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TRIFUNCTIONAL CATALYSTS FOR CONVERSION OF SYNGAS TO ALCOHOLS: ELEVENTH QUARTERLY REPORT FOR PERIOD MARCH 1, 1987 TO MAY 31, 1987

DELAWARE UNIV., NEWARK. CENTER FOR CATALYTIC SCIENCE AND TECHNOLOGY

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Eleventh Quarterly Report for Period March 1,1987 to May 31,1987

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OBJECTIVES

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Task 1. Preparation of catalyst samples

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Task 2. Testing catalysts for syngas conversion

Task 3. Measurement of surface composition and structure

Task 4. Determination of nature of surface complexes

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Task 5. Reaction mechanism determination by isotopic tracers and kinetics

Task 6. Design, prepare and test optimized catalysts

ABSTRACT

Changes in the chemical state of Rh and Mo, and the dispersion of Mo due to different \approx treatments and Mo loadings was studied by X-Ray Phototelectron Spectroscopy. The results show well dispersed Mo on Mo/Al₂O₃ and aggregated Mo on Rh-Mo/Al₂O₃. The crystallite size of Mo-oxide particles in Rh-Mo/Al₂O₃ was estimated using Kerkhof and Moulijn method to be \approx 20A. Electron Spin Resonance Spectroscopy measurements on catalysts show presence of paramagnetic Mo species on reduction and corroborate XPS results. Mo and Rh loadings were determined by X-Ray Fluoresence.

Ethylene hydrogenation was carried out on Rh/Al_2O_2 , Mo/Al_2O_3 and $Rh-Mo/Al_2O_3$ in the presence and in the absence of carbon monoxide in the gas phase. Carbon monoxide in the gas phase acts as an ON/OFF switch for ethylene hydrogenation on Rh/Al_2O_3 . $Rh-Mo/Al_2O_3$ acts like Rh/Al_2O_3 for ethylene hydrogenation in the absence of carbon monoxide and like Mo/Al_2O_3 in the presence of carbon monoxide. Task:3 Measurement of surface complexes

* Task:4 Determination of nature of surface complexes

Task:5 Reaction mechanism determination by isotopic tracers and kinetics

X-Ray Photoelectron Spectroscopy (XPS)

Introduction

XPS is a useful tool to investigate the chemical nature of surfaces. It is sensitive to -- different elements, their oxidation state and their local chemical environment. There are however problems with precise physical and chemical interpretation of the spectra for insulators, porous and heterogenous samples. Due to the insulating nature of oxide supports, they become charged on photoelectron emission. Hence we need a reference peak

) to find the charging correction.

Experimental set-up

A Physical Electronics double pass cylindrical mirror analyzer and ultra-high vaccum chamber with an attached pretreatment chamber was used. An Al anode was used. The X-Ray tube was operated at 10kV and 60mA. Data was collected at 50eV and 100eV pass energy for detailed and survey scans respectively. Powdered samples ground between glass slides were pressed into Al sample holders with an Al die. The sample holder was then mounted onto the tip of the probe. The samples were evacuated with the sample temperature below 70C. The samples were treated insitu in the sample treatment chamber(Figure 1). Hydrogen (\geq 99.999%) and Helium (\geq 99.999%) were further purified using a CuO trap for oxygen removal and a zeolite trap for water removal. Both the gases were then passed through a rotameter and a mass flow controller. Carbon monoxide was purified by passing it through zeolite trap. The pressure in the analyzer chamber was less than 5 X 10⁻⁸ torr. Survey scans were taken for each sample and after each treatment to check for extraneous impurities in the chamber and in the sample. Magnesium was present in the survey scans as an impurity in the chamber. Periodic washing of the sample probe with dilute nitric acid kept the magnesium impurity to low levels. This is necessary because Mg Auger lines are very close to Rh $(3d_{5/2})$ for Al X-rays. Sample treatment

