

**PROGRESS ON DEVELOPING TECHNOLOGY
FOR PRODUCING HIGHER ALCOHOLS
FROM SYNTHESIS GAS**

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ABSTRACT

On September 25, 1990, the Department of Energy awarded Contract Number DE-AC22-90PC90043 to North Carolina State University for a research and development program entitled "Novel Approaches to the Production of Higher Alcohols from Synthesis Gas". The objective of this contract is to develop improved process and catalyst technology for producing higher alcohols from synthesis gas or its derivatives.

A substantial number of catalysts for the direct conversion of synthesis gas to higher alcohols have been prepared, characterized and tested for activity and selectivity. All of these catalysts were of the general composition Rh/MO_x/Al₂O₃, where M denotes a metal that acts as a promoter for the Rh. The promoters studied to date are Nb, Mo, W and Re. The selectivity to total oxygenates, including methanol and formaldehyde, increased in the order: no promoter \equiv Nb \equiv W < Mo < Re. The best total oxygenate selectivity, about 76% based on moles of carbon monoxide converted, was obtained with a catalyst comprised of 1 wt.% Rh/6 wt.% Re/Al₂O₃. Unfortunately, this catalyst had a very low activity, about 0.67 moles CO/kg.(catalyst), hr. at the standard testing conditions of 200°C, 3.4 MPa., 9000 hr.⁻¹ space velocity and 2/1 H₂/CO ratio.

The activity of the promoted catalysts increased in the order: Re < no promoter \equiv W < Nb \equiv Mo. At standard testing conditions, the most active catalyst, 1 wt.% Rh/0.05 wt.% Mo/12 wt.% Re/Al₂O₃, had an activity of about 3.2 moles CO/kg.(catalyst), hr. The selectivity of this catalyst to total oxygenates was 62%. The highest yield of C₂⁺ oxygenates was obtained with the same catalyst. This yield was about 0.84 moles CO/ kg.(catalyst), hr. The C₂⁺ oxygenates consisted mostly of ethanol and acetaldehyde, with smaller quantities of C₃ and C₄ alcohols and aldehydes.

The performance of even the best of these catalysts falls short of the preliminary targets that were established for activity, total oxygenate selectivity and C₂⁺ productivity. Research on the development of Rh-based catalysts has been discontinued.

CONTRACT OVERVIEW

Figure 1 shows the five tasks into which the overall contract is divided. The first four are being performed by North Carolina State University. Task 5 has been subcontracted to Air Products and Chemicals, Inc.

Figure 2 summarizes the status of Task 2. The objective of this task is to extend the research carried out by Air Products and Chemicals, Inc. and Chem Systems, Inc. on the Liquid Phase Methanol Process to the synthesis of higher alcohols. In particular, the task is focused on developing process technology for producing alcohols in a slurry reactor that can operate at higher temperature and pressure than the Liquid Phase Methanol Process. The ultimate objective is to be able to run the reactor at conditions that are representative of the "high pressure" methanol synthesis process, i.e., a temperature in the vicinity of 400°C and a pressure of about 20 MPa.

Currently, the autoclave system is being operated to verify its performance with the Liquid-Phase Methanol Process. Several runs with different gas compositions and space velocities have been recommended by Air Products and Chemicals, Inc. The data from these runs will be compared with data from Air Products' data base to ensure that the results from the NCSU autoclave system reproduce those obtained by Air Products. Some additional data at pressures up to about 20 MPa will also be obtained in order to extend the existing data base on the Liquid Phase Methanol Process to higher pressure.

Mechanical operation of the NCSU autoclave system over the range of variables recommended by Air Products is excellent. The data obtained to date is not directly useful for a combination of three reasons: poisoning of the Cu/ZnO catalyst by iron and nickel carbonyl, problems with the analytical system, and loss of liquid from the autoclave. These problems are under active investigation and appear to be close to being resolved. In the process of diagnosing and correcting the problem of catalyst poisoning, a good deal has been learned about the nature of the poisoning phenomenon. Briefly, it appears that Fe and Ni that have been deposited on the methanol synthesis catalyst in turn catalyze the formation of carbon which eventually fills the pores of the catalyst, blocking its active sites.

The key to extending the existing slurry reactor technology to higher temperatures will be identifying a liquid that is thermally and chemically stable at reaction conditions, and has a low vapor pressure at the operating temperature of the autoclave. Several mineral oils with the required vapor pressure and thermal stability characteristics have been identified and tested in laboratory glassware. Tests in the stirred autoclave have been disappointing because of the afore-mentioned problem of oil loss.

