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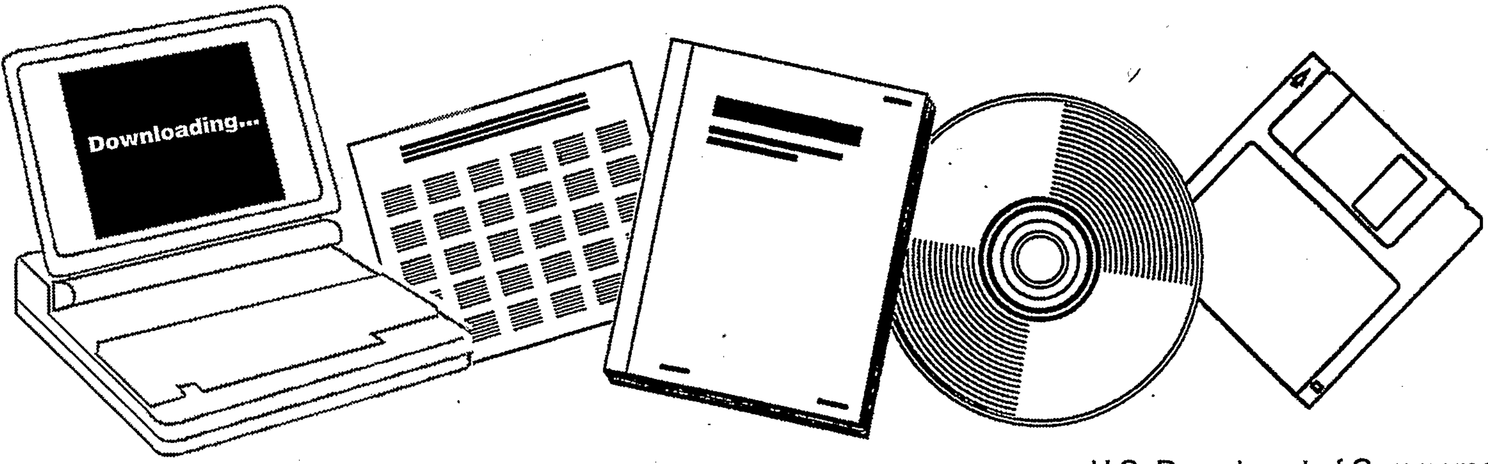

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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

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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, reaction probing, study state rate measurement, and transient kinetic study.

A better understanding of the role of additives 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.

RESULT TO DATE

During the third quarter of 1991, the characterization of coprecipitated Na-Mn-Ni catalysts were carried out. The coprecipitated catalysts have been found to be active and selective for higher alcohol synthesis. The characterization methods included were temperature programmed reaction and x-ray photoelectron spectroscopy. XPS results revealed that the surface concentration of the Na-Mn-Ni catalysts changes with respect to the envoronment. TPR results have revealed that the surface concentration changes may be due to the oxidation of the surface during reaction.

INTRODUCTION

Synthesis gas conversion on Group VIII metal catalysts have been proven to be a promising route for the synthesis of higher aldehydes and alcohols [1,2]. Rh catalysts exhibit the highest activity for higher oxygenate synthesis among the Group VIII metal catalysts [3-6]. Mechanistic studies on Rh catalysts have shown that higher oxygenate selectivity depends on moderate CO dissociation and strong CO insertion activities [5,7,8]. Addition of promoters such as Mn, Ti, Zn, La, Ag, V, and Mo increases the CO insertion activities of Rh/SiO_2 catalysts [5,9-12]. Alkali species have been found to decrease the hydrogenation ability of Rh catalysts while having little effect on the CO insertion activities. This effect results in an enhancement of the higher oxygenate selectivities [13]. The high cost of Rh, however, prevents this process from being economically favorable as compared to conventional alcohol production such as fermentation.

Previous investigations have demonstrated that coprecipitated Ni catalysts possess higher oxygenate synthesis activities from syngas [14-17]. Uchiyama and coworkers [14,15] found that coprecipitated $Ni-TiO_2$ exhibits a high selectivity for C_{2+} oxygenates while coprecipitated Ni-ZnO exhibits a high selectivity for methanol. It is interesting to note that the effect of these oxides parallels, to some extent, that of supported Rh/SiO_2 prepared by impregnation. Recently, coprecipitated Na-Mn-Ni catalysts have been shown to posses good activity and selectivity toward C_{2+} oxygenates from syngas [16,17]. Although the Ni-based catalysts are not as selective as Rh catalysts, they are of particular interest due to their low cost. It has also been found that under specific conditions, the surface of the Na-Mn-Ni catalysts undergo a change in composition and/or structure [17]. The change in surface composition may be of importance to the synthesis of higher alcohol from syngas.

The purpose of this investigation is to characterize coprecipitated Na-Mn-Ni catalysts that have shown a good selectivity toward C_{2+} oxygenates using temperature programmed reaction (TPR) and X-Ray Photoelectron Spectroscopy (XPS) methods. TPR is used to gain information on the active site for CO hydrogenation, particularly the site for methanation, a competing reaction. The TPR spectra are compared to that of Ni/SiO_2 catalyst, a good methanation catalyst. The TPR experiments may also be used to probe the surface of the coprecipitated catalysts and investigate the change in surface concentrations. XPS is used to study the effects of catalyst preparation and the CO hydrogenation reaction on the surface state of the catalyst.

EXPERIMENTAL

The coprecipitated Na-Mn-Ni catalysts were prepared by precipitating $Ni(NO_3)_2{\cdot}6H_2O$ and $MnNO_3{\cdot}XH_2O$ with Na_2CO_3. The precipitate was washed with water to remove excess Na. The catalyst was calcined in air at 250°C for 3 hr and then reduced in flowing hydrogen at 350°C for 7 hr. The resulting catalyst contained Na, Mn, and Ni which had a molar ratio of Na:Mn:Ni = 0.005:0.5:1 (as determined by atomic absorption spectroscopy). To determine the effect of Na on the surface, an increase in the Na content of the catalyst (Na:Mn:Ni = 0.05:0.5:1) was achieved by impregnating the washed catalyst with $NaNO_3$. The catalyst was then calcined and reduced in the same manner as before. Another catalyst was prepared in order to determine the effect of washing the excess Na from the catalyst. This catalyst was made by precipitation as described above; however, the resulting precipitation was not washed with water. The molar ratios of the unwashed catalyst was found to be Na:Mn:Ni = 0.2:0.95:1. For all of the coprecipitated Na-Mn-Ni catalysts, an equimolar amount of Ni and Mn were used in there respective nitrates for the coprecipitation. The unwashed catalyst; however exhibit a molar ratio of Mn to Ni of 0.95:1, while the molar ratio of the washed catalyst was found to be 0.5:1. This difference is due to some of the Mn being washed away along with the Na_2CO_3. A Ni/SiO_2 catalyst of 15wt% was prepared by impregnation of large-pore SiO_2 using $Ni(NO_3)_2{\cdot}6H_2O$. Characterization of these catalysts using BET surface area, H_2 chemisorption, H_2 TPD, XRD, and CO hydrogenation studies are reported elsewhere [16,17].

Temperature Programmed Reaction (TPR) experiments were performed in a stainless steel differential reactor system. Details of the reactor system are given elsewhere [18]. Continuous product analysis was conducted by a Balzers QMG 112 mass spectrometer (MS) interfaced to a microcomputer. This MS system is capable of following up to eight predetermined m/e peak intensities versus time. The minimum amount of detection for a CO pulse in the mass spectrometer was about 0.03 µmol. The mass spectrometer is about ten times more sensitive to the CH_4, CO_2, and H_2O observed in this study.

All the catalysts in this study were reduced in flowing hydrogen at 500°C before each TPR experiment was performed. Carbon monoxide was adsorbed on the catalysts by pulsing CO into flowing He at a flow rate of 50 ml/min upstream of the reactor at 30°C. Temperature programmed desorption experiments were performed by ramping the temperature at a rate of 15°C/min from 30°C to a final temperature of 500°C in the pure He stream at 50 ml/min and monitoring the products on-line with the mass spectrometer. After further reduction in H_2 a TPR experiment was carried out. The catalysts were cooled under He flow to 30°C and CO was adsorbed as before. The carrier flow was switched to a 9.1% H_2 in He flow of 55 ml/min and the temperature was ramped as before to 500°C. A second TPR experiment was performed under the same conditions; however, CO was adsorbed at 400°C and cooled in a pure He flow to 30°C.