The catalyst samples were calcined outside the pretreatment chamber at 500C under air. The reduction of the catalyst was done insitu in the pretreatment chamber under $\approx 30 \text{ scc/min}$ of Hydrogen with the following schedule 200C(1/2 hr), 350C(1/2 hr) and 500C(1hr). The heating rate was 8C/min. The catalyst was then cooled to less than 70C and evacuated. CO chemisorption was done after data was collected for the reduced samples. CO was passed over the catalyst $\approx 30 \text{ scc/min}$ for 15 min at 30C. The reaction was performed on the catalyst by flowing a mixture of $CO/H_2 = 1 : 2$, total flowrate $\approx 50scc/min$ at 200C for 1 hr. For comparison of the method of preparation, samples of 3%Rh 2.8% Mo /Al₂O₃ (3Rh28MoC) prepared by reaction of Mo(CO)₆ with the surface -OH groups , followed by deposition of Rh(CO)₂(acac) were also run. Air calcination was done after each stage at 30C for the above catalyst. This catalyst was provided to us by Prof. H.C. Foley.

Results

(i) Binding Energies

The binding energies of the different element referenced to $Al(2p)^1$ are listed in Table 1. Rhodium is present in the +3 state after air calcination, but after reduction in hydrogen at 500C, it is completely converted to metallic state. The oxidation state of Rh is not affected by subsequent treatments such as CO adsorption and reaction. Molybdenum exists in the +6 state after air calcination. The binding energy of $Mo(3d_{5/2})$ in $3\%Rh2.8\%Mo/Al_2O_3$ is 1 eV higher than that of Mo+6 in MoO₃, This has been explained as a result of the interaction between Mo+6 and the support, where there is donation of electron density from molybdenum to oxygen or the oxygen binding Al and Mo is more electronegative

C(1s) peak is not used because of its weak intensity and poor resolution

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than the oxygen in the bulk MoO₃². On reduction in hydrogen at 500C molybdenum is
reduced from the +6 state to a mixture of +6, +5 and to +4 states(figure 2 and 3). This confirms with the data obtained from ESR experiments, which will be discussed later. The
binding energy and the shape of the Mo peak do not change on subsequent CO adsorption and reaction. The reduction of Mo is increased with increase in Mo loading. The extent of reduction of Mo is not affected by the presence of Rh(figure 2 and 3). In contrast, with Ni and Mo the reduction of Mo is enhanced by presence of Ni³.

(ii) Relative photoelectronic response

Figure 4 shows the relative photoelectronic response of Mo (defined as Intensity of Mo peak/ Intensity of Al) for Rh-Mo/Al₂O₃ and Mo/Al₂O₃. The relative photoelectronic response for Mo is higheron Mo/Al₂O₃ than on Rh-Mo/Al₂O₃ (figure 4). We know from previous work that Mo/Al₂O₃ forms a monolayer⁴. We see that the Mo in 15%Mo/Al₂O₃ is equal to or less than the monolayer coverage since the photoelectronic response curve is still linear. The photoelectronic response is not sensitive to the treatment of catalyst i.e. Mo dispersion is not changed after treatments such as reduction, chemisorption and reaction. At present we are not sure whether this aggregation of Mo-oxide is a surface effect or a pH effect. The relative photoelectronic response is higher for 3Rh28MoC than on 3Rh28Mo, indicating that Mo is more dispersed on the former catalyst.

(iii) Estimation of particle size

Grinding the catalyst does not change the relative phototelectronic response appreciably, hence there is no surface segregation. The absence of surface segregation allows us to

² Holl Y., Tourounde R., Maire G., Muller A., Engelhard P.A. and Grosmangin J.,

³ Grimblot J.G. and Payen E. in "Surface poroperties and catalysis by non-metals" ed.

Bonnelle J.P., Delmon B. and Derouane E., D. Reidel Publishing Co,1983, Boston.

⁴ Hall W.K. in "Proc. of the Climax Fourth Intl. Conf. on Chemistry and Uses of Molybdenum", ed. Barry H.F. and Mitchell P.C.H., Climax Molybdenum Company, Ann Arbor, Michigan, 1982.

J.Catal.1987,104,202.

use the model of Kerkhof and Moulijn to estimate crystallite size(Figure 5)⁵. The model assumes that catalyst support is made of stacked layers with modifier dispersed uniformly over the surface area (either as a monolayer or as crystallites). The incident X-rays and outgoing photoelectron are perpendicular to the surface. This model can estimate the particle size provided the mean free path for the photoelectrons is known. The model does not take concentration gradient and surface segregation into account.

