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A Temperature-Programmed Reaction and X-ray Photoelectron Spectroscopy Study of Coprecipitated Na–Mn–Ni Catalysts

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Temperature-programmed reaction and X-ray photoelectron spectroscopy studies have been employed to investigate coprecipitated Na–Mn–Ni catalysts which are active for higher oxygenate synthesis from syngas. The results were compared to Ni/SiO_2, a good methanation catalyst. XPS results revealed that the reduction of the air-exposed coprecipitated catalysts at 673 K led to the migration of Na_2CO_3 to the catalyst surface; CO hydrogenation at 573 K induced the migration of the Ni and Mn back to the catalyst surface. The changes in surface composition with reduction and reaction condtions gives rise to uncertainty in the estimation of the turnover frequency calculated from the number of Ni surface atoms determined by H_2 chemisorption. It was observed by TPR experiments that oxygen from absorbed CO readily associates with the surface of the coprecipitated catalysts, possibly oxidizing the surface and causing the surface to restructure. Two pools of carbon are present on the surface of the catalyst during TPR experiments as evidenced by two methane peaks. The methanation peak temperatures for the coprecipitated Na–Mn–Ni catalysts were higher than that of Ni/SiO_2; the CO dissociation activity of the coprecipitated catalysts is lower than that of Ni/SiO_2. Lower CO dissociation and methanation activities results in a high selectivity for C_{2+} oxygenates.

INTRODUCTION

Synthesis gas conversion on Group VIII metal catalysts has been proven to be a promising route for the synthesis of higher aldehydes and alcohols (*1*). Previous investigations have demonstrated that coprecipitated Ni catalysts possess higher oxygenate synthesis activities from syngas (*2–5*). Uchiyama and co-workers (*2, 3*) found that coprecipitated Ni-TiO_2 exhibits a high selectivity for C_{2+} oxygenates, while coprecipitated Ni–ZnO exhibits a high selectivity for methanol. Coprecipitated Ni–Al_2O_3 has been found to be active for methanation. It is interesting to note that the effect of these oxides parallels, to some extent, that of supported Rh catalysts prepared by impregnation (*6–13*).

Recently, coprecipitated Na–Mn–Ni catalysts have been shown to possess good activity and selectivity toward C_{2+} oxygenates from syngas (*4, 5*). Although the Ni-based catalysts are not as selective as supported Rh catalysts, they are of particular interest due to their low cost and potential for further improvement in catalyst activity and selectivity. It has also been found that under specific conditions, the surface of the Na–Mn–Ni catalysts undergoes a change in composition (*5*). The change in surface composition may be of importance to the catalysis of higher oxygenate synthesis.

The purpose of this investigation is to characterize coprecipitated Na–Mn–Ni catalysts that have shown a good selectivty 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 to CO insertion. The TPR spectra are compared to that of Ni/SiO_2 catalyst, a good

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methanation catalyst, and are used to determine the differences between the supported Ni and the coprecipitated Ni catalysts. XPS is used to determine the state of the catalytic surface of the coprecipitated Na–Mn–Ni after reduction and reaction. The surface composition of the Na–Mn–Ni catalyst may be instrumental in the synthesis of higher alcohols from synthesis gas.

EXPERIMENTAL

Catalyst Preparation

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 (Johnson Matthey). The $Ni(NO_3)_2$ and $MnNO_3$ were dissolved in water with a 1:1 molar ratio of Ni to Mn. The solution was then added to an aqueous Na_2CO_3 (20% excess Na as compared to the Ni and Mn) to form a precipitate of Ni and Mn carbonate. The resulting slurry was filtered and washed with water to remove the excess Na. The catalyst was calcined in air at 523 K for 3 h and then reduced in flowing hydrogen at 623 K for 7 h. 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 to determine the effect of washing the excess Na from the catalyst. This catalyst was made by precipitation as described above; however, the resulting precipitate was filtered once and 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 their respective nitrates for the coprecipitation. The difference in the Mn/Ni ratio between the washed and unwashed catalysts is due to some of the Mn being washed away along with the Na_2CO_3. A Ni/SiO_2 catalyst of 15 wt% was prepared by impregnation of large-pore SiO_2 (Strem Chemicals) 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 (*4*, *5*).

Temperature-Programmed Reaction

Temperature-programmed reaction experiments were performed in a stainless-steel differential reactor system. Details of the reactor system are similar to that reported by Falconer and Schwarz (*14*) and are described briefly. The TPR system consists of a gas flow section, a reactor section, and a product analysis section. The gas flow section controls the flow of the gases H_2,CO, and He (all gases are Linde, ultra-high purity grade) to the reactor. The H_2 and CO are further purifed by passing over a molecular sieve and the He is passed over a molecular sieve and an oxygen trap. Gas flow to the reactor is controlled by Brooks mass flow controllers (Model 5850E). The gas flow section also consists of a pulsing valve for injecting an adsorbing gas into the He flow. The reactor section contains a stainless-steel tubular reactor (0.95 cm o.d.) with a heating tape wrap. The catalyst powder (100 mg) is supported by glass wool. A thermocouple is inserted into the reactor tube with the tip touching the catalyst bed. The temperature of the reactor is controlled in a linear fashion by Omega temperature controllers (Model 2011k). Effluent of the reactor is continuously sampled through a variable leak valve (Nupro SS-2MA) into a mass spectrometer vacuum chamber via a capillary tube (0.05 cm i.d. and 1 m in length). Both leak valve and capillary tube are maintained at 393 K to prevent condensation of product species. The mass spectrometer (MS) is a Balzers QMG 112 interfaced to a microcomputer. This MS system is capable of following up to eight predetermined *m*/*e* peak intensities versus time.