The X-Ray photoelectron spectroscopy (XPS) of the catalysts was measured by a Leybold LHS-10 system. This system is equipped with a high-pressure sample preparation facility which allows various pretreatments of the catalysts and transfer of the catalyst sample to the vacuum chamber without exposure to air. Each catalyst was analyzed by XPS three times. First the spectrum was taken of a catalyst sample before the reduction process. The catalyst sample was then reduced in H_2 for 90 min and a second spectrum was taken. The third X-Ray photoelectron spectrum was taken after the sample had been exposed to CO/H_2 at a ratio of 1:1 at a temperature of 300°C and a pressure of 1 atm for 60 min.

RESULTS

The adsorption of CO for the temperature programmed experiments were conducted by pulsing CO into the carrier gas stream at the inlet of the reactor. These pulses reveal much information about the state of the surface of the catalyst before each experiment. CO was pulsed at least four times over each catalyst sample before each temperature programmed experiment at each adsorption condition. At room temperature, the Ni/SiO_2 catalyst produced both CO and CO_2 from CO pulsing. For the Na-Mn-Ni catalysts, only CO was observed at the outlet of the reactor after each pulse.

Figure 1 is the CO_2 response to CO TPD of the four catalysts in this study. Desorbed carbon monoxide was not observed from the catalysts tested in this study. The Ni/SiO_2 produced a CO_2 desorption peak at 210°C with a shoulder at 150°C. The CO_2 has been known to desorb from Ni/SiO_2 catalysts as a result of CO TPD at higher temperatures than reported here [19]. Carbon monoxide was also observed to desorb from Ni/SiO_2 in the literature [19]. It appears that the Ni/SiO_2 catalyst exhibits a much higher CO dissociation activity than those in the literature. The TPD spectra for the Na-Mn-Ni catalyst with the ratio of 0.005:0.5:1 did not show any CO or CO_2 desorption profile. This indicates strong CO adsorption to the surface of this catalyst. When more Na was impregnated into this catalyst, a CO_2 desorption peak was observed at 450°C with a shoulder at above 500°C, as seen in the spectra for Na-Mn-Ni (0.05:0.5:1). the unwashed catalyst, Na-Mn-Ni (0.2:0.95:1), exhibited a lower CO_2 desorption peak temperature at 290°C with a shoulder at 160°C.

The responses of CH_4, H_2O, and CO_2 during the TPR experiments when CO was adsorbed at 30°C is presented in Figure 2. A CO desorption peak was not observed. The methane spectrum of the Ni/SiO_2 catalyst has a sharp peak centered at 250°C. The coprecipitated Na-Mn-Ni

(0.005:0.5:1) catalyst produced two distinct methane peaks. The first at 360°C and another at above 500°C. This is an indication that two distinct active sites exist for adsorbed carbon on this catalyst. The phenomena of two distinctive active carbon sites has been observed on other Ni-based catalysts in the literature such as Ni/Al_2O_3 [19-24]. When additional Na was impregnated onto the catalyst (as is the case with Na-Mn-Ni (0.05:0.5:1), the first methane peak was decreased to 310°C while the second peak disappears completely. The unwashed catalyst, Na-Mn-Ni (0.2:0.95:1) produced a methane peak at a temperature of 380°C.

The H_2O response to TPR when CO was adsorbed at 30°C is shown on the middle portion of Figure 2. The Ni/SiO_2 catalyst did not produce H_2O during TPR while the Na-Mn-Ni (0.005:0.5:1) catalyst exhibited a water peak at above 500°C. The Na impregnated Na:Mn:Ni (0.05:0.5:1) catalyst and the unwashed Na-Mn-Ni (0.2:0.95:1) catalyst produced a very small amount of H_2O at above 500°C.

The CO_2 response to TPR when CO was adsorbed at 30°C is also shown is Figure 2. These spectrum show that the Ni/SiO2 catalyst produced CO_2 with a peak temperature of 140°C while the Na-Mn-Ni catalysts did not produce any CO_2 at all during TPR when CO was adsorbed at 30°C.

Figure 3 is the CH_4, H_2O, and CO_2 response when TPR was performed with CO being adsorbed at 400°C. The main product from the adsorption pulses on the catalysts at 400°C was CO_2 [25]. Since oxygen from dissociated CO was leaving the surface as CO2, the surface as CO, surface consisted mainly of adsorbed carbon. The methane spectra for the Ni/SiO_2 catalyst exhibited a peak at above 500°C. The methane TPR spectra for Na-Mn-Ni (0.005:0.5:1) exhibited two distinct peaks for methane formation which is similar to those for CO adsorption at 30°C. The first peak was observed at 360°C and the second at above 500°C. The Na-Mn-Ni (0.05:0.5:1) also exhibited two peaks; however, the peaks were decreased to 300°C and 440°C. The unwashed Na-Mn-Ni (0.2:0.95:1) catalyst produced two methane TPR peaks at 295°C and above 500°C.

The Ni/SiO$_2$ catalyst produced a very small amount of H$_2$O during TPR when CO was adsorbed at 400°C. This H$_2$O peak was at above 500°C. All three Na-Mn-Ni catalysts produced a substantial amount of H$_2$O. All had peaks at above 500°C.

During TPR when CO was adsorbed at 400°C, the Ni/SiO$_2$ produced a CO$_2$ response peak at 140°C, the same as in Figure 2. The Na-Mn-Ni (0.005:0.5:1) catalyst produced CO$_2$ during these adsorption conditions at a much higher temperature of above 500°C. When more Na was impregnated into this catalyst, Na-Mn-Ni (0.05:0.5:1), CO$_2$ was not observed during TPR in this temperature range. The unwashed catalyst, Na-Mn-Ni (0.2:0.95:1), exhibited two CO$_2$ desorption peaks for TPR when CO is adsorbed at 400°C. The first was observed at 210°C and the second at 480°C.

Figures 4 and 5 are the results of the X-ray photoelectron spectroscopy study of the catalyst with additional Na, Na-Mn-Ni (0.05:0.5:1), and the unwashed catalyst, Na-Mn-Ni (0.2:0.95:1). The XPS results for the washed Na-Mn-Ni (0.005:0.05:1) catalyst has been presented elsewhere [17] and was found to be consistent with the spectra presented here.

Shown in Figure 4a is the XPS spectra of the Ni$_{2p}$, Mn$_{2p}$, Na$_{1s}$, and C$_{1s}$ binding energies for the Na-Mn-Ni (0.05:0.5:1) catalyst. The catalyst exposed to air exhibited Ni peaks at 854.6 and 860.7 eV, Mn peaks at 641.8 and 668.0 eV, a Na peak at 1071.4 eV, and two C peaks at 284.9 and 289.3 eV. When this catalyst was exposed to reduction at 400°C conditions, the Ni and the Mn peaks almost completely disappeared, while the Na peak was greatly enhanced and shifted to 1071.4 eV. The C peak was also greatly enhanced and shifted to 291.4 eV under reduction conditions. Following CO hydrogenation at 300°C for 60 min, the Ni peak at 852.5 eV grew slightly while the Mn peaks at 641.2 and 653.8 grew substantially. The Na peak at 1073.1 eV decreased under the CO hydrogenation conditions, as did the two C peaks at 291.2 and 284.4 eV.

The XPS spectra of the unwashed Na-Mn-Ni (0.2:0.95:1) is presented in Figure 5. The data in Figure 5 is consistent with that of Figure 4. The Ni peaks for the exposed to air catalyst were found at 855.1 and 861.4 eV, the peaks for Mn at 641.5 and 653.5 eV, the peak for Na at

1071.9 eV, and the C peaks at 285.1 and 290.7 eV. After reduction, the Ni and Mn peaks disappeared completely while the Na peak is sifted to 1074.9 eV and the intensity is increased. Likewise, reduction caused the C peak at 292.1 eV to increase greatly in intensity. After exposure to the CO hydrogenation atmosphere, the Ni and Mn peaks reappear, the Ni at 856.2 eV and the Mn at 642.3 and 654.0 eV. The Na peak decreased in intensity and shifted to 1073.1 eV, as well as the C peaks at 291.2 and 284.4.

DISCUSSION

The XPS spectra revealed interesting results as to the the state of the surface of the catalysts during reaction conditions. The XPS results are summarized in Table 1. The coprecipitated catalysts exposed to air contained a fair amount of Ni, Mn, Na, oxygen and carbon. The chemical state of surface Ni is assigned to be Ni^+. The chemical state of Mn on the surface of both samples is difficult to discern from the XPS spectra due to poor resolution. From previous results of x-ray diffraction studies, it can be concluded that the surface Mn was in the form of MnO after exposure to air [16]. The Na of both catalysts were in the form of Na_2CO_3 with a little bit of an unknown state of carbon on the surface.