Electron Spin Resonance Spectroscopy(ESR)

The reduction of Mo(+6) to Mo(+5) on Rh-Mo/Al₂O₃ and Mo/Al₂O₃ was reported in the section on XPS. This is cross-checked with ESR. Mo(-6) is not a paramagnetic species while Mo(-5) is a paramagnetic species. Two set of experiments were conducted. Both sets contained Al₂O₃, 3%Rh/Al₂O₃, 15%Mo/Al₂O₃ and 3%Rh 15%Mo/Al₂O₃. In the first set air calcined samples were transferred to a glove box under nitrogen and the sample is loaded into a quartz sample tube. Spectra were collected at 30C and at liquid nitrogen temperature. There were no paramagnetic species in this set of catalyst. The next set of experiments consisted of reducing the above samples under hydrogen at 500C. The adsorbed hydrogen is then removed by flushing the catalyst with flowing helium. The catalyst is then cooled under helium to 30C and then dosed with carbon monoxide. The sample is then transferred to a glove box and packed into a quartz sample tube. Spectra were collected at 30C and at liquid nitrogen temperature. Only 15%Mo/Al₂O₃ and 3%Rh15%Mo/Al₂O₃ showed intense peaks due to Mo(-5). The g value is same for both catalysts and is 1.9611. There is no fine structure on the Mo(+5) peak. The lack of fine structure is due to the unsymmetrical environment around Mo(+5) ion. Figure 6 shows the ESR spectra of 3%Rh15%Mo/Al₂O₃ after CO adsorption.

X-ray Fluorescence(XRF)

Callibration

⁵ Kerkhof F.P.J.M. and Moulijn J.A., J.Phys. Chem. 1979,83,1612.

Mo and Rh loadings were checked with XRF. A Phillips PW1410/80 X- Ray Spectrometer was used. Samples were mixed in an appropriate amount with Orthoboric acid. The samples are then ground and mixed in a ball mill for an hour. Cu K X-Rays are used and LiF(200) crystal is used. The Mo K_{β} and Rh K_{α} lines overlap. Instead of deconvoluting the overlapped peaks, we monitored the weak Rh K_{β} lines for longer times. Rh(NO₃)₃3H₂O was tried as a standard. Due to the hygroscopic nature of the above salt , the results were not repeatable. Then RhCl₃ salt was used as a standard; this salt is from an old batch and the exact amount of hygroscopic water in it may not be accurate. MoO₃ is used as a standard for solid samples. There may be interference between the Rh and Mo apparent cross-sections. This interference is caused due to the higher absorption cross-section of Mo for X-rays emitted by Rh than the absorption cross-section of Rh for X-rays emitted by Mo.

Effect of particle size on the selection of standards

The role of particle size in solid standards is often not appreciated. Solid standards have micron size particles. The average distance between the two particles is of the same order of magnitude as the length scale of absorption of X-rays emitted by Rh and Mo (for e.g. for $60\mu m$ particles; separation between particles is $\approx 0.12 cm$, while the length scale for absorption of X-rays in the sample is $\approx 0.2 cm^6$). Thus a substantial amount of X-rays are absorbed before it reached the other element. This is not true with our catalyst sample because Mo and Rh are dispersed on the atomic scale. Hence non-interference of Rh and Mo peaks in solid standards need not imply non-interference in the catalyst samples. In a fliquid phase solution the Mo and Rh atoms are quite well dispersed on the atomic level. Hence non-interference of peaks should be checked in the liquid phase. Liquid samples are prepared by dissolving Rh nitrate and ammonium molybdate (molybdenum trioxide is spatingly soluble in water). Liquid samples do not show any interference between Rh and

⁶ Estimated from Bertin E.P., "Principles and Practice of X-Ray Spectrometric analysis", Plenum Press, 1975, New York.

Mo peaks.

