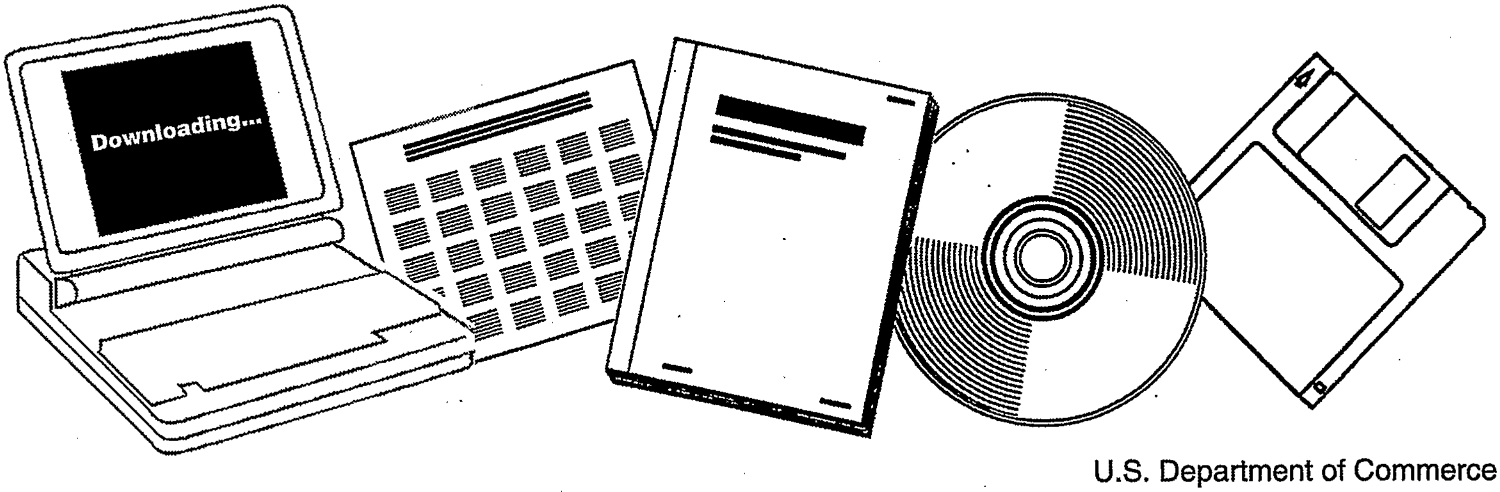
DE86008858

TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS. SIXTH QUARTERLY REPORT, DECEMBER 1, 1985-FEBRUARY 28, 1986

DELAWARE UNIV., NEWARK. DEPT. OF
CHEMICAL ENGINEERING

04 APR 1986



DOE/ET/14880--T10
DE86 008858

TRIFUNCTIONAL CATALYSTS
FOR CONVERSION OF SYNGAS TO ALCOHOLS

Sixth Quarterly Report for Period
December 1, 1985 to Febuary 28, 1986

K.B.Bischoff, William Manogue and G.Alex Mills
Coprincipal Investigators

Sudhakar Chakka, Postdoctoral Fellow
Nazeer, Graduate Student

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19716

Date Published
April 4, 1986

Prepared for
Fossil Energy
Department of Energy

Under Contract No. DE-AC22-79-ET14880

OBJECTIVES

Task 1. Preparation of catalyst samples
2. Testing catalysts for syngas conversion
3 Measurement of surface composition and structure
4 Determination of nature of surface complexes
5 Reaction mechanism determination by isotopic tracers and kinetics
6 Design, prepare and test optimized catalysts

TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS

MOLYBDENA - MODIFIED RHODIUM CATALYSTS

ABSTRACT

The addition of relatively large amounts of molybdena to Rh/Al_2O_3 catalysts (Mo/Rh atom ratio of 2 or greater) was found to increase CO hydrogenation activity by a factor of ten. Moreover, under standard test conditions the selectivity to oxygenates is increased from about 35 to about 85%. The C1/C2 oxygenates ratio is increased. C1 oxygenates include MeOH, MeOMe and MeOEt. The $Rh/Mo/Al_2O_3$ catalysts also show high activity for the water-gas shift reaction.