As evidenced from the XPS spectra, reduction of the coprecipitated catalysts under a hydrogen flow at 300°C for 90 min caused a drastic change on the catalyst surface. This change also occurs on the Na-Mn-Ni (0.005:0.5:1) catalyst under similar conditions [15]. The Ni and Mn peaks for both catalysts almost totally disappear except a small amount of Ni^0 detected in the spectrum of Na:Mn:Ni (0.05:0.5:1). These reduction conditions also caused a significantly higher concentration of Na_2CO_3 on the catalyst surface, as evidenced by the magnitudes of the Na and the carbonate peaks. From the XPS data presented here, it appears that the Na_2CO_3 migrated to the surface of the catalyst during the reduction conditions of H_2 flow at 400°C. This would result in a decrease of the Ni and Mn peaks and an increase in the Na_2CO_3 peaks. The mechanism of the surface migration is yet unclear; however, it is possibly related to a change in surface energies due to different environments [26-27].

After the reaction conditions of a CO/H_2 mixture at 300°C on Na-Mn-Ni (0.05:0.5:1) and Na-Mn-Ni (0.2:0.95:1), the concentration of Na_2CO_3 on the catalyst surface decreased. The decrease of Na_2CO_3 coincided with a substantial increase in the concentration of Mn and a small increase in the concentration of Ni on the surface. The Ni and Mn both appear to be on the forms of Ni^+ and Mn^+ respectively. This result indicates that the direction of the migration on the catalyst surface results from the Ni and Mn being reduced or oxidized. Although the mechanism for migration is still unclear, it is clear that the Mn is uncovered from the Na_2CO_3 surface in a larger proportion than the Ni during CO hydrogenation conditions. It is the surface state of Ni^+, Mn^+, and Na_2CO_3 that appears to be selective for higher oxygenate synthesis on coprecipitated Na-Mn-Ni catalysts.

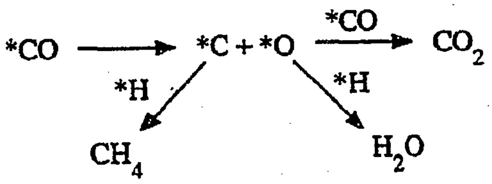
Carbon dioxide was adsorbed for the TPD and TPR experiments under the surface conditions specified above after the reduction conditions were imposed. The pulse data from CO adsorption showed a small amount of CO adsorption at room temperature for the same coprecipitated catalysts [25], while the TPD spectra (Figure 1) exhibited desorption of CO_2 for the coprecipitated Na-Mn-Ni catalysts. The formation of CO_2 is attributable to the Boudouard reaction:

$$2{*}CO \longrightarrow {*}C + CO_2^{\cdot}$$

The small amount of CO adsorption observed during the adsorption process was due to a small amount of Ni metal on the surface, as evidenced from the XPS data. It may be possible that the CO_2 from the TPD experiments is coming from the carbonate on the surface of the catalysts; however, repeated experiments with the same catalyst sample were reproducible without any indication of the CO_2 product being depleted. The high temperature of CO_2 formation on Na-Mn-Ni (0.05:0.5:1) and Na-Mn-Ni (0.2:0.95:1) and no observable CO_2 peak for Na:Mn:Ni

(0.005:0.5:1) as compared to Ni/SiO_2 indicated that, after CO dissociation, the oxygen is strongly adsorbed on the surface of the coprecipitated catalysts.

The mechanism for the TPR reactions is given by:



The pathway of the oxygen from adsorbed CO can take one of two paths. It can react with adsorbed CO to form CO_2 or with hydrogen to form H_2O. During TPR experiments with a CO adsorption temperature of 30°C, the oxygen was readily removed from the surface of Ni/SiO_2 to form CO_2. The coprecipitated catalysts, however, did not exhibit this property. The oxygen was removed from the surface of the coprecipitated catalysts by the reaction with H_2 at high temperatures to form water. This result also confirms the idea that oxygen readily associates with the surface of the coprecipitated catalysts, possibly oxidizing the Ni and/or the Mn. The surface oxidation may a driving force for the surface concentration to change during reaction conditions.

The main product from the pulse CO adsorption procedure at 400°C on all of the catalysts was CO_2, with a small amount of CO [25]. The TPR spectra when CO was adsorbed at 400°C also showed the removal of oxygen at a high temperature; however, the oxygen was removed from the surface of the catalyst by the formation of both H_2O and CO_2. These differences compared to when CO was adsorbed at 30°C is possibly due to a different surface condition caused by adsorption at 400°C or cooling the catalyst samples from 400°C to 30°C. Due to these differences, it is difficult to discern the state of the catalyst surface during TPR.

Carbon monoxide hydrogenation reaction results over the Ni/SiO_2 and coprecipitated Na-Mn-Ni catalysts at 275°C and 10 atm have been reported [16,17]. A summary of the CO hydrogenation results for the Ni/SiO_2 catalyst, the coprecipitated Na-Mn-Ni catalysts, as well as coprecipitated Na-Ni and Mn-Ni are presented in Table 2. The Ni/SiO_2 catalyst produced methane as a major product with C_{2+} hydrocarbons as minor products for the CO hydrogenation reaction. The coprecipitated catalysts exhibited a marked decrease in the methane rate and selectivity as compared to Ni/SiO_2 while high activity and selectivity for the formation of acetaldehyde and propionaldehyde was observed for the CO hydrogenation reaction.

The methane formation on the coprecipitated catalysts during the TPR experiment at an adsorption temperature of 30°C is at higher temperatures than that of Ni/SiO_2. The methanation activity for the coprecipitated catalysts is much less than that for Ni/SiO_2. The lower methane activity observed in this study resulted in an increase in the CO insertion activity observed in previous studies [16,17]. This lower methane activity could be a direct consequence of the Na-Mn-Ni catalysts having a lower CO dissociation activity as compared to Ni/SiO_2. The observation of two forms of methane on the surface of the coprecipitated catalysts is facilitated by higher adsorption temperatures on the Na-Mn-Ni (0.05:0.5:1) and the unwashed Na-Mn-Ni (0.2:0.95:1). The second carbon peak during TPR appears to be suppressed by more Na being added to the surface, as observed in the TPR spectra of Na-Mn-Ni (0.005:0.5:1) and Na-Mn-Ni (0.05:0.5:1). It was found in previous studies that Na enhances the CO insertion activity [16,17]. The CO insertion step during the synthesis of higher alcohols seems to be a product from the carbon that appears first during the TPR experiments. The second form of carbon may be one that primarily reacts to methane during CO hydrogenation.

SUMMARY

The Na-Mn-Ni catalysts are a complicated system in which the surface concentrations were observed to have changed upon a change in the reactin environment. The coprecipitated catalysts exposed to air contained Ni, Mn and Na_2CO_3 on the surface. After the catalysts were exposed to reduction conditions, Na_2CO_3 almost totally covered the surface. Upon exosing the catalysts to CO hydrogenation conditions, the concentrations of Ni and Mn on the surface increased substantially. The TPR results suggest that oxygen readily associates to the surface of the coprecipitated catalysts, possibly oxidizing the Ni and/or Mn. This association is possibly related to the surface concentration differences and to the good activity and selectivity for higher oxygenates during the CO hydrogenation reaction on the these catalysts.

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TABLE 1

Summary of XPS Results on Coprecipitated Na-Mn-Ni Catalysts

Catalyst	Band	Binding Energy (eV)		
		Exposed to air	After Reduction	After Reaction
Na-Mn-Ni[a] (0.005:0.5:1)	Ni	872.8 (Ni$^+$)	Absent	NA
		861.2 (Satellite)	Absent	NA
		855.3	Absent	NA
	Mn		Absent	NA
		653.3 (Mn$^+$)	Absent	NA
		641.8 (Mn$^+$)	Absent	NA
	Na	1071.2 (Na$^-$)	1073.2	NA
	C	NA	NA	NA
Na-Mn-Ni (0.05:0.5:1)	Ni	872.4 (Ni$^+$)	Absent	Absent
		860.7 (Satellite)	Absent	Absent
		854.6	852.5	Absent
	Mn	668.0	Absent	668.7
		653.3 (Mn$^+$)	Absent	653.8 (Mn$^+$)
		641.3	Absent	641.2
	Na	1074.4 (Na^{2+})	1071.4	1071.8
	C	289.3 (CO$_3^{2-}$)	289.6 (CO$_3^{2-}$)	289.9 (CO$_3^{2-}$)
		284.9	286.4	285.7
Na-Mn-Ni (0.2:0.95:1)	Ni	873.1 (Ni$^+$)	Absent	856.2
		861.4 (Satellite)	Absent	Absent
		855.1	Absent	Absent
	Mn	668.0	Absent	668.7
		653.5 (Mn$^+$)	Absent	654.0
		641.5	Absent	642.3
	Na	1071.9 (Na^0)	1070.9 (Na$^+$)	1070.9 (Na$^+$)
	C	290.7	292.1	291.2
		285.1	285.1	284.4

The probable chemical states are in parentheses.

a The data for Na-Mn-Ni (0.005:0.5:1) has been presented in ref. [17].