Results

The Rh loading was lower than expected. However the relative Rh loading was within 10% error The difference in the Mo loading between 3%Rh x%Mo/Al₂O₃ and x%Mo/Al₂O₃ . was again within 10% The table below summarises the results.

· · : ·	Catalyst	Rh ratio	Mo ratio	۰. ۲
: .	3%RhAl2O3	1.00		
	3%Rh2.8%Mo/Al ₂ O ₃	1.05	1.00	
	3%Rh2.8%Mo/Al ₂ O ₃ (+)	ء 1.90	1.33	
	7.5%Mo/Al ₂ O ₃	-	3.40	
	3%Rh7.5%Mo/Al ₂ O ₃	1.25	2.72	
	15%Mo/Al ₂ O ₃		5.61	
-	3%Rh15%Mo/Al ₂ O ₃		U : 5.27	

(+) Prepared from carbonyl clusters

Ethylene Hydrogenation with and without Carbon monoxide

Ethylene hydrogenation was performed to characterize the hydrogenation activity of the catalyst. The overall rate for CO-hydrogenation is less poisoned by carbon monoxide for Rh-Mo/Al₂O₃ as compared to Rh/Al₂O₃(see quarterly report 10). Hence we studied ethylene hydrogenation on Rh/Al₂O₃, Mo/Al₂O₃, Al₂O₃ and Rh-Mo/Al₂O₃. These catalysts were calcined previously. Ethylene is purified by passing it through a CuO trap and a Zeolite trap to remove oxygen and water respectively. The flow rate is monitored with a mass flow controller. A schematic diagram of the flow apparatus is given in figure 7. A glass reactor is used to avoid base hydrogenation activity of aluminized stainless steel (used in high pressure reaction runs). The catalyst is reduced under 25scc/min of hydrogen at 200C for 1/2hr, 350C for 1/2 hr and at 500C for 1hr. The catalyst is then cooled under hydrogen to 30C. The catalyst was contacted with ethylene only in the presence of hydrogen and helium to avoid poisoning of the catalyst. The initial transient of ethylene is suppressed by flowing a large excess of helium with ethylene. The flowrate of helium is then decreased to the required value. The same procedure is used to avoid poisoning due to an initial surge of carbon monoxide.

It is well known that transition metals are very active for ethylene hydrogenation⁷. Presence of carbon monoxide in the gas phase can have a profound effect on ethylene hydrogenation activity. Rh/Al_2O_3 is reported to be a very good ethylene hydrogenation catalyst; this is also seen in our results i.e. ethylene undergoes complete conversion. However in presence of carbon monoxide there is no conversion of ethylene. Carbon monoxide in gas phase acts as an ON/OFF switch for conversion of ethylene at 30C. There is no activity for ethylene hydrogenation due to Al_2O_3 at 30C. There is very little activity by calcined only catalyst. Rh-Mo/Al₂O₃ acts like Rh/Al₂O₃ in the absence of carbon monoxide in Table 2.

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⁷ Bond G.C., "Catalysis by Metals", Academic Press, 1962, London.



Figure 1

FIGURE 2

COMPARISON OF REDUCIBILITY OF Mo IN 3% Rh 7.5% Mo/Al₂O₃ AND 7.5% Mo/Al₂O₃, X PS Reference Peak: Al(2p)=74.7eV



Figure 3

COMPARISON OF REDUCIBILITY OF Mo IN 3% Rh 15% Mo/Al2O3 AND 15% Mo/Al2O3, XPS Reference Peak: Al(2)=74.7eV







In this case, c= 20Å.



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EXPERIMENTAL SET-UP



BA CUD TRAP

" Table 1: Uncorrected Feak positions(xps) :

