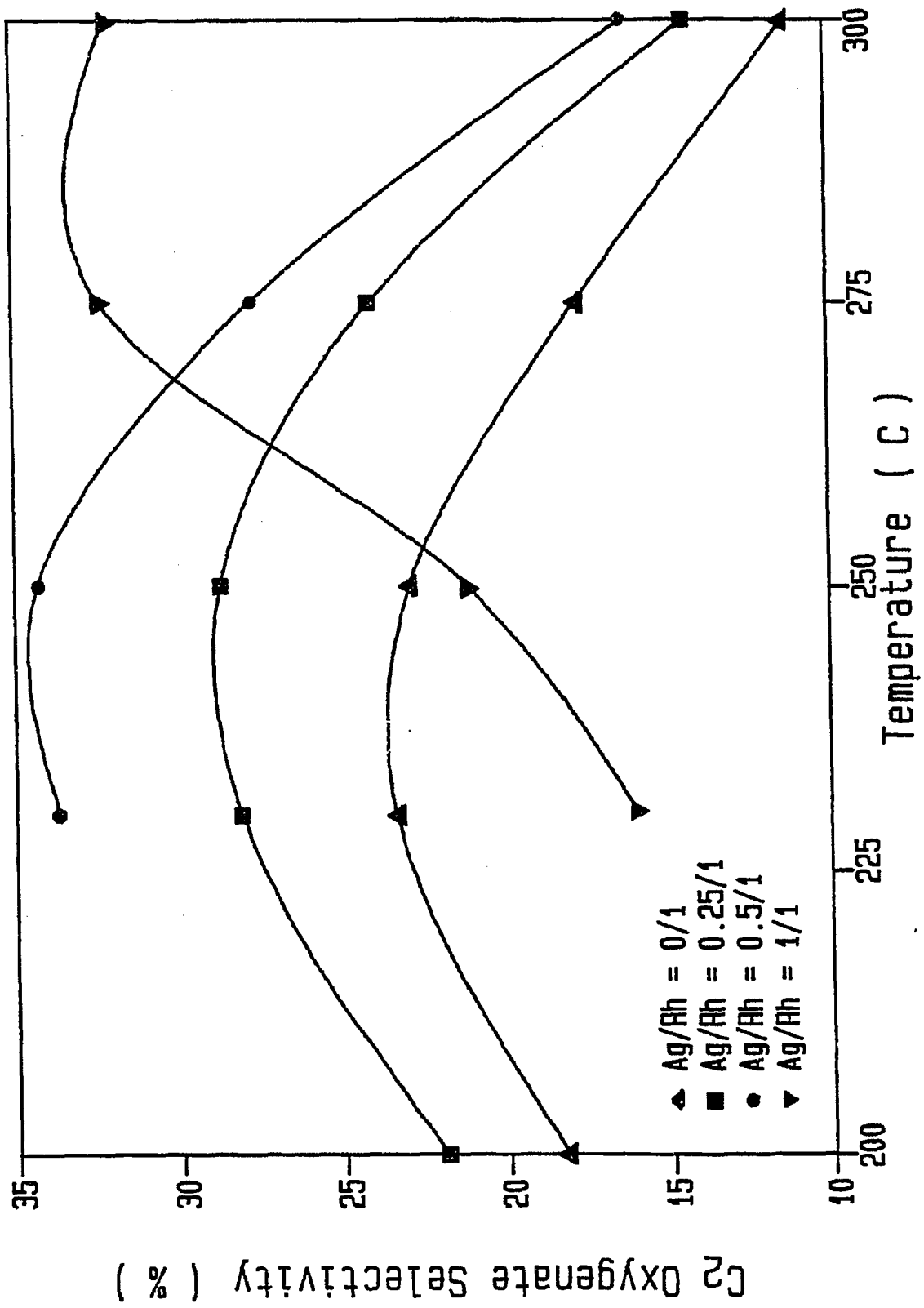
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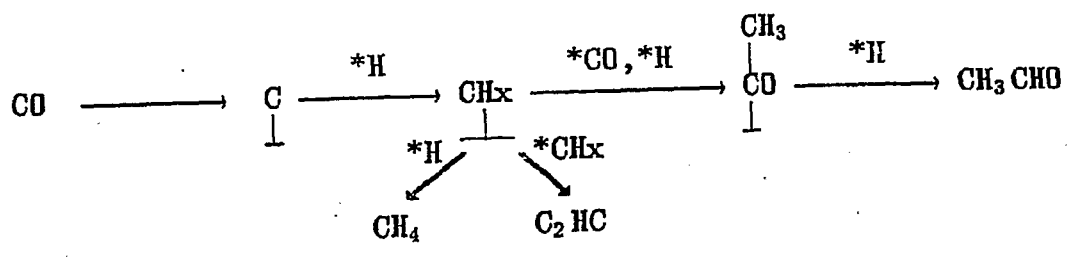
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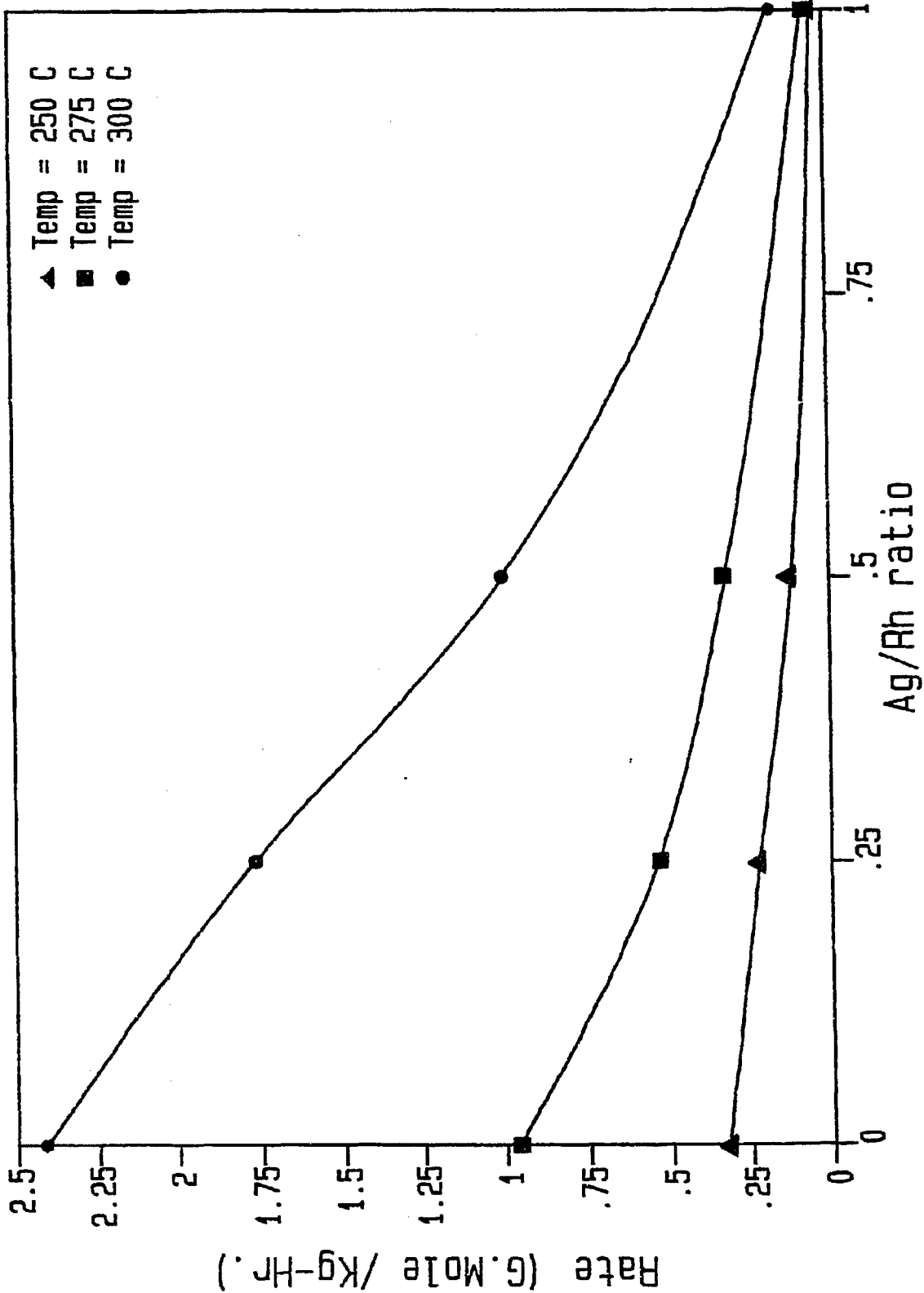