NA Data Not Available.

TABLE 2

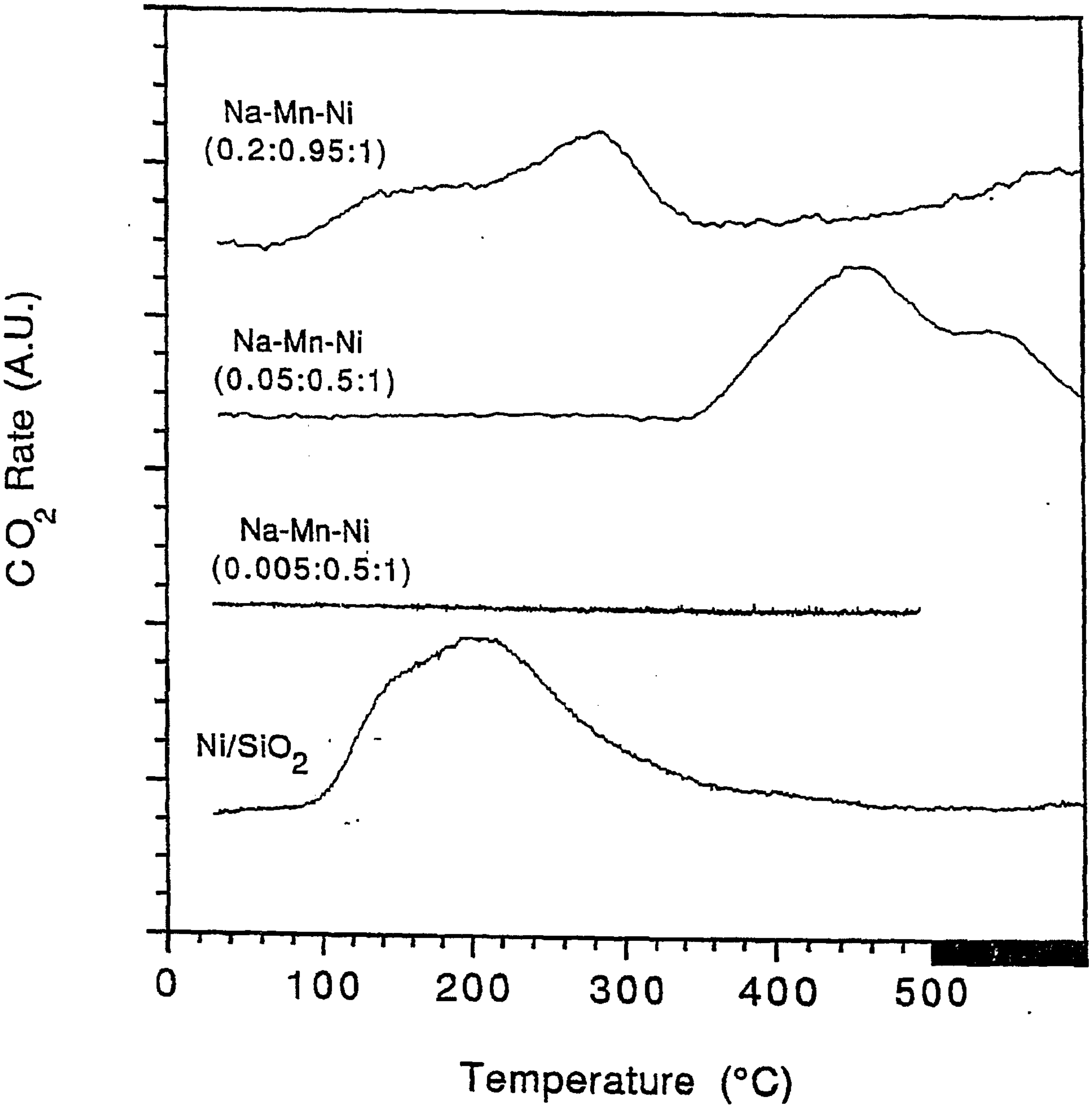
Rates of Product Formation and Selectivities from CO Hydrogenation

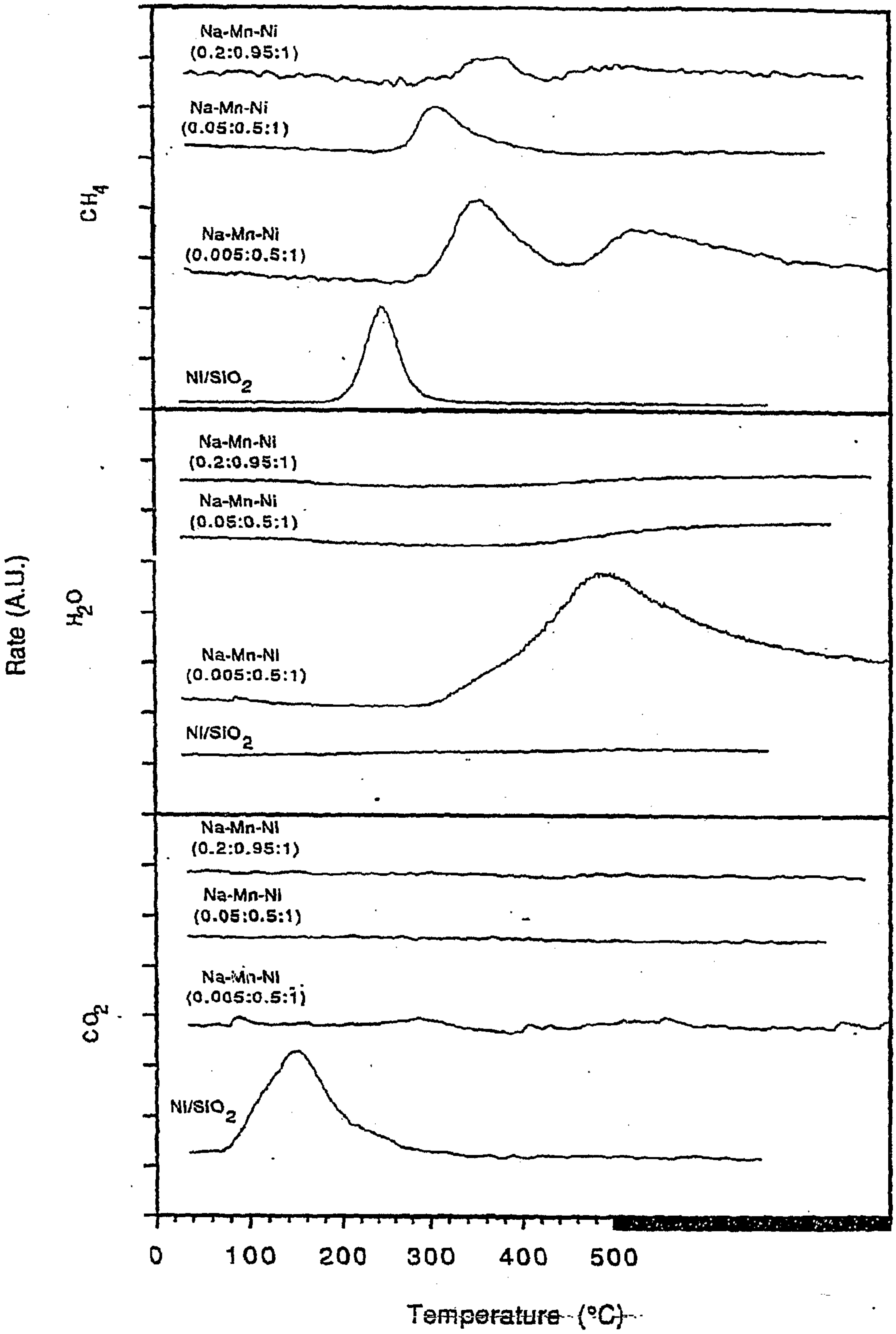
Species	Ni/SiO_2	Na-Ni	Mn-Ni	Na-Mn-Ni (0.005:0.5:1)	Na-Mn-Ni (0.05:0.5:1)	Na-Mn-Ni (0.2:0.95:1)
	Rate of Product Formation (mol/kg-hr)					
CH_4	32.50	0.31	3.75	0.39	0.15	0.29
C_2H_4	0.02	0.04	0.04	0.03	0.01	0.047
C_2H_6	1.35	0.004	0.70	0.011	0.0065	0.012
$C_{3+}HC$	0.51	0.002	0.35	0.038	0.012	0.045
CH_3CHO	0.00	0.005	0.00	0.19	0.052	0.14
C_2H_5CHO	0.00	0.00	0.00	0.031	0.021	0.068
	Selectivity					
CH_3CHO/CH_4	0.00	0.016	0.00	0.49	0.35	0.48
C_2H_5CHO/C_2H_6	0.00	0.00	0.00	2.80	3.20	0.23
$C_{2+}HC/CH_4$	0.06	0.15	0.29	0.20	0.19	0.36