Figure 3 shows the chemistry that underlies Task 4. The overall objective is to develop a one-step process for converting methanol into higher alcohols, as indicated in the first reaction. Both of the reactions in the following example are known. Olefins are known intermediates in the conversion of methanol into aromatics over acidic catalysts such as ZSM-5. The hydration of olefins to alcohols is a standard commercial method of production using various catalysts based on phosphoric acid. Individually, these two reactions are practiced at about the same temperature, but at different pressures and, obviously, with different feed gases.

Figure 4 summarizes the current status of Task 4. The process is thermodynamically feasible, but requires a relatively high partial pressure of steam in the feed. One catalyst that is very selective for olefin formation from methanol has been identified from batch, temperature programmed desorption experiments. Finally, a continuous screening reactor is now on stream and will be used to test various catalyst combinations in an attempt to demonstrate the one-step reaction of methanol to higher alcohols shown in Figure 3.

The remainder of this report will be devoted to a detailed discussion of the results of Task 3 - Novel Catalysts For Synthesis of Higher Alcohols.

RESULTS OF TASK 3

Figure 5 outlines the technical approach on which Task 3 was based. All of the catalysts synthesized, characterized and tested were of the general composition $\text{Rh}/\text{MO}_x/\text{Al}_2\text{O}_3 (\text{SiO}_2)$. The rationale behind exploration of this general composition is as follows. First, rhodium is a known catalyst for chain growth and carbon monoxide insertion reactions. In earlier research by other investigators, Rh has shown some promise for the direct synthesis of higher alcohols from carbon monoxide/hydrogen mixtures. Second, certain metal oxides are

known to interact with rhodium to increase the selectivity and/or activity towards mixed alcohol formation.

In this research, a number of variables associated with catalyst composition and/or preparation were studied including: the source of rhodium, either $\text{Rh}(\text{NO}_3)_3$ or $\text{Rh}_4(\text{CO})_{12}$; the source of the support; the nature of the promoter; the concentration of the promoter, and; the source of the promoter, either a salt or a carbonyl compound. In addition, a number of variables associated with reactor operation were studied, including temperature, pressure and H_2/CO ratio.

Four different promoters: niobium, molybdenum, tungsten and rhenium, were investigated. Only Mo and Re are discussed further in this paper. Catalysts involving Nb and W as promoters showed much less promise than those containing Mo and Re. Moreover, all of the catalysts discussed in this paper are based on various Al_2O_3 supports; attempts to deposit controlled amounts of promoter on silica were largely unsuccessful.

Figure 6 shows the targets that have been established for catalyst performance. These targets are not based on economic trade-off studies. Rather, they derive from qualitative comparisons with existing commercial technology, complemented by qualitative "guesstimates" where necessary. The value of these targets is as a benchmark to evaluate the progress of the catalyst development effort. When one or more catalysts achieves all of these targets, or comes close to achieving them, a detailed economic evaluation will be required.

The criterion for catalyst activity is based primarily on the results achieved by Air Products in the Liquid-Phase Methanol program, where catalyst activities in excess of 15 moles $\text{CO}/\text{kg}(\text{catalyst}), \text{hr.}$ are routinely observed. The lower target for higher alcohols reflects the higher value of these alcohols relative to methanol. The selectivity target for methane is based on the very low economic value of this product, especially in plants based on natural gas. The target for total oxygenate selectivity effectively defines the total quantity of hydrocarbon products that are tolerable, and the target for C_2^+ oxygenate selectivity arises from the need to produce higher alcohols as a primary product, rather than as a by-product of methanol manufacture. Of all of the targets in Figure 6, this one is probably the most judgmental and subject to the most uncertainty. It should be noted that the total oxygenate and C_2^+ selectivities are

based on the moles of CO converted, e.g., total oxygenate selectivity = (moles of CO converted to oxygenated hydrocarbons of any kind/total moles of CO converted to all products). The C_2^+ productivity is not an independent parameter, but is the product of the targets for activity and C_2^+ oxygenate selectivity.

The target for catalyst life is reasonably consistent with the catalyst deactivation results that have been achieved with the Liquid-Phase Methanol Process. Catalyst life testing has not been part of this research program. All catalyst testing has been carried out for relatively short periods of time, approximately one or two days.

Figure 7 shows the best results that have been achieved to date for each of the first, third, fourth and fifth criteria in Figure 6. All of the results shown are at a standard set of testing conditions: 200°C, a total pressure of 3.4 MPa, a feed consisting of only H₂ and CO in a 2/1 ratio and a space velocity of 9000 sLiters/kg.(catalyst), hr. Catalyst testing was carried out in a gas-phase, packed-bed reactor containing 0.5 grams of catalyst. The conversion of CO was very low in all cases, typically less than 1%, so that the reactor operated under essentially differential conditions.