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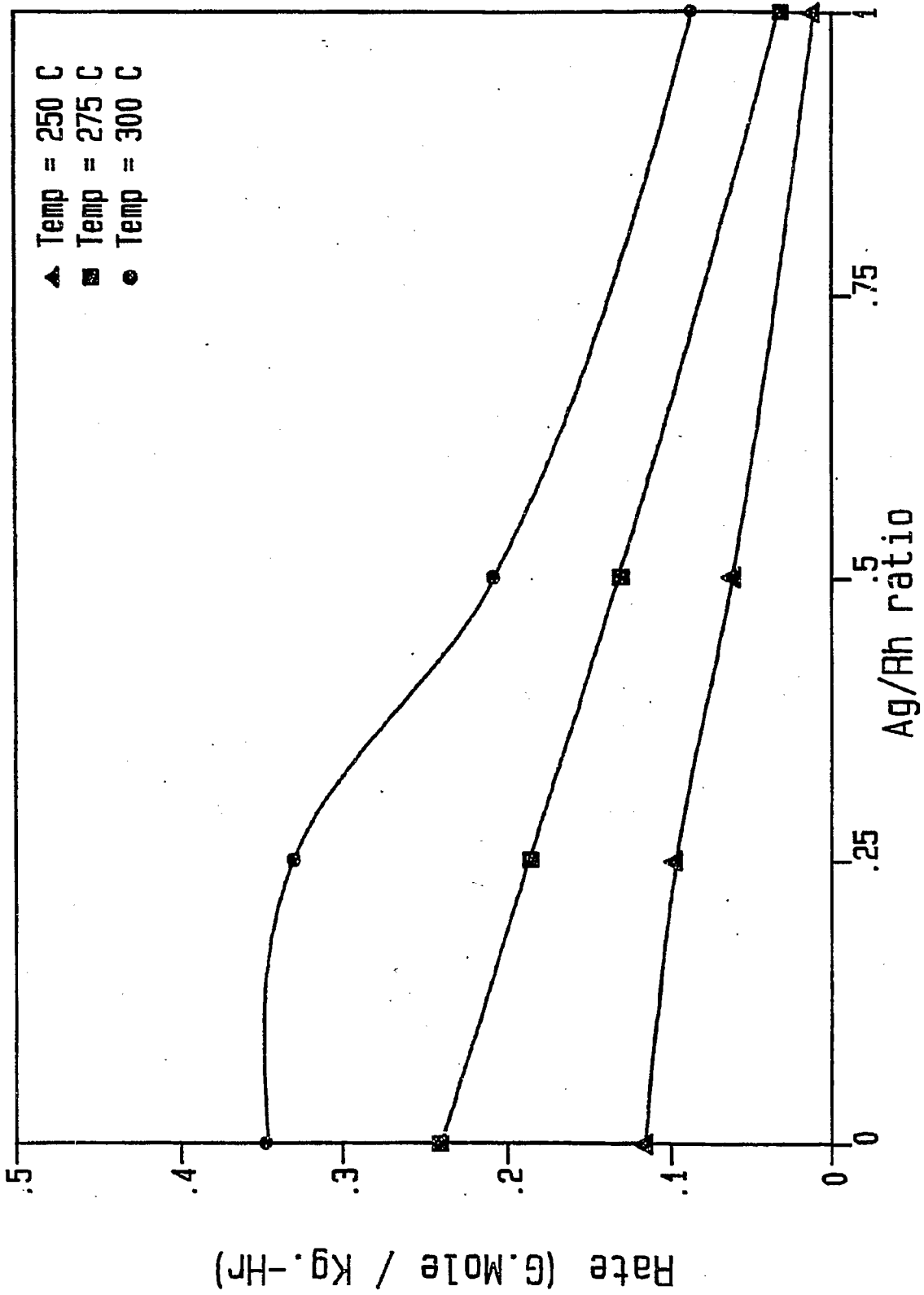
1. Infrared spectra of CO adsorption on Rh/SiO₂ and AgRh/SiO₂ at 510 K and 1.01 MPa.
2. The effect of temperature on C₂ oxygenate selectivity over Rh/SiO₂ and AgRh/SiO₂.
3. Reaction pathway for the formation of C₂ oxygenates from CO hydrogenation.
4. The rate of methane formation as a function of Ag/Rh.
5. The rate of C₂ oxygenate formation as a function of Ag/Rh.
6. Reaction pathway for the formation of C₃ oxygenates from the reaction of ethylene with syngas.