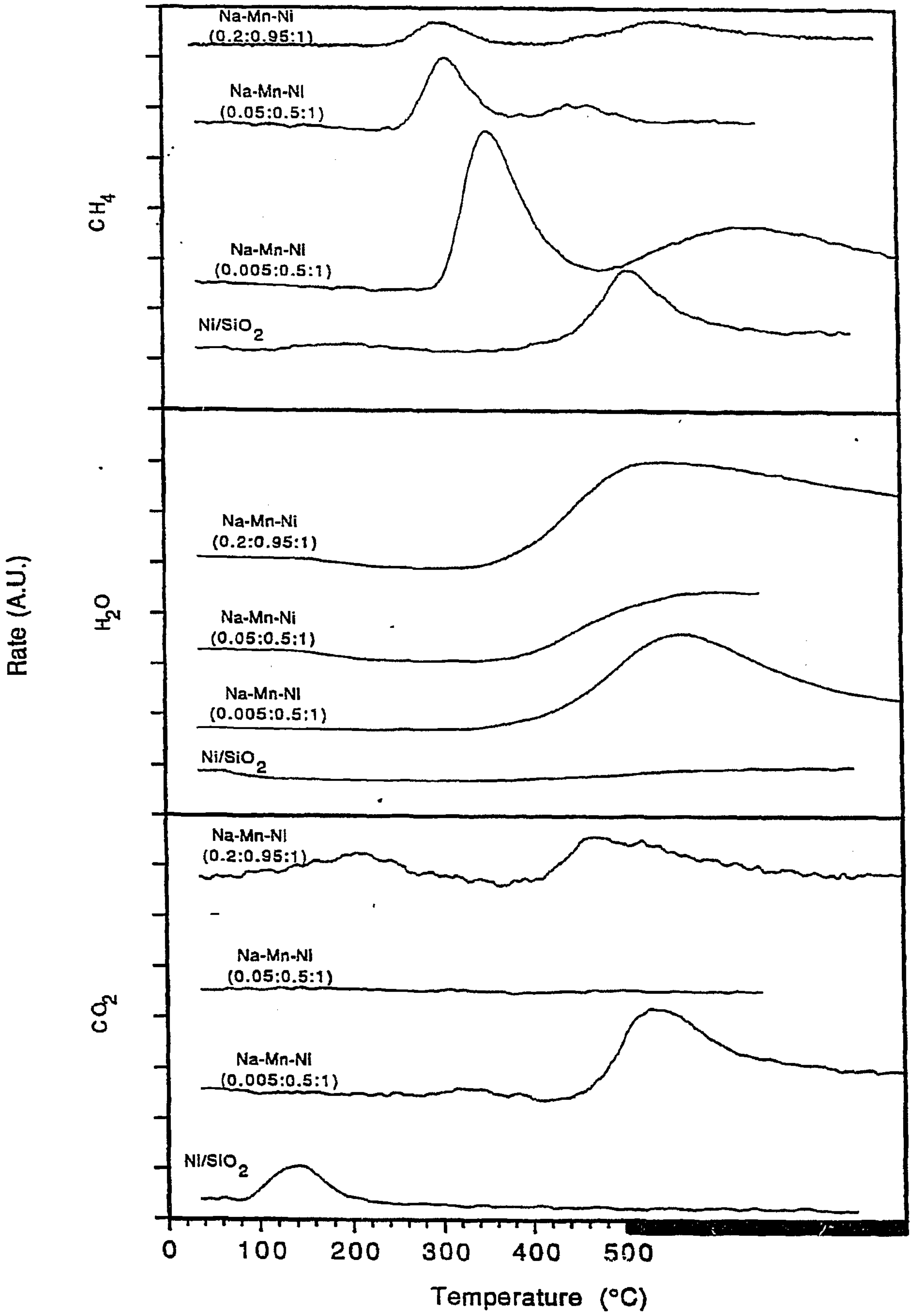
Note: $H2:CO$ - 1:1 at 275°C, 10 atm.

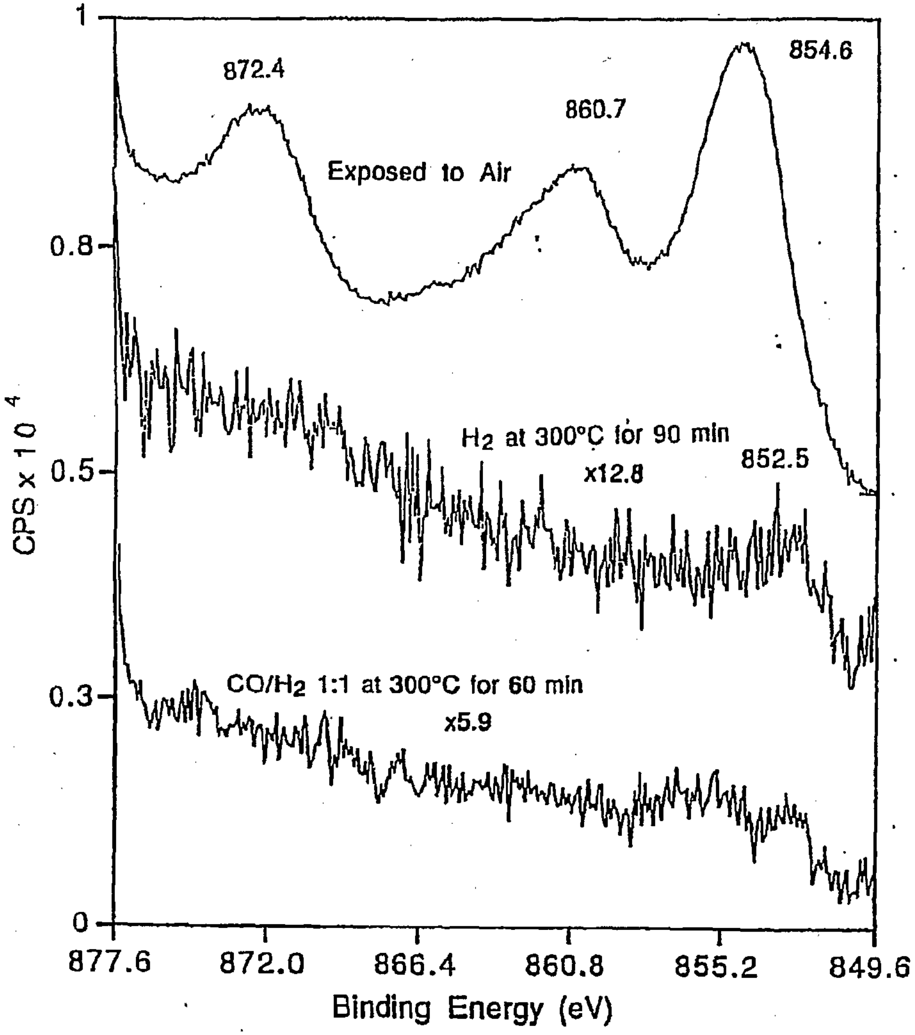
$$\text{Selectivity} = \frac{\text{Rate of formation of species i (mol/kg-hr)}}{\text{Rate of formation of species j (mol/kg-hr)}}$$