All the catalysts in this study were reduced in flowing hydrogen at 773 K before each TPR experiment was performed. Carbon monoxide was adsorbed on the catalysts by pulsing (4–10 pulses) CO into flowing He at a flow rate of 50 ml/min upstream of the reactor at 303 K until equal size eluted CO peaks were obtained. The carrier flow was switched to a 9.1% H_2 in He flow of 55 ml/min and the temperature was ramped at a rate of 15 K/min from 303 K to a final temperature of 773 K while monitoring the products on-line with the mass spectrometer. After reaching 773 K, the temperature was held at this temperature for 15 min. A second TPR experiment was performed under the same conditions; however, CO was adsorbed (4–10 pulses) at 673 K and cooled in a pure He flow to 303 K. The TPR experiment conducted when CO was adsorbed at 303 K is denoted as TPR(303 K) and the experiment conducted when CO was adsorbed at 673 K is denoted as TPR(673 K). All TPR experiments were checked for diffusional limitation by the criteria developed by Gorte (*15*). The resulting TPR spectra were normalized to units per gram of catalyst and a calibration factor.

X-Ray Photoelectron Spectroscopy

The X-ray photoelectron spectroscopy 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 of a catalyst sample exposed to air was taken. The catalyst sample was then reduced in H_2 at 673 K 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 573 K and a pressure of 0.1 MPa for 60 min.

RESULTS

Temperature-Programmed Reaction

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. Carbon monoxide was pulsed over each catalyst at 303 and 673 K. The eluted peaks from pulsing CO over the Ni-based catalyst include CO and CO_2. CO_2 is produced by the CO disproportionation reaction,

$$2CO \rightarrow CO_2 + C.$$

Formation of a CO_2 molecule would leave a carbon atom deposited on the catalyst surface (*16, 17*). Tables 1 and 2 list the amount of CO adsorbed and carbon deposited on the surface resulting from CO pulse chemisorption at 303 and 673 K, respectively. The CO disproportionation activity, which is equivalent to the CO dissociation activity (*17–19*), can be compared by the ratio of surface carbon to adsorbed CO. The Ni/SiO_2 catalyst exhibited CO disproportionation activity producing surface carbon while the coprecipitated Na–Mn–Ni showed little activity for the reaction at 303 K. At 673 K, the coprecipitated Na–Mn–Ni catalysts exhibited higher activity for the CO disproportionation than the Ni/SiO_2 catalysts. Among Na–Mn–Ni catalysts, the CO disproportionation activity decreased in the order Na–Mn–Ni (0.005 : 0.5 : 1) > Na–Mn–Ni (0.2 : 0.95 : 1) > Na–Mn–Ni (0.05 : 0.5 : 1).

The responses of CH_4, H_2O, and CO_2 during the TPR experiments when CO was adsorbed at 303 and 673 K on the Ni/SiO_2 is presented in Fig. 1. The vertical bars on the graph are the relative intensities of the MS signal normalized by the weight of catalyst in the reactor and a calibration factor for the comparison of the relative rate among different Ni catalysts. The heavy bar on the *x*-axis signifies that the temperature was held constant at the last temperature shown on the axis. A CO desorption peak was not observed. A variation of CO concentration

TABLE 1

Carbon Balances for Pulse Chemisorption at 303 K and TPR (303 K)

Catalyst	Pulse CO chemisorption (μmol/g-catalyst)			TPR (μmol/g-catalyst)		
	CO	C[a]	Total carbon[c]	CH_4	CO_2	Total carbon[c]
Ni/SiO_2	28.4	4.6	33.0 (0.46)	28.9	0.6	29.5 (0.41)
Na–Mn–Ni (0.005 : 0.5 : 1)	4.4	0.0	4.4 (0.12)	3.4	0.8	4.2 (0.12)
Na–Mn–Ni (0.05 : 0.5 : 1)	<0.3[b]	0.0	<0.3[b] (<0.08)	0.5	0.0	0.5 (0.03)
Na–Mn–Ni (0.2 : 0.95 : 1)	<0.3[b]	0.0	<0.3[b] (—)	<0.3[b]	0.0	<0.3[a] (—)

[a] Carbon deposits on the catalyst surface.
[b] Amount of chemisorbed CO was below measurement error of ±0.3 μmol/g-catalyst.
[c] The number in parentheses is the μmol of total carbon/μmol of surface Ni based on H_2 chemisorption.

corresponding to ±0.3 μmol/g-catalyst cannot be discerned from the MS response. The methane response to TPR(303 K) produced a sharp peak at 523 K while the CO_2 response produced a peak at 413 K. The CO_2 response peak to the TPR(673 K) remained at 413 K while the methane peak was shifted to a temperature above 773 K. It has been suggested that the high-temperature methane peak may be due to a less reactive graphitic carbon which can be slowly converted from the active surface carbon at temperatures above 600 K (*16*). The amount of CH_4 and CO_2 produced during TPR, which can be estimated from the area under methane and CO_2 profiles, is also listed in Tables 1 and 2. The amount of CH_4 and CO_2 on the Ni/SiO_2 catalyst was much greater during TPR(303 K) than TPR(673 K).