One catalyst, 0.05 wt.% Mo/1 wt.% Rh/12 wt. % Re/Al₂O₃, gave the highest overall activity and the highest C_2^+ productivity. A second catalyst, 1 wt.% Rh/6 wt.% Re/Al₂O₃, produced the highest total oxygenate selectivity and the highest C_2^+ oxygenate selectivity. For all of the experimental catalysts evaluated in this program, the C_2^+ oxygenates were composed primarily of ethanol and acetaldehyde, with much smaller amounts of C₃ alcohols and aldehydes and only trace concentrations of C₄ oxygenates. All of the experimentally-measured selectivities shown in this paper are exclusive of CO₂. Carbon dioxide was not accurately measured in the catalyst screening program.

None of the four targets was achieved, although the performance of the 1%Rh/6%Re/Al₂O₃ catalyst was close to the 80% target for total oxygenate selectivity. No single catalyst came close to meeting all four selectivity and activity targets simultaneously.

Figure 8 shows a more complete set of results for the two catalysts of Figure 7. All of these data are at the standard testing conditions, as defined above, except that the reactor temperature was changed

from 200 to 250°C for one run on each catalyst. The most active catalyst, Mo/Rh/Re/Al₂O₃, has a reasonably balanced performance. Its methane selectivity is only slightly above the target shown in Figure 6 and its C₂⁺ oxygenate selectivity is comparable to that of the best catalyst in this regard, the Rh/Re/Al₂O₃ catalyst. The total oxygenate selectivity of 62% is significantly below that of the Rh/Re/Al₂O₃ catalyst. The Mo/Rh/Re/Al₂O₃ catalyst does not satisfy any one of the targets established in Figure 6.

The 1%Rh/6%Re/Al₂O₃ catalyst does meet the CH₄ selectivity target, and it almost meets the total oxygenates selectivity target. However, its overall activity and its C₂⁺ productivity are substantially below their respective targets.

The data at 250°C shown in Figure 8 are disappointing. Raising the reactor temperature increases the activity of both catalysts substantially, to the point that the overall activity of the Mo/Rh/Re/Al₂O₃ catalyst is above the target of Figure 6 and the C₂⁺ productivity is essentially equal to its target. However, these increases are accompanied by a significant decrease in the total oxygenate selectivity and a significant increase in the CH₄ selectivity.

Figure 9 shows some selected data that illustrates the important effect that the alumina support has on catalyst performance. The "base catalyst" in this figure is 1wt.%Rh, deposited from [Rh₄(CO)₁₀], on the indicated alumina. Although there is little difference in the activity of the three base catalysts, the catalyst based on Catapal alumina has a substantially higher selectivity. The columns labeled "most selective catalyst" show the performance of the catalyst with the highest total oxygenate selectivity that was prepared on each support. These three catalysts do not necessarily have the same composition. Note that the most selective catalyst prepared on the Catapal alumina is still more than 10 percentage points more selective than the most selective catalysts prepared on the other two aluminas. Within the admittedly limited scope of the catalyst development conducted to date, it was not possible to prepare a catalyst on either the Grace alumina or the Degussa alumina that overcame the apparent intrinsic selectivity advantage of the Catapal alumina. The selectivity advantage of the latter support is also apparent in the data for the "most active catalyst".

Figures 10 through 13 show some details of the overall activity and total oxygenate selectivity results for the rhenium-promoted and the molybdenum-promoted catalysts. Figure 10 reveals the increased overall catalyst activity that results from increasing the concentration of rhenium on the catalyst by impregnating the support with ammonium perrhenate. Depending on the type of alumina, the catalyst activity was increased by a factor of roughly three at the highest Re concentrations. Based on the one data point shown, it does not appear as though rhenium carbonyl is as effective a means to add rhenium as the perrhenate.

Figure 11 demonstrates that the activity increase associated with increased rhenium concentrations is achieved with little or no impact on overall oxygenate selectivity. With both the Catapal alumina and the MI-307 alumina, there is essentially no effect of Re loading on selectivity, when the Re is applied from the perrhenate. The one data point for Re application from rhenium carbonyl suggests that this approach may lead to a slightly higher selectivity, at the expense of overall catalyst activity, as noted in the discussion of Figure 10. The Catapal alumina produces a significantly higher selectivity than the MI-307 alumina, over the whole range of Re concentration.

