Synthesis of Aldehydes from Synthesis Gas over Na-Promoted Mn–Ni Catalysts

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The synthesis of acetaldehyde and propionaldehyde from CO hydrogenation over Na–Mn–Ni catalysts has been studied. Coprecipitated Na–Mn–Ni catalysts exhibited high activities for the synthesis of acetaldehyde from CO hydrogenation and the synthesis of propionaldehyde from addition of ethylene to CO hydrogenation. In contrast, Na–Mn–Ni/SiO_2 catalysts prepared from coimpregnation showed mainly methanation and ethylene hydrogenation activities. The selectivities to acetaldehyde in CO hydrogenation were found to parallel the selectivities to propionaldehyde in ethylene addition. X-ray photoelectron spectroscopic studies revealed that reduction of the coprecipitated Na–Mn–Ni catalyst at 350°C led to the migration of Na ions onto the surface of the catalyst resulting in the suppression of hydrogen chemisorption on the catalyst. © 1991 Academic Press, Inc.

INTRODUCTION

The activity of Group VIII metal catalysts for higher aldehyde and alcohol (oxygenate) synthesis has been shown to depend on their moderate CO dissociation and strong CO insertion activities (*1–4*). Various additives have been employed as promoters to increase the selectivity toward higher oxygenates on Group VIII metals. Addition of promoters such as Mn, Ti, Zn, La, Ag, V, and Mo to Rh/SiO_2 catalysts promoted CO insertion activities resulting in increases in the rate of formation of higher oxygenates (*2, 5–10*). By contrast, additives such as alkali species suppressed hydrogenation activity of Rh, while they had little effect on the CO insertion activity (*11*). Such an effect led to the enhancement of C_{2+} oxygenate selectivity.

In a recent investigation, the Ni/SiO_2 catalyst, a methanation catalyst, was demonstrated to possess the CO insertion activity (*12*). The catalyst is capable of catalyzing the formation of propionaldehyde from reaction of ethylene with syngas. Extensive

studies of CO hydrogenation on the Ni-based catalysts have revealed that the coprecipitated Na–Ni–TiO_2 and alkali Ni–Cu–Zn catalysts are active for higher alcohol synthesis (*13–15*). In the present work, we report the results of a study on the activity and selectivity of Na–Mn–Ni catalysts for higher aldehyde synthesis.

EXPERIMENTAL

Ni/SiO_2, 15 wt%, was prepared by impregnation of large-pore SiO_2 (surface area: 350 m^2/g, Strem Chemicals) using Ni$(NO_3)_2 \cdot 6H_2O$ (Johnson Matthey). Na–Mn–Ni/SiO_2 of which Ni loading is 5 wt% with the ratio of Na : Mn : Ni = 0.2 : 0.5 : 1 was prepared by coimpregnation of SiO_2 using Ni$(NO_3)_2 \cdot 6H_2O$, MnNO$_3 \cdot$ XH_2O, and NaNO$_3$ (Johnson Matthey). After impregnation, the sample was reduced in flowing hydrogen at 400°C for 16 hr. The coprecipitated Na–Ni catalyst was prepared by precipitating Ni$(NO_3)_2 \cdot 6H_2O$ with Na$_2CO_3$. The coprecipitated Na–Mn–Ni catalyst was prepared by precipitating Mn$(NO)_3 \cdot$ XH_2O and Ni$(NO_3)_3 \cdot 6H_2O$ with Na$_2CO_3$. The resulting precipitate was washed with water to remove excess Na.

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The catalyst contained Na, Mn, and Ni which had a molar ratio of Na : Mn : Ni = 0.005 : 0.5 : 1 (determined by Atomic absorption spectroscopy). The catalyst was calcined in flowing air at 250°C for 3 hr and then reduced in flowing hydrogen at 350°C for 7 hr.

The X-ray photoelectron spectroscopy (XPS) of the catalyst was measured by a Leybold LHS-10 system 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. Average Ni particle size for these catalysts was determined by X-ray diffraction (XRD) line broadening; hydrogen uptake was measured by hydrogen temperature-programmed desorption (TPD). Adsorption of H_2 for TPD was conducted by cooling of the catalyst in H_2 from 400 to 30°C. TPD experiments were performed in a flow of Ar from 30 to 400°C at a heating rate of 20°C/min. The catalysts were reduced again in a differential reactor at 350°C for 2 hr before reaction studies. CO hydrogenation (CO : H_2 = 1 : 1) was performed at 180–300°C and 10 atm. Following CO hydrogenation studies, the reaction of ethylene with syngas was employed to determine the activity of the catalysts for CO insertion and hydrogenation (2, 4, 11).