The coprecipitated Na–Mn–Ni catalysts (good higher oxygenate catalysts) exhibited drastic differences from the Ni/SiO_2 catalyst

TABLE 2

Carbon Balances for Pulse Chemisorption at 673 K and TPR (673 K)

Catalyst	Pulse CO chemisorption (μmol/g-catalyst)			TPR (μmol/g-catalyst)		
	CO	C[a]	Total carbon[b]	CH_4	CO_2	Total carbon[b]
Ni/SiO_2	2.3	1.0	3.3 (0.05)	1.5	0.7	2.2 (0.03)
Na–Mn–Ni (0.005 : 0.5 : 1)	0.8	6.0	6.8 (0.19)	5.6	0.8	6.4 (0.18)
Na–Mn–Ni (0.05 : 0.5 : 1)	<0.3[c]	0.4[d]	0.4[d]	0.8	0.0	0.8 (0.05)
Na–Mn–Ni (0.2 : 0.95 : 1)	0.4	1.2	1.6 (—)	1.9	0.3	2.2 (—)

[a] Carbon deposited on the catalyst surface.
[b] The number in parentheses is the μmol of total carbon/μmol of surface Ni based on H_2 chemisorption.
[c] Amount of chemisorbed CO was below measurement error of ±0.3 μmol/g-catalyst.
[d] The error on the amount of total carbon is rather high.

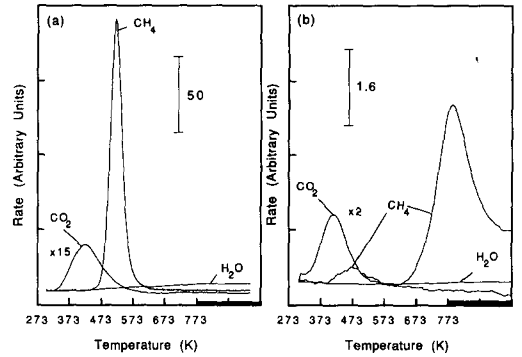


FIG. 1. (a) TPR(303 K) and (b) TPR(673 K) spectra of 15 wt% Ni/SiO_2.

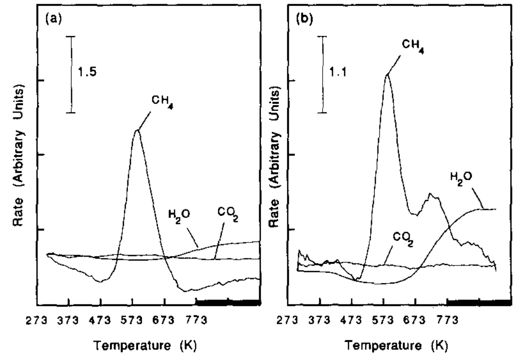


FIG. 3. (a) TPR(303 K) and (b) TPR(673 K) spectra of coprecipitated Na–Mn–Ni (0.05 : 0.5 : 1).

(a good methanation catalyst) in the TPR spectra. The Ni/SiO_2 produced CH_4 and CO_2 during TPR while the coprecipitated catalysts produced CH_4, H_2O, and only a small amount of CO_2 during TPR. Figure 2 is the results from the TPR experiments on the coprecipitated Na–Mn–Ni (0.005 : 0.5 : 1) catalyst. The TPR(673 K) experiment produced a substantially larger amount of CH_4, H_2O, and CO_2 than the TPR(303 K) experiment. The same trend was also observed for the other two coprecipitated Na–Mn–Ni catalysts. The response of CH_4 for both TPR experiments on Na–Mn–Ni (0.005 : 0.5 : 1) produced two peaks, indicating two different pools of carbon on the surface. The phenomenon of two distinct pools of carbon has been observed on other Ni-based catalysts in the literature (*14, 16, 20—25*). The first methane peak for both TPR experiments was at 633 K and the second was above 773 K. The peak temperature for H_2O was above 700 K for both TPR spectra. Only the TPR(673 K) produced a small amount of CO_2 at 500°C.

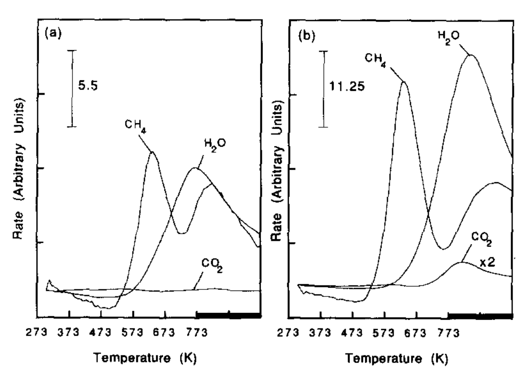


FIG. 2. (a) TPR(303 K) and (b) TPR(673 K) spectra of coprecipitated Na–Mn–Ni (0.005 : 0.5 : 1).