Figure 12 is a plot of the overall catalyst activity versus the molybdenum concentration on the catalyst for a family of molybdenum-promoted catalysts. When the Mo is applied to the catalyst via ammonium heptamolybdate, the activity increases regularly up to a loading of about 11 weight percent Mo. The Degussa alumina seems to respond more strongly to promotion by Mo, with over a five-fold increase in activity between the base catalyst with no Mo and the catalyst with the highest Mo loading of about 11 wt. %. However, the activity increase with Catapal alumina is also an impressive four fold. Application of low levels of Mo from molybdenum carbonyl produced exceptionally high activity increases on both aluminas, relative to the expectations based on the catalysts impregnated with Mo salt.

Figure 13 shows that the impressive gains in catalyst activity with increasing Mo concentration were achieved at the expense of some selectivity loss. Interestingly, the selectivities of the three catalysts prepared with molybdenum carbonyl were above those of their respective base catalysts, and above the curve for their respective aluminas impregnated with Mo salt. Once again, the Catapal alumina

gave the highest selectivity over the whole range of promoter concentration.

CONCLUSIONS

Many interesting results have been achieved from the catalyst development effort that has been carried out under Task 3. The results that probably have the most long-term potential for further exploitation are: 1) the strong effect of the type of alumina on overall oxygenate selectivity; 2) the significant promoting effect of rhenium on overall catalyst activity, and; 3) the significant promoting effect of molybdenum on overall oxygenate selectivity. In connection with the last two items, it should be noted that the catalyst with the highest overall activity and the highest C_2^+ productivity at standard conditions contained both Re and Mo. Nevertheless, even after the significant effort that was involved in Task 3, there is no single catalyst composition that closely approaches all of the established targets. For this reason, the catalyst development effort has been terminated, as noted in Figure 14.

Future research under this contract will be concentrated on Task 2 and Task 4. Under Task 2, after reproducing a limited set of Liquid-Phase Methanol results, some data will be taken for this process at total pressures that exceed those in the current data base. Work will then be focused on extending the region of operation of slurry reactors for alcohol synthesis to higher temperatures, with the objective of testing "high-pressure" methanol synthesis catalysts and modifications thereof. Under Task 4, the continuous screening reactor will be operated at various process conditions and with various catalyst mixtures in order to demonstrate the feasibility of a "one step" synthesis of C_2^+ alcohols from methanol or dimethyl ether.

FIGURE 1

**Novel Approaches to the Production of
Higher Alcohols from Synthesis Gas**

- Task 1: Program Management**
- Task 2: Liquid-Phase, Higher Alcohol Process
with Recycle of Lower Alcohols**
- Task 3: Novel Catalysts for Synthesis of
Higher Alcohols**
- Task 4: Synthesis of Higher Alcohols via
Acid-Base Catalysis**
- Task 5: Technology Evaluation**

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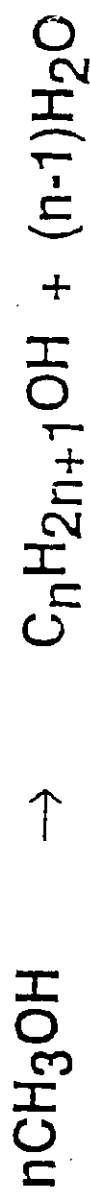
Status

Task 2:

- Stirred Autoclave System Designed, Constructed, Started Up
- Liquid - Phase Methanol Tests Performed
 - Air Products' low-pressure data reproduced
 - Process extended to higher pressure (ca. 20 MPa)
 - Better understanding of catalyst deactivation by $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$
- Several High Temperature (ca. 400 °C) Oils Screened

FIGURE 3

Desired Task 4 Chemistry (One-Step)



For example:



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FIGURE 4

Status

Task 4:

- **Thermodynamic Calculations Performed to Define Region of Process Feasibility**
- **9 Acid Catalysts Screened for Olefin Formation via Temperature Programmed Desorption (TPD)**
- **Continuous Screening Reactor Designed, Constructed, Started Up**

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FIGURE 5

Task 3

- **Technical Approach**
- **Rh/MO_x/Al₂O₃ (SiO₂)**
- **Variables Studied**
 - **Source of Rh (salt, carbonyl)**
 - **Type of Al₂O₃**
 - **Nature of Promoter**
 - M = Nb, Mo, W, Re**
 - **Concentration of Promoter**
 - **Source of Promoter (salt, carbonyl)**
 - **Operating Conditions**

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FIGURE 6

Task 3

- Preliminary Catalyst Targets

Activity: > 10 moles CO/kg.(cat.), hr.

Selectivity (Carbon Efficiency):

a) $\text{CH}_4 < 10\%$

b) Oxygenate Selectivity

Total > 80%

$\text{C}_2^+ > 40\%$

c) C_2^+ Productivity: > 4 moles CO/kg.(cat.), hr.