MoO_3/Al_2O_3 tested under similar conditions (250° C, 30 atmos., $H_2/CO = 2$, 3,000 GHSV) displayed low activity ; only hydrocarbons were produced.

Rh/TiO_2 is more active than Rh/Al_2O_3, Rh/SiO_2, Rh/MgO or Rh/La_2O_3. However, $Rh/Mo/TiO_2$ was less active than $Rh/Mo/Al_2O_3$.

During the course of this work, a few patents were located which also point to the high activity of catalyst containing Rh and Mo. However these patents do not provide a systematic study nor an understanding of the nature of this enhancement. Our research is directed to identifying the surface chemistry which gives rise to such strong activity and selectivity enhancement. It is conjectured that hydrogen activation is particularily increased, possibly on MoO_3 with transfer to CO chemisorbed on the Rh.

TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS
MOLYBDENUM - MODIFIED CATALYSTS

Hydrogenation of CO by rhodium catalysts is under intensive investigation worldwide (1,2). Remarkable changes in activity and selectivity can be induced by variations in support and/or by the addition of chemical modifiers.

Recently we have found that the addition of relatively large amounts of molybdena to Rh/Al_2O_3 (Mo/Rh atom ratio of about 2) increases the activity for CO hydrogenation by a factor of ten, that the selectivity to oxygenates is increased from about 35 to 85%, and that the activity for promoting the water-gas shift reaction is also greatly enhanced (important in generating H_2 in syngas of low H_2/CO ratios).

Experimental.

Supports were : CATAPAL® gamma alumina (extrudate from Air Products and Chemicals Inc.) calcined at 500 (all temperatures C), 200 m2/gm; Davison silica gel grade 57; titania P-25 from Degussa. Commercial $Co/Mo/Al_2O_3$, American Cyanamid Co. catalyst HDS-16A, 5.6%CoO,11.2% MoO_3 was also used as 'support'. Rhodium nitrate was sulfate-free 10 wt.% Rh solution from Engelhard. Ammonium molybdate was from Alfa Products, Puratonic grade. All catalysts except Mo/Al_2O_3 contained 3 wt. % Rh.

Catalysts were prepared by the incipient wetness method. 3% Rh, 2.8% Mo/Al_2O_3 was prepared by coimpregnation (pH ca 1). The 7.5 and 15% Mo catalysts were prepared by first depositing molybdena on alumina using ammonium molybdate solution adjusted to pH 1-2 using HNO_3, drying and calcining at 500 , followed by impregnation with Rh nitrate solution. For the catalyst containing 15% Mo, the Mo was deposited in two steps with a 500 calcination in between. The % Mo quoted is for the metal by wt.; Mo is undoubtedly present in an oxide form.

Catalyst testing was in a flow reactor system (ca. 0.5 gm. catalyst) 200° - 275° , H_2/CO = 2, 2,500 -36,000 GHSV, at 30 atmos. Analysis was by on-line GC using a single Teflon^R lined SS column packed with Porapak QS. A porapak T column was used to resolve three peaks each having a pair of compounds. Conversion of CO is reported on a total basis. Selectivity is on a CO_2-free basis, as others have done; this applies to individual compounds and to % of CO converted which goes to oxygenates, reported as % OXY., and the percentage of oxygenates greater than C1, which is reported as %C2OXY.

Activity Results

Rh/Mo/Al_2O_3. The effect of incorporating increasing amounts of molybdena in the Rh/Al_2O_3 system is shown in series A, Table 1. Activity increases such that when the Mo/Rh atom ratio reaches 2.7 (7.5 wt.% Mo/3 % Rh) the same CO conversion is reached at 36,000 GHSV as with Rh/Al_2O_3 at 3,600 GHSV.

Mo/Al_2O_3. In order to determine the effect of molydena on alumina, Mo/Al_2O_3 catalyst B was investigated. Activity was found to be at a comparatively low level and, significantly, only hydrocarbons were formed.

Rh/Co/Mo/Al_2O_3. While catalyst C showed high activity as expected, no unusual results attributable to the Co were observed.