The product profile of the TPR experiments on the coprecipitated Na–Mn–Ni (0.05 : 0.5 : 1) catalyst is presented in Fig. 3. The methane response produced one peak at 583 K on the TPR(303 K) and TPR(673 K) spectra, while the TPR(673 K) experiments produced a second methane peak at 713 K. Water was formed during TPR in both cases at temperatures above 773 K. Carbon dioxide was not produced during TPR.

Figure 4 shows the TPR profile of the unwashed Na–Mn–Ni (0.2 : 0.95 : 1) catalyst. During the TPR(303 K) experiment, very little product was observed. Methane produced two peaks, the first at 673 K and the second at temperatures above 773 K. A larger amount of methane was produced during TPR(673 K). Water was observed at temperatures above 773 K for both TPR experiments. Carbon dioxide was not observed during TPR(303 K); however, CO_2 peaks was observed during TPR(673 K). The first CO_2 peak was at 483 K and the second at 753 K.

The three coprecipitated catalysts all had

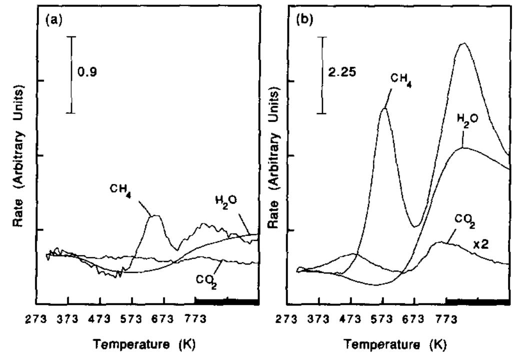


FIG. 4. (a) TPR(303 K) and (b) TPR(673 K) spectra of coprecipitated Na–Mn–Ni (0.2 : 0.95 : 1).

similar product characteristics during the TPR experiments. The coprecipitated catalysts exhibited two pools of carbon. Water was formed at temperatures above 700 K on the coprecipitated catalysts. A low activity for the CO disproportionation reaction was observed during TPR of the coprecipitated catalysts. The addition of Na to the Na–Mn–Ni (0.005 : 0.5 : 1) catalyst resulted in lowering of the methane peak temperature and lowering of the amount of CH_4, H_2O, and possibly graphitic carbon. The unwashed catalyst further lowered the amount of product formation in TPR(303 K).

It should be noted that the amount of H_2O produced over the coprecipitated Na–Mn–Ni catalysts was not quantified due to the difficulty in calibration of H_2O response in the mass spectrum. Pulse injection of H_2O for calibration often leads to plugging of the capillary tubing in the sampling system. Further improvement in sampling is required for the quantification of the H_2O peak. However, the relative amount of H_2O produced from TPR on each catalyst can be compared by the area under the H_2O spectrum.

X-Ray Photoelectron Spectroscopy

Figures 5 and 6 are the results of the X-ray photoelectron spectroscopy study of the Na-impregnated 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 before and after H_2 reduction are similar to Fig. 5 in this study and have been presented elsewhere (*5*). The XPS spectra of Ni/SiO_2 and impregnated Na–Mn–Ni/SiO_2 catalysts were recorded to compare with the coprecipitated catalyst. The spectra recorded for the impregnated catalysts exhibited no observable surface concentration change under CO hydrogenation conditions at 573 K.

Shown in Figs. 5a and 5b are 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 following H_2 reduction and exposed to air exhibited Ni peaks at 854.6 and 872.4 eV, Mn peaks at 641.8 and 653.3 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 conditions at 673 K, the Ni and the Mn peaks almost completely disappeared, while the Na peak at 1071.4 eV was greatly enhanced. The C_{1s} peak at this position is from a carbonate species. Following CO hydrogenation at 573 K 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 1071.8 eV decreased under the CO hydrogenation conditions, as did the C peak resulting from carbonates at 289.9 eV.

The XPS spectra of the unwashed Na–Mn–Ni (0.2 : 0.95 : 1) is presented in Fig. 6. The behavior of the catalyst surface is similar to that of Na–Mn–Ni (0.05 : 0.5 : 1). The Ni peaks for the air-exposed catalyst were found at 855.1 and 873.1 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 was sifted to 1070.9 eV and the intensity was increased. Likewise, reduction caused the carbonate peak at 292.1 eV to increase greatly in intensity. After exposure to the CO hydrogenation atmosphere, the Ni and Mn peaks reap-