Life: > 2 Years

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FIGURE 7

Best Results to Date(1)

	<u>Target</u>	<u>Result</u>	<u>Catalyst(2)</u>
Activity $\left(\frac{\text{moles CO}}{\text{kg., hr.}}\right)$	>10	3.2	0.05%Mo/1%Rh/12%Re/Al ₂ O ₃
Oxygenate Selectivity			
Total (%)	80	76	1%Rh/6%Re/Al ₂ O ₃
C ₂ ⁺ (%)	40	27	1%Rh/6%Re/Al ₂ O ₃
C ₂ ⁺ Productivity $\left(\frac{\text{moles CO}}{\text{kg., hr.}}\right)$	4	0.84	0.05%Mo/1%Rh/12%Re/Al ₂ O ₃

(1) At standard testing conditions

(200°C; P=3.4MPa; H₂/CO=2; SV=9000L/kg.(cat.), hr.)

(2) Percents are by weight

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FIGURE 8

Effect of Temperature

Catalyst*	<u>0.05%Mo/1%Rh/12%Re</u>	<u>200</u>	<u>250</u>	<u>200</u>	<u>250</u>	<u>1%Rh/6%Re</u>
Temperature(°C)						
Performance:						
Activity ($\frac{\text{moles CO}}{\text{kg., hr.}}$)	3.2	19	0.67	6.8		
Oxygenate Selectivity						
Total (%)	62	34	76	31		
C ₂ (%)	26	21	27	19		
C ₂ Productivity ($\frac{\text{moles CO}}{\text{kg., hr.}}$)	0.84	3.9	0.18	1.3		
CH ₄ Selectivity (%)	15	43	10	45		

* Al₂O₃ Support

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FIGURE 9

Effect of Al₂O₃

Type	Base Catalysts(1)			Most Selective(1)			Most Active(1)		
	Activity(2)	Selectivity(3)	Catalyst	Activity(2)	Selectivity(3)	Catalyst	Activity(2)	Selectivity(3)	Catalyst
Degussa C (100 m ² /gr.)	0.24	54		0.63	62		1.2	35	
Grace MI-307 (170 m ² /gr.)	0.27	53		0.15	62		0.80	53	
Catapal (300 m ² /gr.)	0.21	70		0.67	76		1.3	74	

(1) At standard testing conditions (200°C)

(2) (moles CO/kg., hr.)