Rh/ Other Supports. Rh/TiO_2 is the most active of Rh/TiO_2, Rh/Al_2O_3 or Rh/SiO_2 (or indeed Rh/MgO or Rh/La_2O_3, not shown).It was thought that possibly Rh/Mo/TiO_2 would have superactivity. However, while more active than Rh/TiO_2 it was not as active as Rh/Mo/Al_2O_3.

Selectivity Results.

The influence of catalyst composition on selecivity is of special interest. First it should be noted that the addition of MoO_3 greatly increases the water-gas shift reaction. Indeed, with the higher amounts of Mo, 20 to 35% of CO reacted under the test conditions was converted to CO_2.The water needed for the shift reaction came from the synthesis of hydrocarbons and higher alcohols.

It was previously established that the selectivity of supported rhodium catalysts for oxygenates synthesis is dependent on conversion level (3). This is illustrated in the figure by the line for Rh/Al_2O_3. Also evident is the major increase in selectivity for catalysts of various Mo contents. This figure also demonstrates the decrease in selectivity on increasing the reaction temperature from 200° to 225-250° for the 7.5% Mo catalyst.

The distribution of individual oxygenates is shifted significantly by the addition of Mo to Rh/Al_2O_3. The percentage of C2+ oxygenates decreases from about 75% to 28% (Table 1). A more detailed comparison of the distribution of individual compounds is shown in Table 2. Note for the Mo catalyst not only the relatively high MeOH but also the high ether and low ester formation.

Discussion.

The scientific interpretation of rhodium catalysts and the effects of supports and modifiers has been controversial. Considerable evidence points to the criticality of the oxidation state of the Rh on control of oxygenates through a mechanism which involves non-dissociative CO chemisorption (1,2).

The concept of an " ensemble " of Rh atoms has been advocated. Such an ensemble is believed to have a minimum number of atoms necessary to act as an adequate catalyst site for activaton of the CO and H2 molecules (4,5).

A general picture of the promoter partly covering the Rh atoms has also been put forward (6) in which a Metal-O-Rh interaction assists in CO activation. It has also been proposed (7) that the CO chemisorption is weakened, thereby increasing the surface concentration of hydrogen atoms.

Our previous work has shown that for Rh/Al2O3 catalysts the Rh is essentially completely dispersed. Thus the effect of the Mo is not to increase Rh dispersion. It is persuasive that the effect of the Mo is to accelerate CO hydrogenation by making more effective use of the H2. Early work by Natta (8) showed that the reaction

$$CO + 2H_2 \longrightarrow CH_3OH$$

fitted the termolecular kinetic expression :

$$\text{(initial) rate} = \frac{a_{CO} \cdot a^2_{H_2}}{(A + Ba_{CO} + Ca_{H_2})^3}$$

where 'a' represents activities of CO and H2.

Thus if the concentration of surface hydrogen atoms is limiting because of the strong chemisorption of CO, then an increase in available H by the Mo would enhance the rate of reaction. This might occur by a " weakening" of CO chemisorption on the Rh, or what seems more likely, by the activation of H2 on the MoO3 adjacent to Rh with a sort of 'reverse spillover' to the Rh active site where CO is chemisorbed. Thus the ' ensemble' might be a dual-metal/metal oxide ensemble. Also the effect of Rh may be to assist partial reduction of MoO3 with increased activity. To explain the great increase in oxygenates selectivitly may require that CH3OH formation is favored from the oxygenated surface intermediate which is common for formation of both methane and methanol, due to the presence of Mo.

During the course of this work, a few patents were located which also point to high activity of catalysts which contaim Mo and Rh. Multicomponent catalysts have been described which contain a wide array on elements, including Mo and Rh. (eg 9,10).More significantly for the present report is a patent application (11) in which Rh on MoO3 is shown to be active at relatively low temperatures for CO hydrogenation with production of oxygenates.. Also, a US patent (12) which claims Rh/Fe/Mo/Al2O3 catalysts includes an example of Rh/Mo/Al2O3, active in the formation of oxygenates.