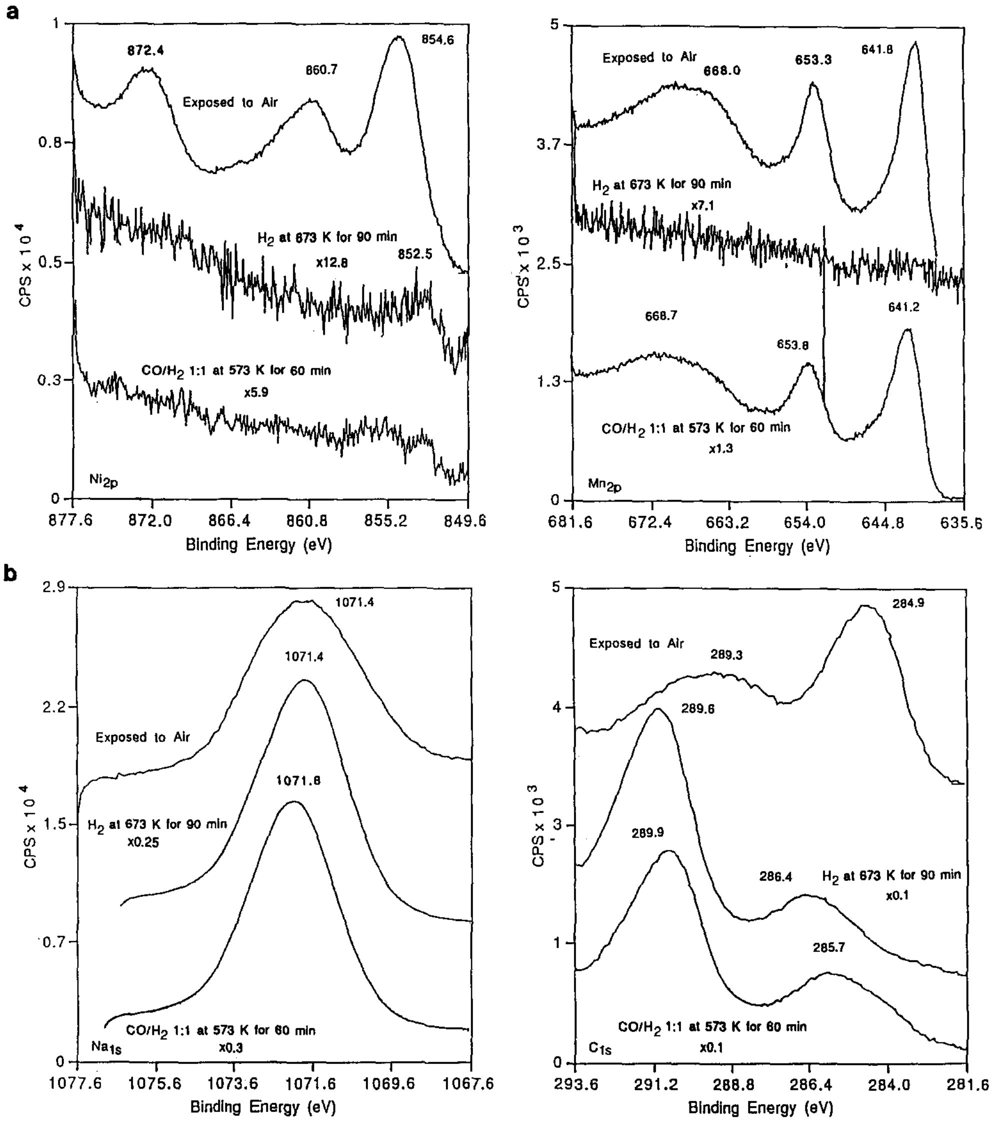


FIG. 5. X-ray photoelectron spectra of (a) the Ni_{2p} and the Mn_{2p} bands of Na–Mn–Ni (0.05 : 0.5 : 1) and (b) the Na_{1s} and the C_{1s} bands of Na–Mn–Ni (0.05 : 0.5 : 1).

peared, 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 1071.3 eV, as well as the C peaks at 291.2 and 284.4 eV.

DISCUSSION

Our previous studies have shown that coprecipitated Na–Mn–Ni catalysts exhibited good selectivity toward higher oxygenated products from syngas (*4*, *5*). Table 3 summarizes foregoing results of these catalysts at 573 K and 1.0 MPa (*4*). Included in this table are the results from an impregnated Na–Mn–Ni/SiO_2 that displayed very little C_{2+} oxygenate activity. The selectivities for the higher oxygenates over the coprecipitated catalysts are significantly higher than those of the supported catalysts. The number of Ni surface atoms for the calculation of the turnover frequency (TOF) was deter-