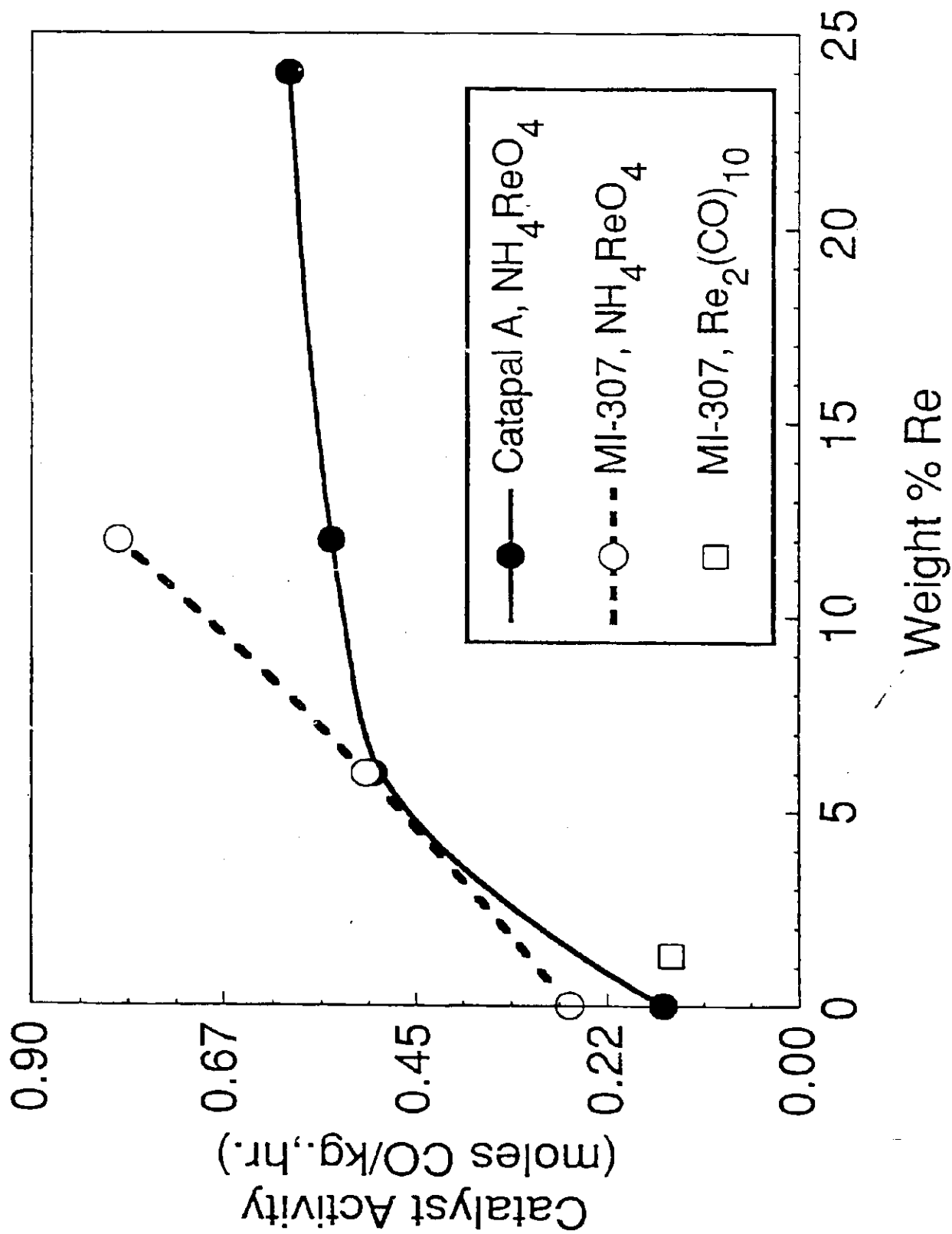
(3) Total Oxygenate Selectivity

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Activity of Rh/Re/Al₂O₃ Catalysts (1 wt.% Rh)

