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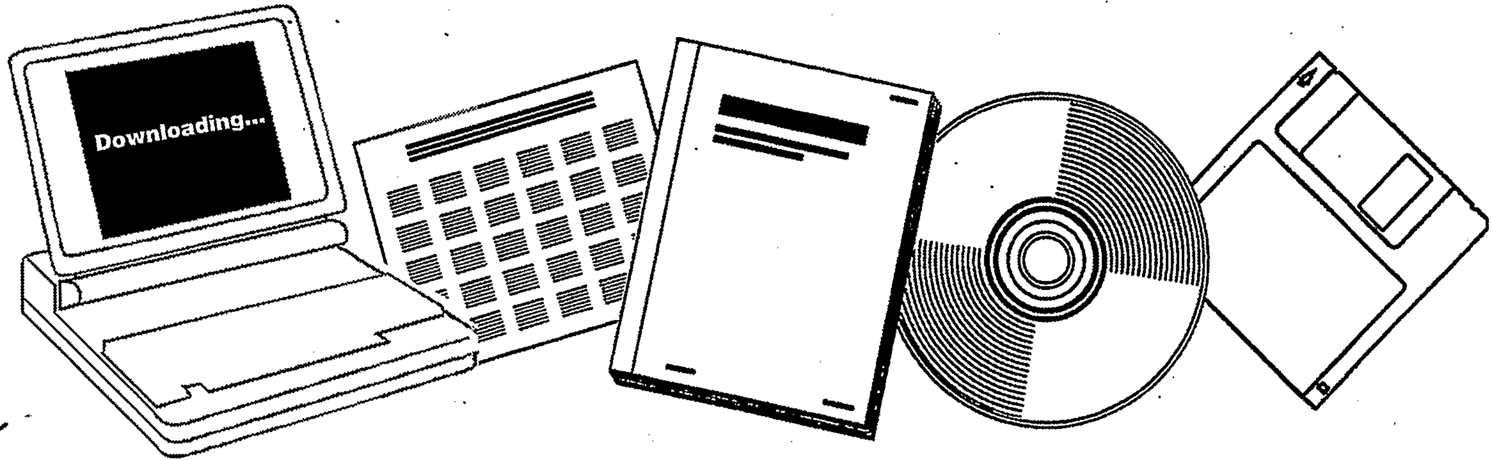

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SUMMARY

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 additive 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 fourth quarter of 1989, the effect of Na on the C_2+ oxygenate selectivity from CO hydrogenation over the Na-Mn-Ni catalysts has been studied. Reaction and X-ray photoelectron spectroscopic studies showed that reduction of coprecipitated Na-Mn-Ni resulted in the migration of Na species to the surface of the catalyst which exhibited high selectivity and activity for the synthesis of C_2+ oxygenates.

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). In a recent investigation, the Ni/SiO_2, a methanation catalyst, was demonstrated to possess the CO insertion activity (5). The catalyst is capable of catalyzing the fromation of propionaldehyde from the reaction of ethylene with syngas. Extensive studies of CO hydorgenation on the Ni-based catalysts have revealed that the coprecipitated $Ni-TiO_2$ and alkali Ni-Cu-Zn catalysts are active for higher alcohol synthesis (6-8).

Various additives have been employed as promoters to increase the selectivity toward higher oxygenates on Group VIII metals. Addition of promoters, such as Mn, Fe, Ti, Zn, La, Ag, V and Mo to Rh/SiO_2 promoted CO insertion activities resulting in increasing in the rate of formation of higher oxygenates (2,9-14). In contrast, additives such as alkali species suppressed hydrogenation activity of Rh, while it had little effect on the CO insertion activity (15). Such an effect led to the enhancement of C_2+ oxygenate selectivity. 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.

15 wt % Ni/SiO_2 were 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 whcih Ni loading is 15 wt % with the ratio of Na:Mn:Ni=0.2:0.5:1 was prepared by coimpregantion of SiO_2 using $Ni(NO_3)_2$ $6H_2O$, $MnNO_3XH_2O$ and $NaNO_3$ (Johnson Matthey). After impregnation, the sample was reduced in flowing hydrogen at 400 °C for 16 hr. Coprecipitated Na-Ni catalyst was prepared by preicpitating $Ni(NO_3)_2$ $6H_2O$ with Na_2CO_3.