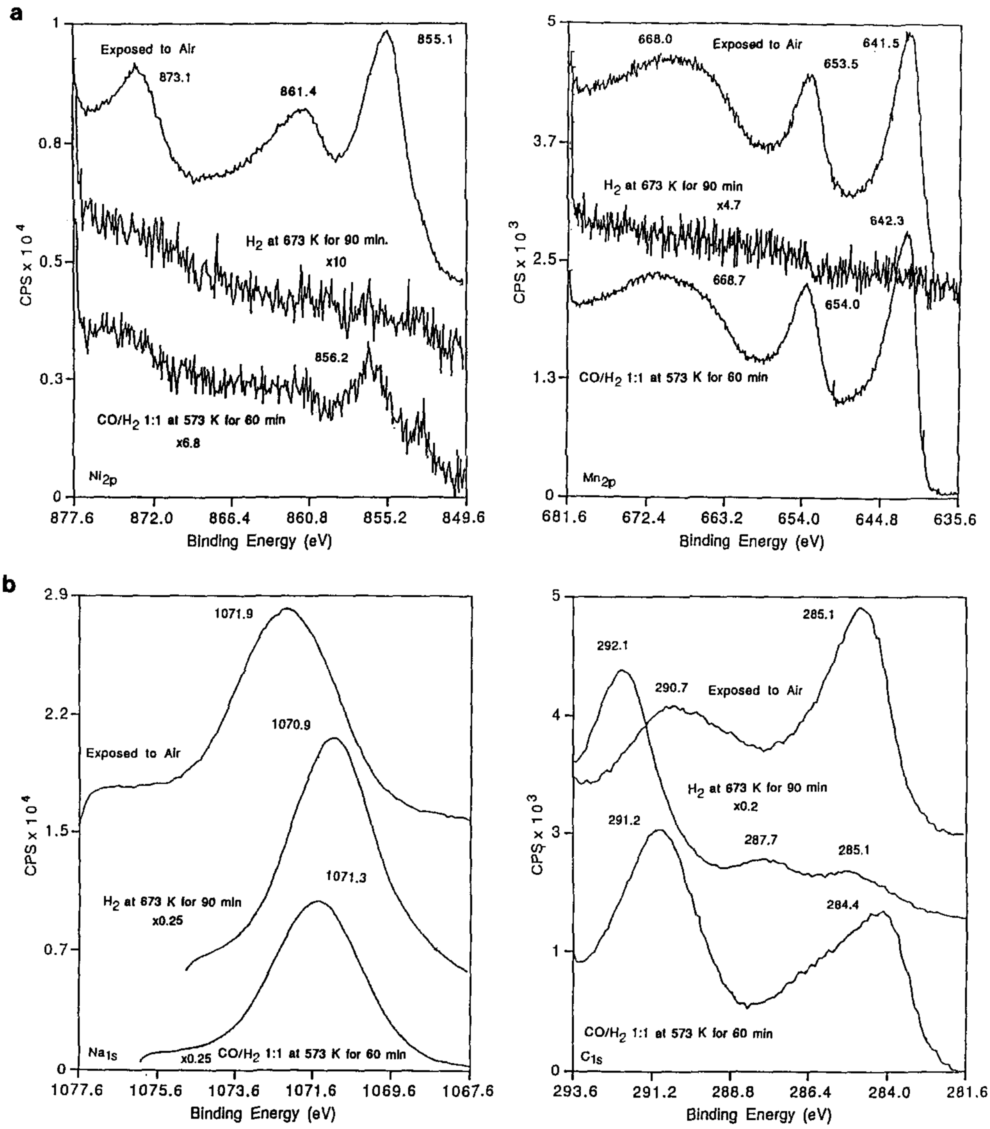


FIG. 6. X-ray photoelectron spectra of (a) the Ni_{2p} and the Mn_{2p} bands of Na-Mn-Ni (0.2 : 0.95 : 1) and (b) the Na_{1s} and the C_{1s} bands of Na-Mn-Ni (0.2 : 0.95 : 1).

mined from H_2 TPD results (*4*). The TOF for CO conversion on the Ni/SiO_2 catalyst is much higher than those of the coimpregnated catalysts. It should be noted that the number of Ni surface atoms determined by H_2 chemisorption may not correspond to those under reaction conditions because of a change in the surface composition during CO hydrogenation.

The XPS spectra revealed interesting changes in the state of the surface of the catalysts during reduction and reaction conditions. The XPS results are summarized in Table 4. The surface of the coprecipitated catalysts exposed to air contained Ni, Mn, Na, O, and C elements. The chemical state of both surface Ni and Mn is assigned to be in the +1 state. From previous results of

TABLE 3

Rates of Product Formation, TOF, and Selectivities from CO Hydrogenation

Species	Ni/SiO_2	Na-Mn-Ni/SiO_2	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 CO conversion (mol/kg-h)	33.0	3.0	5.5	3.2	5.6
TOF (s^{-1})	0.065	0.020	0.021	0.026	—
			Selectivity		
CH_3CHO/CH_4	0.00	0.033	0.42	0.65	0.30
C_2H_5CHO/C_2H_6	0.00	0.01	5.02	8.14	3.61
$C_{2+}HC/CH_4$	0.045	0.37	0.27	0.35	0.38

Note. From Refs. (*4, 35*). $H_2:CO = 1:1$ at 573 K, 1.0 MPa.

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

X-ray diffraction studies, the Mn was found to be in the form of MnO in the bulk of the catalyst after exposure to air; the Na of both catalysts was in the form of Na_2CO_3 (*4*).

As evidenced from the XPS spectra, reduction of the coprecipitated catalysts under a hydrogen flow at 673 K for 90 min caused a drastic change on the catalyst surface. 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 significant increase in the concentration of Na_2CO_3 on the catalyst surface, as evidenced by the magnitudes of the Na and the carbonate peaks (C^{4+} peak at 289.6 eV). From the XPS data presented here, it appears that the Na_2CO_3 migrated to the surface of the catalyst under the reduction conditions of H_2 flow at 673 K, resulting in a decrease of the Ni and Mn peaks and an increase in the peaks due to Na_2CO_3. It has been shown that this type of migration also occurs on the Na-Mn-Ni (0.005 : 0.5 : 1) catalysts at 623 K under hydrogen flow (*5*).