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Sample description	Sample treatment.	A1 (25)	0(15)
77657 A) 203 (rb3)	as rec	79.5	541.3
	reduced	77.2	536.0
	CO-chemisorbed	. 79.1	₍ 535.9
	reaction	79.3	536.1
	1 662,0100	<i>.</i>	
	as rec	30.5	- 537.4
oamithizuo (1.507	eaduced	· 30.0	536.7
· · ·	CO_shami corbed	77.8	534.5
· · · · · ·		77.9	537.1
•	reaction		
	المراح ورراحه المراجع	Ξ 0.4	537.0
3%56 2.5%67A1203(FA2)			and a second
	required		
	·.	77.3	536.4
3%Rh 7.5%M5/A1203(mm// %	as rec.	TR 0	5555.7
· · ·	reduced	70 0	535.7
	Cu-chemisorbea		0.2.07
		50.0	534.9
7.5%No/A1203(m75)	as rec		575.7
	reduced	9.0	
1	•	70 7	535 8
3%Rh 15%Mo/A1203 (rm1)	as rec	· · · · · · · · · · · · · · · · · · ·	ಜ್ಞಾನ ಸ
	reduced		500.0 R75 4
	CO-chemisorbaú	76.0	
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			534 A
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i i	reduced	×7.0	303.0 ST4 0
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•••	:	70 %	57.4 5
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	CO- chemisorled	= /	0.000
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	reduced _{* *}	7.0	
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3%8h 0.67%Na/A1203(rn6)	as rec	212 - 21 21 - 21	3.7.9 57 - 7
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	reaction		
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•		BINDING ENERG	IY (EV)		. ·	
	C(1s) - I	C(15)-II	Rh(3d)-I	Rh(3d)-11	Ma(3d)—I 👘 M	o(3d)-II
	796.5	289.0	315.3	· · · ·	-	
	10010	288 0	-312.4	•• ••		•
•	207.0	2971V 2004 7		•		
	286.4	290.3	312.0			
	286.5	287.8	312.0	•••	*	
		•			•	
	286.5	_290.S	316.5	· •		
		290.5	312.6	318.0		
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		287.0	315.0		233.1	240.7
	287.0	287.0	311.4	•	237.2	240.4
	785 4	289.1	312.0		237.2	240.0
		700 C			238.3	241.0
	200-2	27V-V 000 8			234.9	240.0
	-287.0	287.4		•		-
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		270.0	312.6	377.5	237.3	240.7
						**
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		. 289.5	512.0	7 : . 3		
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Table 1: Uncorrected Feak positions(xps)

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Table 1: Uncorrected Peak positions(xps). . Na(15)-I Almand 0 peaks have shoulders ---- Al- and O peaks have shoulders Al and O peaks have shoulders Al and O peaks have shoulders. ave ____ C-1 narraw C-1 narrow, C-II broad Rh peak ratio not right C peaks well separated good peak resolution Mo yeaks sep C-T peak as shoulder. No spectrum isrnois. " Mo-II as sh., not acc - Al-an sh, Mo-II not acc. Rh-I may be Mg auger. CyI Al-an sh, Mo-II not acc, Rh-I may be Mg auger, C-I C-I peak as sh, wafer broke after reduction C spec too noisy, Mo-II pk sh not acc Al and C peak have an sh,Mo-II not acc Al and O peak have an sh, Mo-I-I not act Al and O an sh, Mo-II not acc, Cr.1.1 not acc : - J has sh, Mo. peaks overlapping Mo peaks well resolved Rh pk ratio not right C- has an sh, Mo-overlap, Rh pk ratio not right Al,O an sh, Mo pk resolved. C overlap Al.O an sh. Mo pk overlap, C-I nerrow. C-II broad Al.O an sh. 'No pk overlap.C beak overlap. • ·.. · . Mo- pk not resolved. C ph well res 1079.0 1078.0

1078.4

substantial surface exidation to MOCS

Table 2

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Test Reactions:

Ethylene Hydrogenation

-without CO in gas phase

-with CO in gas phase

Reaction conditions:	T= 30C	GHSV-9750 hr
· · · - •	pH2 =0.30atm	pEthylene=0.03atm
	total pressure=1 .atm	🐭 Rest is Helium

Catalyst	pCO(atm)	Ethylene conv(%)
	L	00.000/
3% Hh/ Al 20 3	0.0	>99.99%
	.0.08	<0.01%
7.5%Mo/Al ₂ O3	0.0	~40.0%
	0.08	~5.30%*
3%Rh 7.5%Mo/ Al _O _	- 0:0 -	>99.99%
6 Z J	0.08	~5.50%*

* deactivation within 4 hours

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