The patents cited do not provide a systemmatic study nor do they attempt to explain the nature of this enhancement. Our research is being directed towards answering possilities raised above and to identifying the surface chemistry which gives rise to such strong activity and selectivity enhancement.

TABLE I

CO Hydrogenation over 3%Rh Catalysts
(30 atmos., $H_2/CO = 2$)

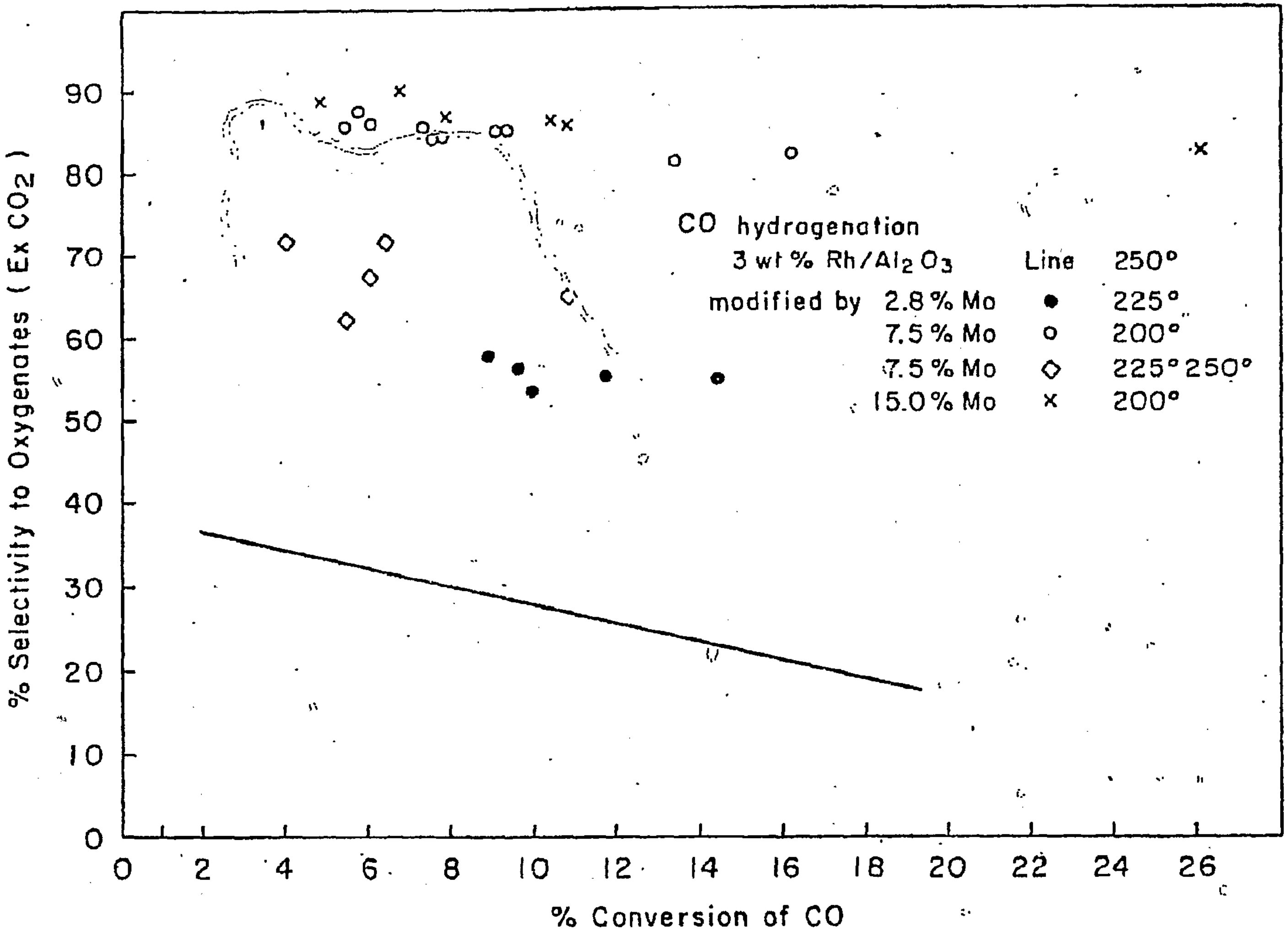
SERIES	Catalyst comp - Wt%	t°C	GHSV	%CO conv.	%CO conv.to		C_{2+}Oxy %of Oxy
					CO_2	Oxy	
A	Rh/Al_2O_3	250	4000	6	1	33	80
	$Rh,2.8Mo/Al_2O_3$	225	3000	9	21	59	42
	$Rh/7.5Mo/Al_2O_3$	200	3000	7	24	86	17
		250	36000	5	25	65	27
	$Rh/15Mo/Al_2O_3$	200	3000	7	23	91	21
		225	3000	27	37	83	14
B	$15Mo/Al_2O_3$	225	3000	<1	61	0	-
		250	3000	2	50	0	-
		275	3000	5	51	0	-
C	$Rh/Mo/Co/Al_2O_3$	250	3000	9	23	51	18
D	Rh/SiO_2	250	3000	1	0	58	94
	Rh/TiO_2	225	2500	9		27	90
E	$Rh/6Mo/TiO_2$	225	4700	11	33	56	19