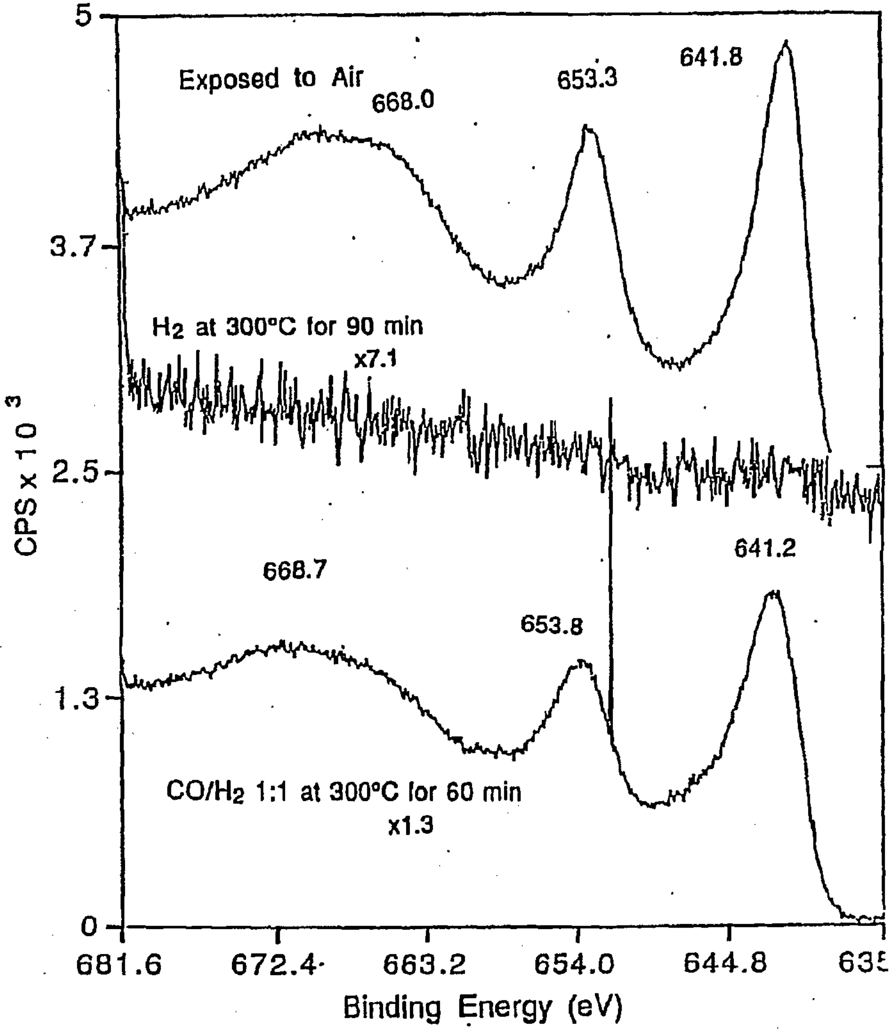
LIST OF FIGURES

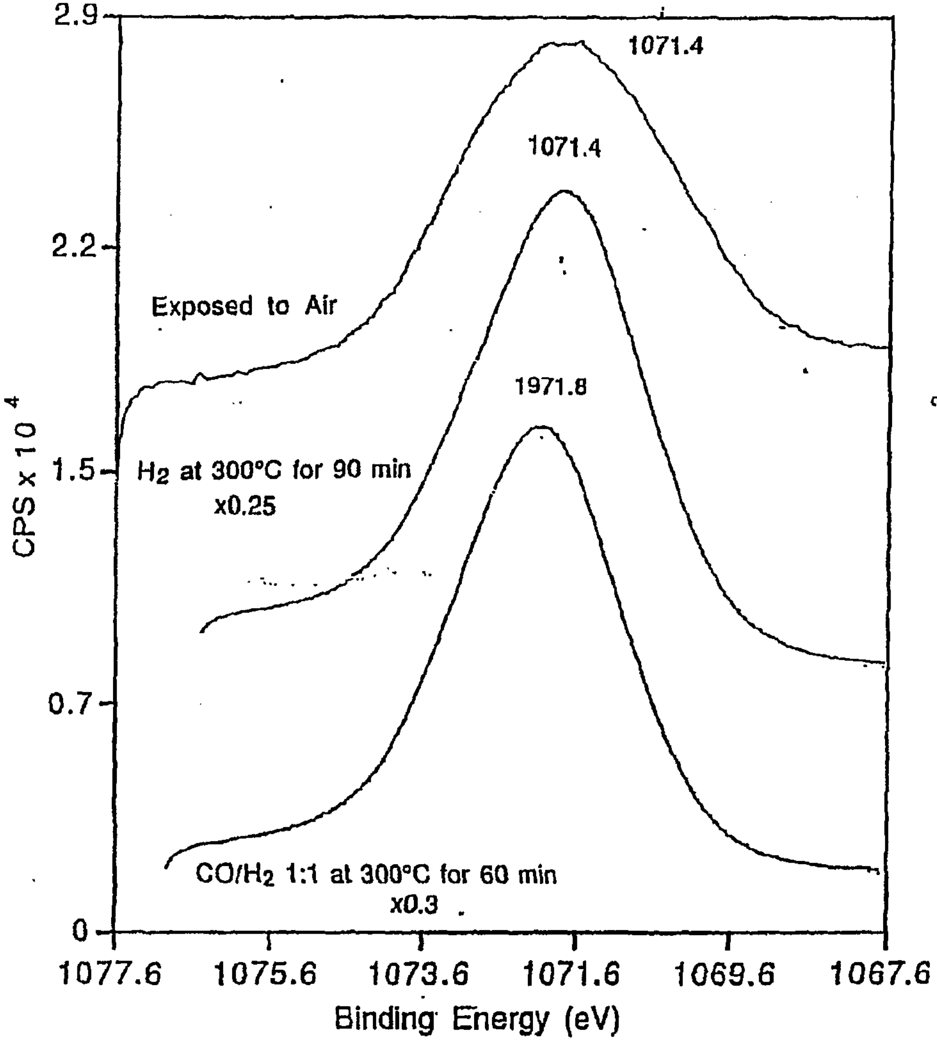

Na-Mn-Ni
(0.2:0.95:1)
Na-Mn-Ni
(0.05:0.5:1)
Na-Mn-Ni
(0.005:0.5:1)
Ni/SiO2
CO2 Rate (A.U.)
0
100
200
300
400
500
Temperature (°C)