Although the Na content in the Na-Mn-Ni (0.05 : 0.5 : 1) catalyst is only 3.2 at.% with respect to Mn and Ni, an estimation of Na coverage on the catalyst surface shows that the amount of Na_2CO_3 in the catalyst is sufficient enough to form 10 monolayers on the catalyst surface. This estimation is based on the density of Na_2CO_3 of 2.53 g/cm^3 and a catalyst BET surface area of 2.7 m^2/g (*4*). It should be noted that the surface restructuring would ultimately change the BET surface area of the catalyst.

After CO hydrogenation at 573 K 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 of both catalysts. The Mn is uncovered from the Na_2CO_3 surface in a larger proportion than the Ni under CO hydrogenation conditions.

The XPS results have shown that under reaction conditions, a surface composition change takes place. The mechanism for surface migration is still unclear, yet it may relate to a change in surface energies due to different environments (*26, 27*). The restructuring of catalyst surfaces in response to a change of its chemical environment has been summarized in the literature (*28*). This surface restructuring makes it difficult to estimate the number of Ni surface atoms by

TABLE 4

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$^+$)[b]	Absent	NA[c]
		861.2 (Satellite)	Absent	NA
		855.3	Absent	NA
	Mn	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$^+$, Ni^0)	Absent	Absent
		860.7 (Satellite)	Absent	Absent
		854.6	852.5	855.2
	Mn	653.3 (Mn$^+$)	Absent	653.8 (Mn$^+$)
		641.2	Absent	641.2
	Na	1071.4 (Na^{2+})	1071.4	1071.8
	C	289.3 (C^{4+})	289.6 (C^{4+})	289.9 (C^{4+})
		284.9	286.4	285.7
Na–Mn–Ni (0.2 : 0.95 : 1)	Ni	873.1 (Ni$^+$)	Absent	Absent
		861.4 (Satellite)	Absent	Absent
		855.1	Absent	856.2 (Ni$^+$)
	Mn	653.5 (Mn$^+$)	Absent	654.0
		641.5	Absent	642.3
	Na	1071.9 (unknown)	1070.9 (Na$^+$)	1070.9 (Na$^+$)
	C	290.7	292.1	291.2
		285.1	285.1	284.4

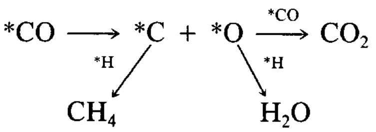
[a] The data for Na–Mn–Ni (0.005 : 0.5 : 1) has been presented in Ref. (*5*).

[b] The probable chemical states are in parentheses.

[c] NA, data not available.

H_2 chemisorption. It should be noted here that a potential error in the H_2 chemisorption measurements can be caused by the presence of Na on the surface because of suppression of and/or slow uptake of H_2 on alkali-promoted metal surface (*29–31*). Due to the uncertainties involved in the estimation of the number of Ni surface atoms on the coprecipitated catalyst surface, caution should be taken in comparing the activity of these catalysts by the TOF reported in Table 3. The true number of Ni surface atoms and active sites for the coprecipitated Na–Mn–Ni catalysts must be determined during reaction conditions. This can be achieved by using the steady-state isotopic transient analysis method (*32*).

Temperature-programmed reaction of CO on Ni-based catalysts produced CH_4, H_2O, and CO_2. The pathway leading to these products from the TPR reactions is as follows:



The oxygen dissociated 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 the TPR(303 K) experiments, the oxygen was readily removed from the surface of Ni/SiO_2 to form CO_2 at a peak temperature of 413 K. The peak for the CH_4 formation is at 523 K, which is significantly higher than that for CO_2 formation, indicating that oxygen from the dissociation of CO was removed by reaction with CO before carbon was hydrogenated to CH_4. The coprecipitated catalysts, however, did not exhibit this property. Carbon from the dissociation of CO was removed by hydrogenation to CH_4 before oxygen was hydrogenated to H_2O on coprecipitated Na–Mn–Ni catalysts as shown by both TPR(303) and TPR(673). The peaks for H_2O are above 700 K, which are higher than those for CH_4 on coprecipitated catalysts and for CH_4 and CO_2 on Ni/SiO_2. This results suggests that oxygen from CO readily associates with the surface of the coprecipitated catalysts, possibly oxidizing the Ni. The surface oxidation may be a driving force for the changes in surface concentration under reaction conditions.

The observation of two methane peaks in most of the Na–Mn–Ni TPR(303) and TPR(673) profiles suggest that two forms of carbon are produced from CO pulse chemisorption. Those peaks below 673 K in the TPR profile result from the active form of carbon; CH_4 peaks above 673 K are produced from the less active form of carbon which is probably inactive under CO hydrogenation conditions at 573 K. Comparison of TPR(303) and TPR(673) shows that pulse CO adsorption at 673 K produced a significantly greater amount of the less active form of carbon than adsorption at 303 K as evidenced by the intensity of the high-temperature CH_4 peaks in TPR(673).

Comparison of total carbon for the Ni/SiO_2 catalyst in Tables 1 and 2 shows that more than 89% of the carbon (including adsorbed CO and surface carbon) produced from pulsing CO at 303 K was converted to CH_4 and CO_2 during TPR(303 K). In contrast, less than 66% carbon was converted to CH_4 and CO_2 during TPR(673 K). Pulsing CO over the Ni/SiO_2 catalyst at 673 K may lead to the formation of graphitic carbon causing catalyst deactivation which results in the following: (i) a less active catalyst for the formation of CO_2 and CH_4, (ii) a high methane peak temperature in the TPR spectrum, (iii) less C and CO on the surface, and (iv) a low CO dissociation activity compared to the coprecipitated Na–Mn–Ni at 673 K.