TABLE 2
EFFECT ON PRODUCTS DISTRIBUTION OF ADDITION OF MO TO RH/AL2O3

CO HYDROGENATION, 30 ATMOS., $H_2/CO = 2$

CONDITION/ PRODUCT	RH/AL2O3	RH/MO/AL2O3		PRODUCT	RH/AL2O3	RH/MO/AL2O3	
		(1)	(2)			(1)	(2)
TEMP. C	250	200	250	MEOH	2	38	16
GHSV	3000	3000	36000	MEOAC	1	30	27
% CO CONV	6	7	5	MECHO	2	0	0
% TO CO2	1	24	25	ETOH	11	6	7
%OXY.	29	86	65	MEOAC	3	1	1
%C+ OXYG.	82	17	27	ACOH	0	0	0
CH4	60	9	27	ETCHO	0.4	0	0
C2H6	4	3	6	N-PRTOH	2.7	2	1
C3H6	0	0	0	MEOET	3	10	15
C3H8	5	1	2	ETOAC	3	0	0
C4H10	2	0.	0	N-BUOH	0	0	0

3 WT % RH, 7.5 WT% MO


CO hydrogenation
3 wt % Rh/Al₂O₃ Line 250°
modified by 2.8 % Mo ● 225°
7.5 % Mo ○ 200°
7.5 % Mo ◇ 225° 250°
15.0 % Mo × 200°
% Selectivity to Oxygenates (Ex CO₂)
0
10
20
30
40
50
60
70
80
90
% Conversion of CO
0
2
4
6
8
10
12
14
16
18
20
22
24
26

References

1 S.M.Davis and G.A..Somerjai. Bull. de la Societe Chimique de France. No. 3, p271 May-June (1985).

2 M.Kawai, M.Uda and M.Ichikawa, J.Phys. Chem. 89,1654 (1985)

3 C. Sudhakar, N. Bhore, K.B.Bischoff, W.H.Manogue and G.A.Mills, Am.Chem.Soc., Pet.Div. Preprints vol. 31 No.1 p 133 April (1986).

4 W.M.H.Sachtler, D.F.Shriver, W.B.Hollenberg and A.F.Lang, J.Catal., 92, 429 (1985).

5 M.M.McClory and R.D.Gonzalez, J.Catal.,89, 392 (1984).

6 M.Ichikawa and T.Fukushima, J.Phys.Chem.89, 1564 (1985).

7 F.G.A.Van den Berg, J.H.E.Glezer and W.M.H.Sachtler, J.Catal., 93, 340 (1985).

8 G. Natta, Catalysis, P.H.Emmett, Ed. Reinhold Pub. Co. Vol. 3 p 391 (1955).

9 P.C.Ellgen and M.M.Bhasin, U.S. Patent 4,096,164 (1978).

10 W.J,Ball.L.Cotton and D.G.StewartU.S.Pat. 4,492,772 (1985).

11 S.J.Jackson, Pat. Application G.B.2,151,616A (1985).

12 Yun-Yang Huang, U.S.Pat.4,328,129 (1982).