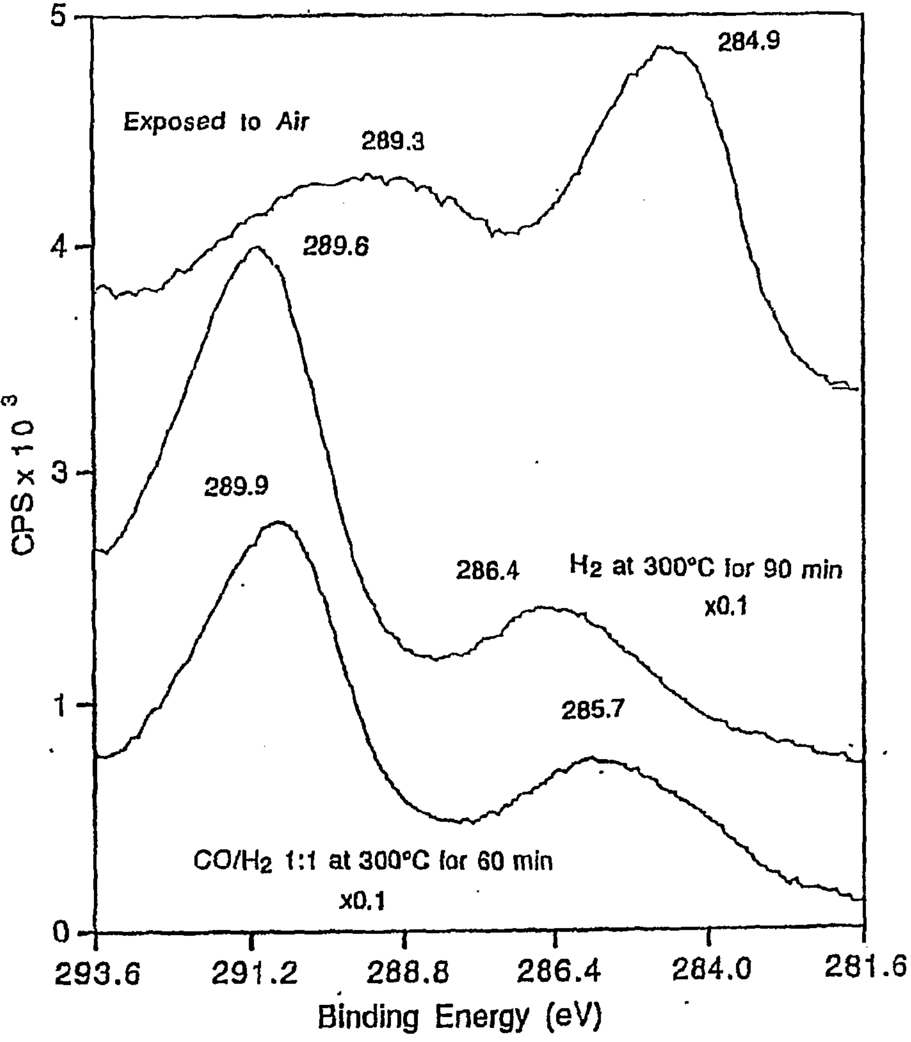

Na-Mn-Ni
(0.2:0.95:1)
Na-Mn-Ni
(0.05:0.5:1)
CH_4
Na-Mn-Ni
(0.005:0.5:1)
Ni/SiO$_2$
Na-Mn-Ni
(0.2:0.95:1)
Na-Mn-Ni
(0.05:0.5:1)
Rate (A.U.)
H_2O
Na-Mn-Ni
(0.005:0.5:1)
Ni/SiO$_2$
Na-Mn-Ni
(0.2:0.95:1)
Na-Mn-Ni
(0.05:0.5:1)
Na-Mn-Ni
(0.005:0.5:1)
CO_2
Ni/SiO$_2$
0
100
200
300
400
500
Temperature (°C)

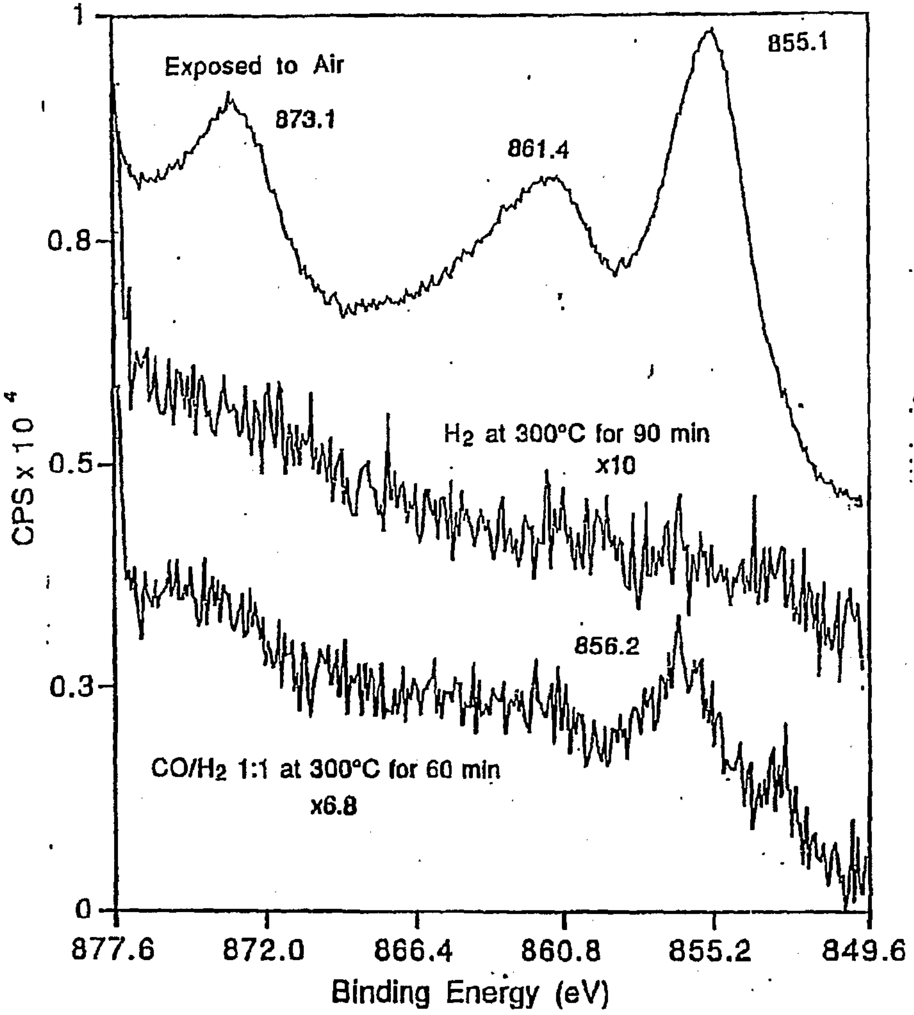

Rate (A.U.)
CH4
Na-Mn-Ni
(0.2:0.95:1)
Na-Mn-Ni
(0.05:0.5:1)
Na-Mn-Ni
(0.005:0.5:1)
Ni/SiO2
H2O
Na-Mn-Ni
(0.2:0.95:1)
Na-Mn-Ni
(0.05:0.5:1)
Na-Mn-Ni
(0.005:0.5:1)
Ni/SiO2
CO2
Na-Mn-Ni
(0.2:0.95:1)
Na-Mn-Ni
(0.05:0.5:1)
Na-Mn-Ni
(0.005:0.5:1)
Ni/SiO2
0
100
200
300
400
500
Temperature (°C)

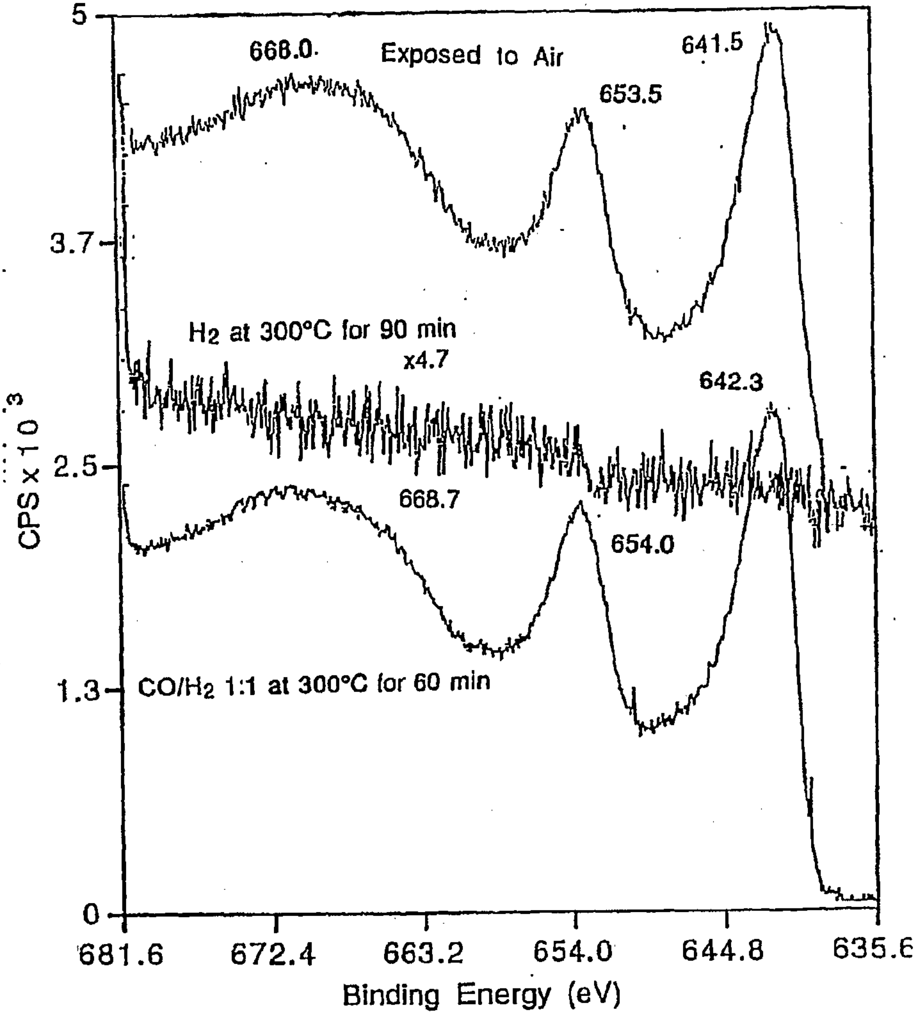

1
0.8
0.5
0.3
0
CPS x 10 4
872.4
860.7
854.6
Exposed to Air
H2 at 300°C for 90 min
x12.8
852.5
CO/H2 1:1 at 300°C for 60 min
x5.9
877.6
872.0
866.4
860.8
855.2
849.6
Binding Energy (eV)