The methane peaks produced from the active form of carbon in the TPR(303 K) profiles should be closely related to the rate of formation and selectivity for CH_4 during steady-state CO hydrogenation. TPR(303 K) is used as a basis for comparison of catalyst activity since pulsing CO over the Ni/SiO_2 catalyst at 673 K resulted in catalyst deactivation. The CH_4 peak temperature for the coprecipitated catalysts was higher than that of Ni/SiO_2; the amount of CH_4 produced from TPR(303 K) on the coprecipitated catalysts is significantly less than that of Ni/SiO_2, as shown in Table 1. The results clearly show that Ni/SiO_2 is much more active for methanation than the coprecipitated catalysts. The first CH_4 peak temperature for the three coprecipitated catalysts are in the range of 583–643 K. The amount of CH_4 produced per gram of catalyst from TPR(303) decreased with the addition of Na on the washed Na–Mn–Ni (0.005 : 0.5 : 1) catalyst. The decreasing order parallels the decreasing methanation activity of the Na–Mn–Ni (0.005 : 0.5 : 1) and the Na–Mn–Ni (0.05 : 0.5 : 1) catalysts during CO hydrogenation.

The activity and selectivity of the Ni-based catalysts, shown in Table 3, strongly depend on the catalyst compositions. High C_2 oxygenate selectivity of the coprecipitated Na–Mn–Ni catalysts can be attributed to a high concentration of Na and Mn species on the catalyst surface. Sodium is known to be effective in suppressing hydrogen chemisorption and hydrogenation. The presence of Na on the catalyst surface could reduce methanation activity during CO hydrogenation. The methane peak temperatures in the TPR spectra, however, decreased with an increase of Na on the Na–Mn–Ni (0.005 : 0.5 : 1) catalyst. In contrast, the addition of an alkali to Ni/Al_2O_3 and Ni/SiO_2 increased the methanation peak temperature in the TPR spectra (*33, 34*). Due to the presence of Mn and the close interaction among Na–Mn–Ni, the effect of Na on the product selectivity is more complicated than those of Na on a single metal system. Ethylene addition studies have shown that the activity of the coprecipitated Na–Mn–Ni catalysts for ethylene hydrogenation was lower than that of Ni/SiO_2 and Na–Mn–Ni/SiO_2 (*35*). Low methanation and hydrogenation activities could provide the intermediate CH_x species a high probability for carbon monoxide insertion for the formation of C_{2+} oxygenates.

The low methanation activity of the coprecipitated Na–Mn–Ni catalysts is due not only to their poor hydrogenation activity but also to their low CO dissociation activity. The Na–Mn–Ni catalysts have a lower CO dissociation activity as compared to Ni/SiO_2 at 303 K. A lower CO dissociation activity results in a high concentration of undissociated CO on the surface, therefore increasing the CO insertion observed in previous studies (*4, 5*).

Although the suppression of methanation can effectively enhance C_2 oxygenate selectivity, the formation of C_2 oxygenates ultimately depends on the activity of the catalyst for CO insertion. The presence of a high concentration of Mn on the surface of the coprecipitated catalysts may play an important role in promoting CO insertion. MnO is considered to be an oxophilic promoter, which enhances CO dissociation and CO insertion on Rh/SiO_2 catalysts (*36*). The promotion effect of Mn is not observed on Na–Mn–Ni/SiO_2, but is observed on the coprecipitated Na–Mn–Ni catalysts. It has been suggested that the interface of MnO–Ni resembles that of MnO–Rh (*37*), which promotes CO insertion. Such an interaction may play an important role in C_2 oxygenate synthesis on the coprecipitated Na–Mn–Ni catalysts. Further study is required to elucidate the origin of CO insertion activity and the nature of the active site for CO insertion on the coprecipitated Na–Mn–Ni catalysts.

CONCLUSIONS

The surface concentration changes with the reduction and reaction environment. The coprecipitated catalysts exposed to air contained Ni, Mn, and Na_2CO_3 on the surface. The XPS study suggests that exposing the coprecipitated catalysts to reduction conditions causes the migration of Na_2CO_3 to the surface. CO hydrogenation conditions cause the concentration of Mn on the surface to increase substantially while that of Ni to increase a small extent. The change in surface concentrations makes it difficult to estimate the turnover frequency using the number of active sites determined by H_2 chemisorption technique before reaction. The TPR results show that oxygen from CO strongly associates to the surface of the coprecipitated catalysts, possibly oxidizing the surface Ni. The strong association of oxygen to the surface of the coprecipitated catalysts may play a role in the surface restructuring. In contrast, the oxygen from CO on the Ni/SiO_2 surface reacts with CO to form CO_2 at lower temperatures than the methanation reaction. The coprecipitated catalysts have two pools of carbon, exhibiting higher peak temperatures than that of the Ni/SiO_2. High methane peak temperatures in TPR spectra reflect a low methanation activity. Low methanation activity is one of the factors that enhance C_2 oxygenate selectivity.

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