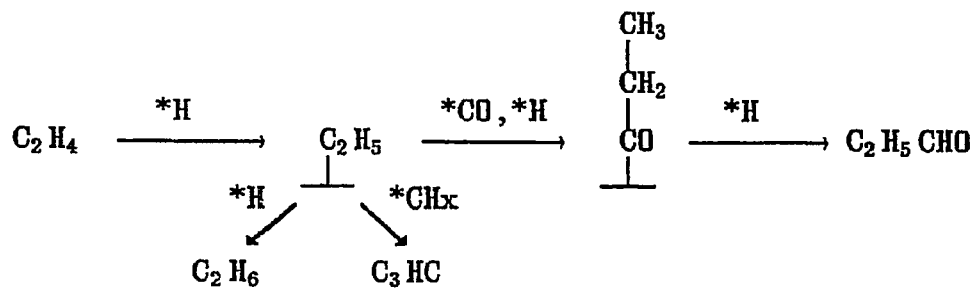


Table 1

Average Crystallite Size and H₂ Chemisorption
for Various Ag/Rh Ratio

Ag/Rh Ratio	Crystallite Size (A°) Rh(H ₂ Chemisorption)	Ag/Rh(XRD)	H ₂ Chemisorbed μ mole/g
0	96*	-	13.7
0.5	97	468/85	13.5
1.0	100	395/136	12.9

* Average particle size was estimated from H₂ chemisorption, assuming the ratio of H_s to Rh to be 1 and the particle to be cubic with five sides exposed to hydrogen.

Table 2

Product Distribution from CO Hydrogenation
for Rh/SiO₂ at Various Temperatures

Temperature (K)	473	503	523	548	573
Rate of CO conv. (mol/kg-hr)	0.13	0.34	0.73	1.87	3.93
TOF ($\times 10^3$) (Sec ⁻¹)	1.3	3.4	7.4	18.9	39.3
Selectivity (mol %)					
C ₁	69.4	63.7	64.6	70.8	78.8
C ₂₊ Hydrocarbons	12.4	12.9	11.6	10.5	9.2
CH ₃ OH	-	-	0.88	0.93	0.67
MeCHO + C ₂ H ₅ OH (C ₂ Oxygenates)	18.2	23.4	22.9	17.7	11.3

TOF: Turnover Frequency

Reaction Pressure: 1.01 MPa

Table 3

Apparent Activation Energies for Major Products
from CO Hydrogenation

Ag/Rh Ratio	Temp. Range (K)	CH ₄	C ₂ ⁺ (Kcal/Mole)	CH ₃ CHO	C ₂ H ₅ OH
0	473/573	23	19	15	29
0.25	473/573	24	20	16	29
0.5	473/573	26	20	12	28
1.0	473/573	24	16	22	--
Literature Value					
Rh/SiO ₂ (31)	393/473	20	19	16	--
Rh-Na/SiO ₂ (31)	433/523	23	21	21	--
LaRhO ₃ (24)	513/613	27	27	28	26
Rh ₂ O ₃ (9)	513/573	26	26	26	--

Table 4

Rate of Product Formation from Reaction of Ethylene
with Syngas ($C_2H_4/CO/H_2$) on AgRh/SiO₂

Ag/Rh Ratio	0	0.25	0.5	1
Rate of Product Formation (mol/kg-hr)				
CH ₄	1.91	1.7	0.84	0.24
C ₂ H ₆	23.1	23.1	15.7	11.2
C ₃ +HC	0.34	0.2	0.07	0.026
CH ₃ CHO	0.28	0.35	0.22	.11
C ₂ H ₅ CHO	2.4	3.1	2.7	4.6
1-C ₃ H ₇ OH	0.27	0.3	0.4	0.13

Temperature: 573 K

Pressure: 1.01 MPa

CO:H₂:C₂H₄ = 25:25:1



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