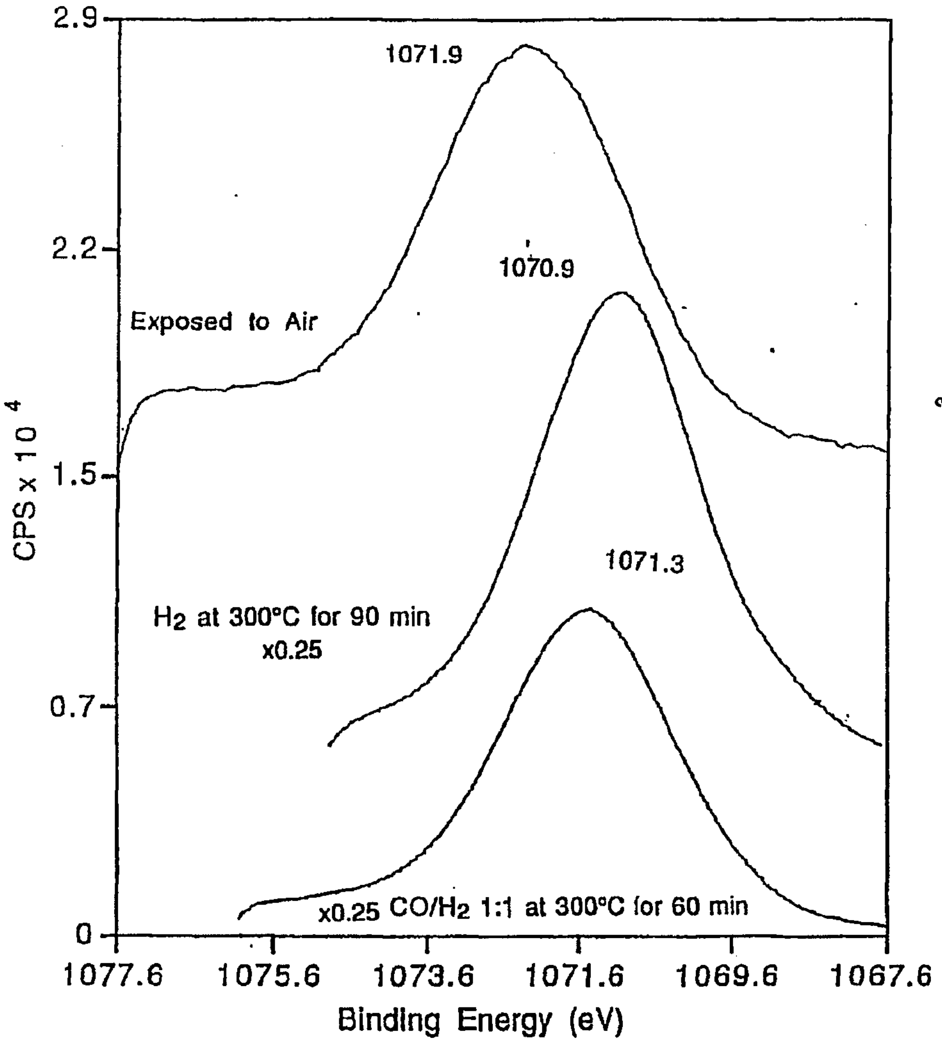

5
3.7
2.5
1.3
0
CPS x 10 3
Exposed to Air
668.0
653.3
641.8
H2 at 300°C for 90 min
x7.1
668.7
653.8
641.2
CO/H2 1:1 at 300°C for 60 min
x1.3
681.6
672.4
663.2
654.0
644.8
63
Binding Energy (eV)

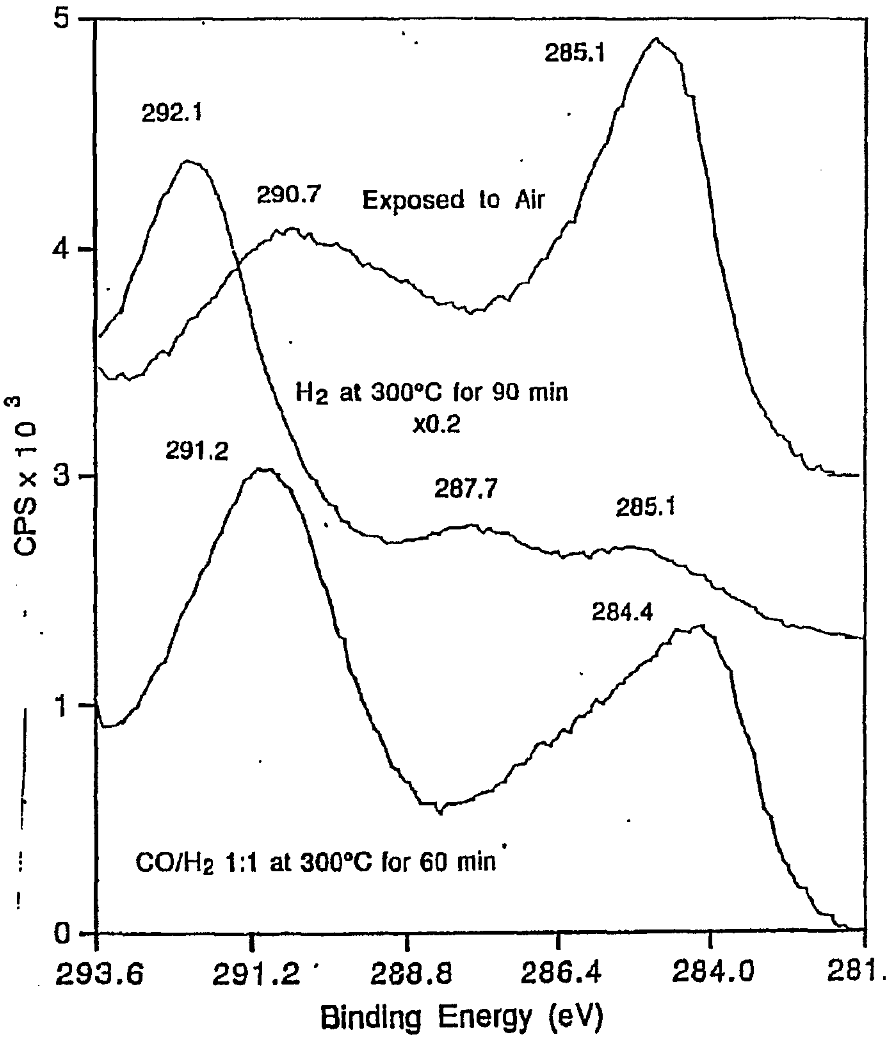

2.9
2.2
1.5
0.7
0
CPS x 10 ^{4}
1071.4
1071.4
1971.8
Exposed to Air
H_2 at 300°C for 90 min
x0.25
CO/H_2 1:1 at 300°C for 60 min
x0.3
1077.6
1075.6
1073.6
1071.6
1069.6
1067.6
Binding Energy (eV)


5
4
3
1
0
CPS x 10 ^{3}
284.9
Exposed to Air
289.3
289.6
289.9
286.4
H_2 at 300°C for 90 min
x0.1
285.7
CO/H_2 1:1 at 300°C for 60 min
x0.1
293.6
291.2
288.8
286.4
284.0
281.6
Binding Energy (eV)


Exposed to Air
873.1
861.4
855.1
H2 at 300°C for 90 min
x10
856.2
CO/H2 1:1 at 300°C for 60 min
x6.8
CPS x 10 4
1
0.8
0.5
0.3
0
877.6
872.0
866.4
860.8
855.2
849.6
Binding Energy (eV)


668.0
Exposed to Air
641.5
653.5
H2 at 300°C for 90 min
x4.7
642.3
668.7
654.0
CO/H2 1:1 at 300°C for 60 min
CPS x 10 3
5
3.7
2.5
1.3
0
681.6
672.4
663.2
654.0
644.8
635.6
Binding Energy (eV)


1071.9
1070.9
1071.3
Exposed to Air
H2 at 300°C for 90 min
x0.25
x0.25 CO/H2 1:1 at 300°C for 60 min
CPS x 10 4
2.9
2.2
1.5
0.7
0
1077.6
1075.6
1073.6
1071.6
1069.6
1067.6
Binding Energy (eV)


292.1
285.1
290.7
Exposed to Air
H2 at 300°C for 90 min
x0.2
291.2
287.7
285.1
284.4
CO/H2 1:1 at 300°C for 60 min
CPS x 10 3
5
4
3
1
0
293.6
291.2
288.8
286.4
284.0
281.
Binding Energy (eV)

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