at Standard Conditions

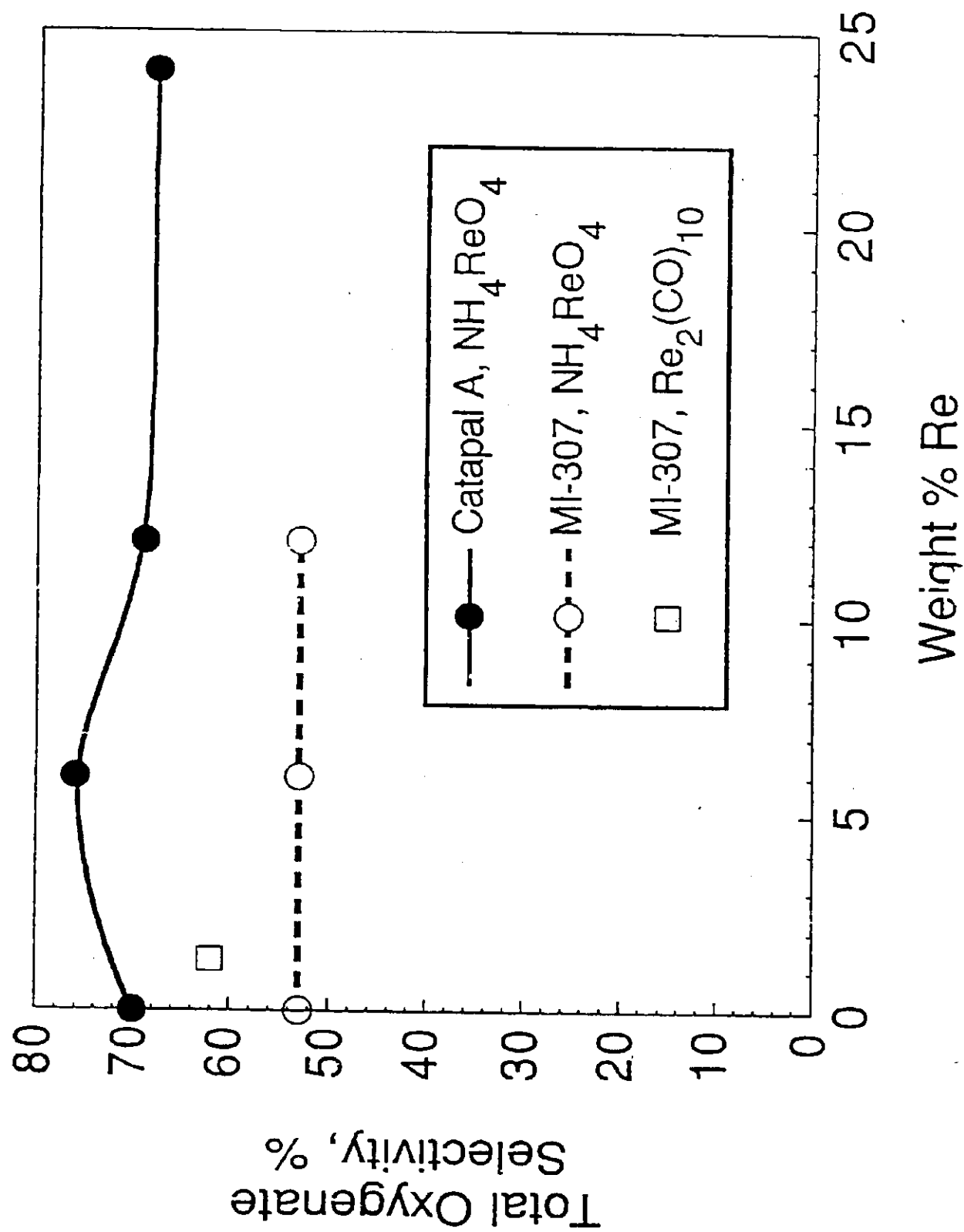
FIGURE 10



Selectivity of Rh/Re/Al₂O₃ Catalysts (1 wt.% Rh)