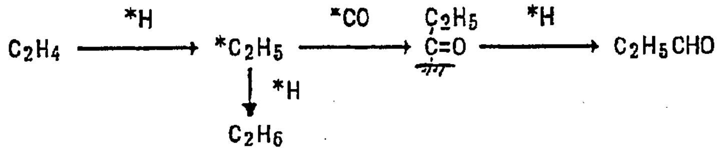
Coprecipitated Na-Mn-Ni catalyst was prepared by precipitating $Mn(NO)_3$

XH_2O and $Ni(NO_3)_2$ $6H_2O$ with Na_2CO_3. The resulting precipitate was washed with water to remove excess Na. The catalyst was calcined in flowing air at 250 °C for 3 hrs and then reduced in flowing hydrogen at 350 °C for 7 hrs. The catalyst contains Na, Mn, and Ni which has a molar ratio of Na:Mn:Ni=0.005:0.5:1 (determined by Atomic Absorption). 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 vaccum chamber without exposure to air. Average Ni particle size for these catalysts was determined by X-ray diffraction line-broadening; hydrogen uptake was measured by hydrogen temperature programmed desorption, as shown in Table 1.

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 in 180 - 300 °C and 10 atm. Product distribution was determined using an HP-5890A gas chromatograph. Following CO hydrogenation studies, the reaction of ethylene with syngas was employed to determine the activity of the catalysts for CO insertion and hydrogenation (2,4,13).

CO Hydrogenation Table 1 shows the product formation rates 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 (15-17), the activity of the catalyst is expressed in term of mole/kg-hr. The performance of the catalysts is compared on the basis of the relative rates and the selectivities. 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 continue 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. Coprecipitated Na-Ni cataylsts produced methane as a major product. By contrast, the coprecipitated Na-Mn-Ni catalysts exhibited high activity and selectivity for the formation of acetaldehyde and propionaldehyde.

Ethylene Addition Ethylene addition was performed after 3 hr of steady-state CO hydrogenation. Table 2 shows the rate of product formation from ethylene addition to CO hydrogenation. The addition of ethylene to syngas over 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 (1,2,13).



$$\begin{tikzcd} C_2H_4 \arrow[r, "*H"] & {*C_2H_5} \arrow[r, "*CO"] \arrow[d, "*H"] & \overset{C_2H_5}{C}=O \arrow[r, "*H"] & C_2H_5CHO \\ & C_2H_6 & & \end{tikzcd}$$

In contrast to the increases in the product formation, there is a marked decrease in the rates of formation of methane and C_{3+} hydrocarbons on the Ni/SiO_2 due to the severe deactivation of the Ni/SiO_2 via the formation of volatile $Ni(CO)_4$ under reaction conditions of this study (5). Despite of significant decreases in the hydrocarbon formation, the Ni/SiO_2 remains active for catalyzing propionaldehyde formation.

The formation of propionaldehyde was observed over all four catalysts. The selectivity for CO insertion is expected in term of the ratio of the C_2H_5CHO rate to the C_2H_6 rate. Coprecipitated Na-Mn-Ni showed the highest selectivity for CO insertion. Comparison of [C_2H_5CHO/C_2H_6] in ethylene addition with [CH_3CHO/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 (13) and V-Rh/SiO_2 catalysts (14).

X-ray Photoelectron Spectroscopy Figure 1 shows the XPS spectra of the coprecipitated Na-Mn-Ni catalyst before and after reduction at 350 °C for 2 hr. The air-exposed catalysts 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 center at 1071.2 eV. Although the results did not provide the quantitative information on the surface concentration and surface state, this spectra show that the catalyst surface contains primarily Ni^+, Ni^o, and Mn^+ with a small amount of unknown state of Na. Reduction of the catalyst in hydrogen resulted in the growth of Na peak and in the loss of Mn and Ni peaks. The results suggest that the reduction led to the migration of Na to the surface of the catalysts. Mn and Ni remained undetectable following exposure of the catalyst to CO and H_2 mixture at 300 °C. Exposure to CO and H_2 led to increase in the intensity of carbon peak. The similiar 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-Mi/SiO_2, most Ni was in reduced Ni^o state and no migration of Na was observed. Work is currently undertaken to study the effect of calcination/oxidation and reduction cycles on the surface state of the coprecipitated Na-Mn-Ni.