RESULTS AND DISCUSSION

Catalyst Characterization

Table 1 shows results of hydrogen uptake and crystallite size for the Ni-based catalysts. The Ni surface area per gram of the catalyst was calculated from hydrogen uptake with an assumption of a stoichiometry of H/Ni = 1. Crystallite sizes of Ni were determined by XRD line broadening and by using hydrogen uptake data and the relation as shown in Table 1. A comparison of crystallite sizes determined from XRD and from hydrogen uptake shows that Ni crystallite sizes for Na–Mn–Ni/SiO$_2$ and Na–Mn–Ni estimated from hydrogen uptake are greater than those determined by XRD. The inconsistency reflects the overestimation of Ni

TABLE 1

Catalyst Characterization

Catalyst	BET Surface area (m²/g cat.)	H₂ Uptake (μmol/g cat.)	Ni Surface area (m²/g cat.)	Crystallite size (Ni/MnO) Å	
15 wt% Ni/SiO₂	—	72.5	8.5	99[a]	92[b]
Na–Mn–Ni/SiO₂ (0.2 : 0.5 : 1)	195.3	20.7	2.4	117[a]	<40[b]
Na–Ni	—	—	—	—	320[b]
Na–Mn–Ni (0.005 : 0.5 : 1)	6.7	35.8	4.2	910[a]	170/220[b]

[a] $d = 5/(S \cdot \rho)$ from Ref. (24). d: Average crystallite size; S: surface area of Ni (m²/g cat.); ρ: density of the bulk Ni.
[b] Determined by X-ray diffraction line-broadening technique.

crystallite size for alkali-promoted catalysts from hydrogen uptake data. This could be due to the suppression of hydrogen chemisorption on the alkali-promoted catalysts (16–17).

CO Hydrogenation

Table 2 shows the rates of product formation and selectivities after 2 hr of steady-state CO hydrogenation studies. Due to the uncertainty in the estimation of the number of Ni surface atoms as a result of the suppression of hydrogen chemisorption on the alkali-promoted catalysts (16, 17), the activity of the catalyst is expressed in term of mol/kg-hr. The performance of the catalysts is compared on the basis of relative rates and selectivities. The Ni/SiO$_2$ catalyst produced methane as a major product with C$_{2+}$ hydrocarbons as minor products. In contrast to other catalysts, the activity of Ni/SiO$_2$ continued to decline since the onset of the reaction. Addition of Na and Mn to the Ni/SiO$_2$ resulted in increases in the selectivity to C$_{2+}$ hydrocarbon as indicated by the increase in the ratio of C$_{2+}$ HC to CH$_4$. Both Na and Mn also promoted the formation of a small amount of acetaldehyde and propionaldehyde. The coprecipitated Na–Ni catalyst produced methane as a major product. By contrast, the coprecipitated Na–Mn–Ni catalyst exhibited high activity and selectivity for the formation of acetaldehyde and propionaldehyde.

TABLE 2

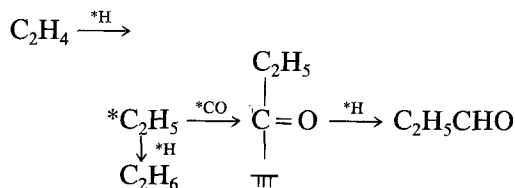Rates of Product Formation and Selectivities from CO Hydrogenation

	Ni/SiO$_2$	Na–Mn–Ni/SiO$_2$	Na–Ni	Na–Mn–Ni
	Rate of product formation (mol/kg-hr)			
CH$_4$	32.5	1.0	0.31	0.39
C$_2$H$_4$	0.02	0.105	0.04	0.03
C$_2$H$_6$	1.35	0.12	0.004	0.011
C$_{3+}$HC	0.51	0.073	0.002	0.038
CH$_3$CHO	0.0	0.033	0.005	0.19
C$_2$H$_5$CHO	0.0	0.006	0.0	0.031
	Selectivity			
CH$_3$CHO/CH$_4$	0.0	0.033	0.016	0.49
C$_2$H$_5$CHO/C$_2$H$_6$	0.0	0.05	0.0	2.8
C$_{2+}$HC/CH$_4$	0.058	0.29	0.15	0.2

Note. H$_2$:CO = 1:1 at 275°C, 10 atm.