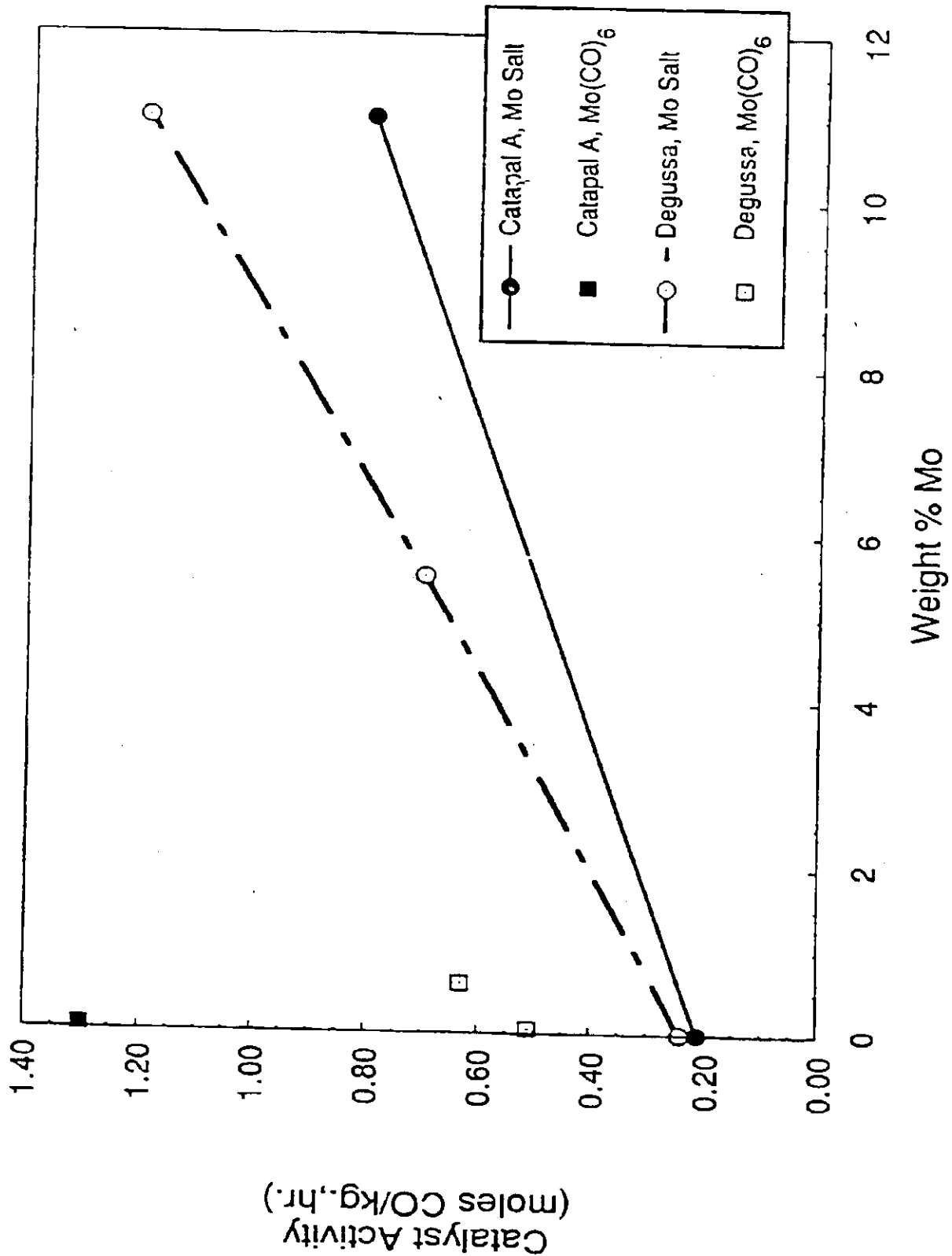
at Standard Conditions

FIGURE 11



Activity of Rh/Mo/Al₂O₃ Catalysts (1 wt.% Rh) at Standard Conditions

FIGURE 12



Selectivity of Rh/Mo/Al₂O₃ Catalysts (1 wt.% Rh)
at Standard Conditions

FIGURE 13

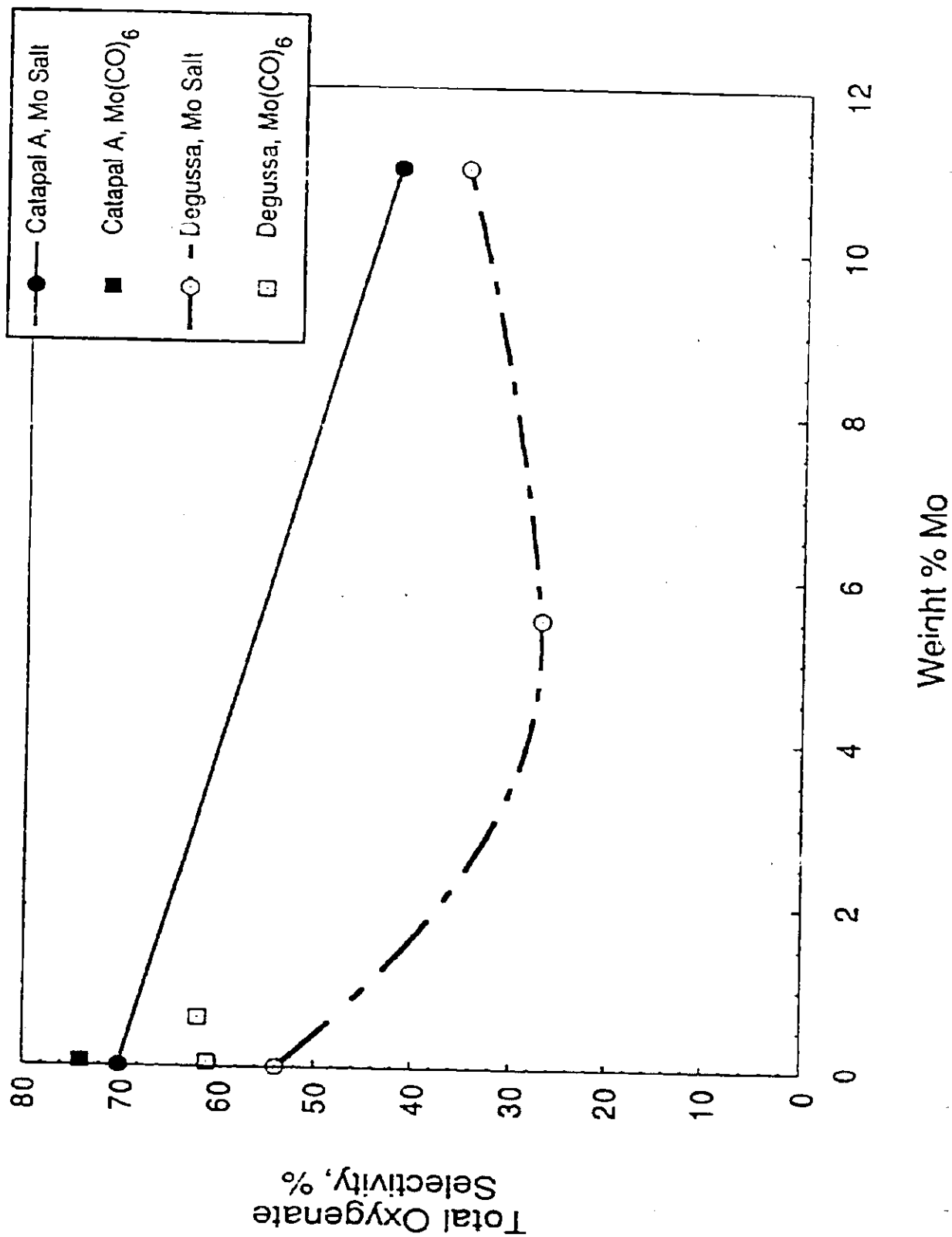


FIGURE 14

WORK PLAN

- **Rh/MO_x / Al₂O₃**
- **CATALYST DEVELOPMENT HAS BEEN TERMINATED**
- **CONCLUDE FEASIBILITY TESTING OF MeOH (DME) → HIGHER ALCOHOLS CONCEPT**
- **CONCENTRATE ON MODIFIED "HIGH PRESSURE" MeOH CATALYSTS IN STIRRED AUTOCLAVE**

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