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

Ethylene Addition

Ethylene addition was performed after 3 hr of steady-state CO hydrogenation. Table 3 shows the rates of product formation from ethylene addition to CO hydrogenation. Addition of ethylene to syngas over the Ni/SiO$_2$ led to increases in the rate of ethane formation as well as the production of propionaldehyde. The significant increases in the rates of formation for these products indicates that the major competitive reactions for the added ethylene are ethylene hydrogenation and CO insertion as shown in the proposed reaction scheme (1–3),

$$C_2H_4 \xrightarrow{\ *H\ }$$

$$*C_2H_5 \xrightarrow{\ *CO\ } \underset{\underset{III}{C_2H_6}}{\overset{\overset{C_2H_5}{|}}{C}}=O \xrightarrow{\ *H\ } C_2H_5CHO$$

$$*C_2H_5 \xrightarrow{\ \downarrow\ *H\ } C_2H_6$$

A marked decrease in the rates of formation of methane and C$_{3+}$ hydrocarbons was observed for the ethylene addition on the Ni/SiO$_2$. This is due to the severe deactivation of the Ni/SiO$_2$ via the formation of volatile Ni(CO)$_4$ under reaction conditions of this study (12). Despite significant decreases in the hydrocarbon formation, the Ni/SiO$_2$

remains active for catalyzing the formation of propionaldehyde.

The formation of propionaldehyde was observed over all four catalysts. The selectivity for CO insertion is expressed in terms of the ratio of the C$_2$H$_5$CHO rate to the C$_2$H$_6$ rate. The coprecipitated Na–Mn–Ni catalyst showed the highest selectivity for CO insertion. Comparison of [C$_2$H$_5$CHO/C$_2$H$_6$] in ethylene addition with [CH$_3$CHO/CH$_4$] in CO hydrogenation shows that C$_3$ oxygenate selectivity in ethylene addition parallels C$_2$ oxygenate selectivity in CO hydrogenation. A similar correlation has also been reported for Ag–Rh/SiO$_2$ (9) and V–Rh/SiO$_2$ catalysts (10).

X-Ray Photoelectron Spectroscopy

Figure 1 shows the XPS spectra of the coprecipitated Na–Mn–Ni catalyst. The air-exposed catalyst exhibited Mn peaks at 641.8 and 653.3 eV and Ni peaks at 855.3 and 872.8 eV as well as a weak, broad Na peak at 1071.2 eV. Although the results did not provide quantitative information on the surface concentration and surface states, these spectra show that the catalyst surface contains primarily Ni$^+$, Ni^0, and Mn$^+$ with a small amount of an unknown state of Na. Reduction of the catalyst in hydrogen at

TABLE 3

Rates of Product Formation and Selectivities form Ethylene Addition

	Ni/SiO$_2$	Na–Mn–Ni/SiO$_2$	Na–Ni	Na–Mn–Ni
	Rate of product formation (mol/kg-hr)			
CH$_4$	0.35	0.604	0.65	0.645
C$_2$H$_6$	13.1	0.19	0.59	0.102
C$_{3+}$HC	0.07	0.004	0.003	0.033
CH$_3$CHO	0.0	0.0	0.001	0.25
C$_2$H$_5$CHO	1.1	0.067	0.11	0.17
	Selectivity			
C$_2$H$_5$CHO/C$_2$H$_6$	0.084	0.35	0.18	1.7
Rate enhancement factor:	9.7	1.58	147	9.2

Note. H$_2$:CO:C$_2$H$_4$ = 1:1:0.02 at 275°C and 10 atm.

$$\text{Rate enhancement factor} = \frac{[C_2H_6] \text{ from } CO/H_2/C_2H_4}{[C_2H_6] \text{ from } CO/H_2}.$$
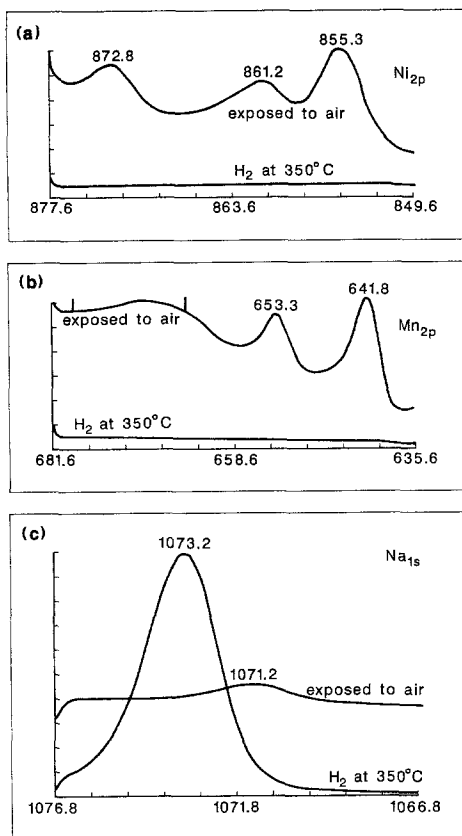
FIG. 1. X-ray photoelectron spectra of Na–Mn–Ni catalysts (a) Ni_{2p}, (b) Mn_{2p}, and (c) Na_{1s}.

350°C for 2 hr resulted in the growth of Na peak and in the loss of Mn and Ni peaks. The results suggest that the reduction led to a migration of Na onto the surface of the catalysts. The migration of Na onto the catalyst surface appeared to result in the suppression of hydrogen chemisorption as shown by the low hydrogen uptake capacity of the catalyst. Mn and Ni remained undetectable following exposure of the catalyst to the CO and H_2 mixture at 300°C. Exposure to CO and H_2 led to an increase in the intensity of the carbon peak. The similar migration of Na was also observed on the Na–Mn–Ni containing the ratio of Na : Mn : Ni : = 0.05 : 0.5 : 1. For the reduced Na–Mn–Ni/SiO_2, most Ni was in reduced Ni^0 state and no migration of Na was observed. Work is being undertaken to study the effect of calcination/oxidation and reduction cycles on the surface state of the coprecipitated Na–Mn–Ni catalyst.

Although the Ni/SiO_2 exhibited the CO insertion activity, the Ni/SiO_2 catalyst is not active for the synthesis of C_2 oxygenates from syngas. This can be attributed to the high hydrogenation activity of the Ni/SiO_2 on which hydrogenation predominated over CO insertion. The presence of Na and Mn on the Ni/SiO_2 decreased hydrogenation activity of the catalyst as indicated by the low value of rate enhancement factor for ethane formation as shown in Table 3. The major effects of alkali promoters on the CO hydrogenation reaction have been identified as (i) the suppression of hydrogen chemisorption and hydrogenation, (ii) the enhancement of CO dissociation, and (iii) the increases in selectivity toward olefin and higher hydrocarbons (16–21). While the suppression of hydrogenation may play a role in enhancing CO insertion selectivities (11), the high activity on the Na–Mn–Ni catalyst for the synthesis of aldehydes appears to lie in its high activity for the CO insertion. Because of the high coverage of Na on the surface of the coprecipitated catalyst, the state of Mn and Ni cannot be determined from XPS. The active site responsible for the aldehyde formation remains unclear.

MnO has been considered to be an oxophilic promoter, which enhances CO dissociation and CO insertion on Rh/SiO_2 catalysts (22). The promoting effect of MnO has been suggested to be due to an interaction of the oxophilic Mn ion with the oxygen of the adsorbed CO on the Rh/SiO_2. The observed CO-stretching frequency in the range of 1500–1600 cm^{-1} has been ascribed to such an interaction (22). Similar frequencies have been reported for the adsorbed CO on the MnO/Ni(111) single crystal (23). Based on the similarity in the vibrational frequency between the adsorbed CO on the MnO–Rh and on the MnO–Ni, it would be reasonable to postulate that MnO may play a similar role in both Rh and Ni catalysts in promoting CO insertion.

In conclusion, reduction of Na–Mn–Ni resulted in the migration of Na species to the surface of the coprecipitated Na–Mn–Ni catalyst which exhibited high activities and selectivities for the synthesis of acetaldehyde from syngas and the synthesis of propionaldehyde from ethylene addition.

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