Although Ni/SiO_2 exhibited the CO insertion activity, the Ni/SiO_2 catalyst is not active for the synthesis of C_2 oxygeantes from syngas. This can be attributed to the great hydrogenation activity of Ni/SiO_2 on which hydrogenation predominates over CO insertion. The presence of Na and Mn decreases the hydrogenation activity of the catalysts as indicated by the low value of rate enhancement factor for ethane formation as shown in Table 2. The major effects of alkali promoters on the CO hydrogenation reaction have been identified to be (i) the suppression of hydrogen chemisorption and hydrogenation, (ii) the enhancement of CO dissociation, and (iii) the increases in selectivity toward olefin and higher hydrocarbon (16-21). The Na appears to have a less singnificant effect on the suppression of ethylene hydrogenation on the coprecipitated Na-Mn-Ni than the Na-Mn-Ni/SiO_2 since the coprecipitated Na-Mn-Ni show a high value of rate enhancement factor for ethane formation during ethylene addition.

Although the suppression of hydrogenation may enhance CO selectivity to produce high yields of C_2 oxygenates (15), the enhancement of CO insertion activity on the Na-Mn-Ni catalyst prepared by the coprecipitation method play a key role in the high yield of aldehydes. Because the high coverage Na on the surface of the coprecipitated catalyst, the state of Mn and Ni can not be determined from XPS. The active site reponsible for the aldehyde formation remains unclear. In conclusion, reduction of Na-Mn-Ni resulted in the migration of Na species to the surface of the coprecipitated Na-Mn-Ni atalysts which exhibited high activity and selectivity for the synthesis of acetaldyde from syngas and propionaldehyde from ethylene addition..

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Table 1 Catalyst Characterization [a]

Catalyst	BET Surface Area (m^2/g)	H_2 Uptake (μmol/g)	Ni Surface Area (m^2/g)	Crystallite Size (Ni/MnO) °A
15 wt% Ni/SiO_2	-	72.5	8.5	92
Na-Mn-Ni/SiO_2 (0.2:0.5:1)	195.3	20.7	2.4	>40
Na-Ni				320
Na-Mn-Ni (0.005:0.5:1)	6.7	35.8	2.4	170/220

a: Determine by X-ray diffration line-broadening technique.

Table 2 Rate of Product Formation and Selectivity from CO Hydrogenation

	Ni/SiO_2	$Na-Mn-Ni/SiO_2$	Na-Ni	Na-Mn-Ni
TOF of CO Conv. (sec^{-1})	37	2.05		1.19
Rate of Product Formation (mol/kg-hr)				
CH_4	32.5	1.0	0.31	0.39
C_2H_4	0.02	0.105	0.04	0.03
C_2H_6	1.35	0.12	0.004	0.011
$C_{3+}HC$	0.51	0.073	0.002	0.038
CH_3CHO	0	0.033	0.005	0.19
C_2H_5CHO	0	0.006		0.031
Selectivity				
CH_3CHO/CH_4	0	0.038		0.49
C_2H_5CHO/C_2H_4	0	0.57		2.8
$C_{2+}HC/CH_4$	0.058	0.29		0.2

H_2:CO= 1:1
at 275°C, 10 atm

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

Table 3 Rate of Product Formation and Selectivity form Ethylene Addition

	Ni/SiO_2	$Na\text{-}Mn\text{-}Ni/SiO_2$	Na-Ni	Na-Mn-Ni
Rate of Product Formation (mol/kg-hr)				
CH_4	0.35	0.604	0.65	0.645
C_2H_6	13.1	0.19	0.59	0.102
$C_{3+}HC$	0.07	0.004	0.003	0.033
CH_3CHO	0	0	0.001	0.25
C_2H_5CHO	1.1	0.067	0.11	0.17
Selectivity				
C_2H_5CHO/C_2H_4	0.084	0.35		1.7
Rate Enhancement Factor	9.7	1.58		9.2

$H_2:CO:C_2H_4 = 1:1:0.02$
at 275°C and 10 atm

$$\text{Rate enhancement factor} = \frac{[C_2H_6] \text{ from } CO/H_2/C_2H_4}{[C_2H_6] \text{ from } CO/H_2}$$

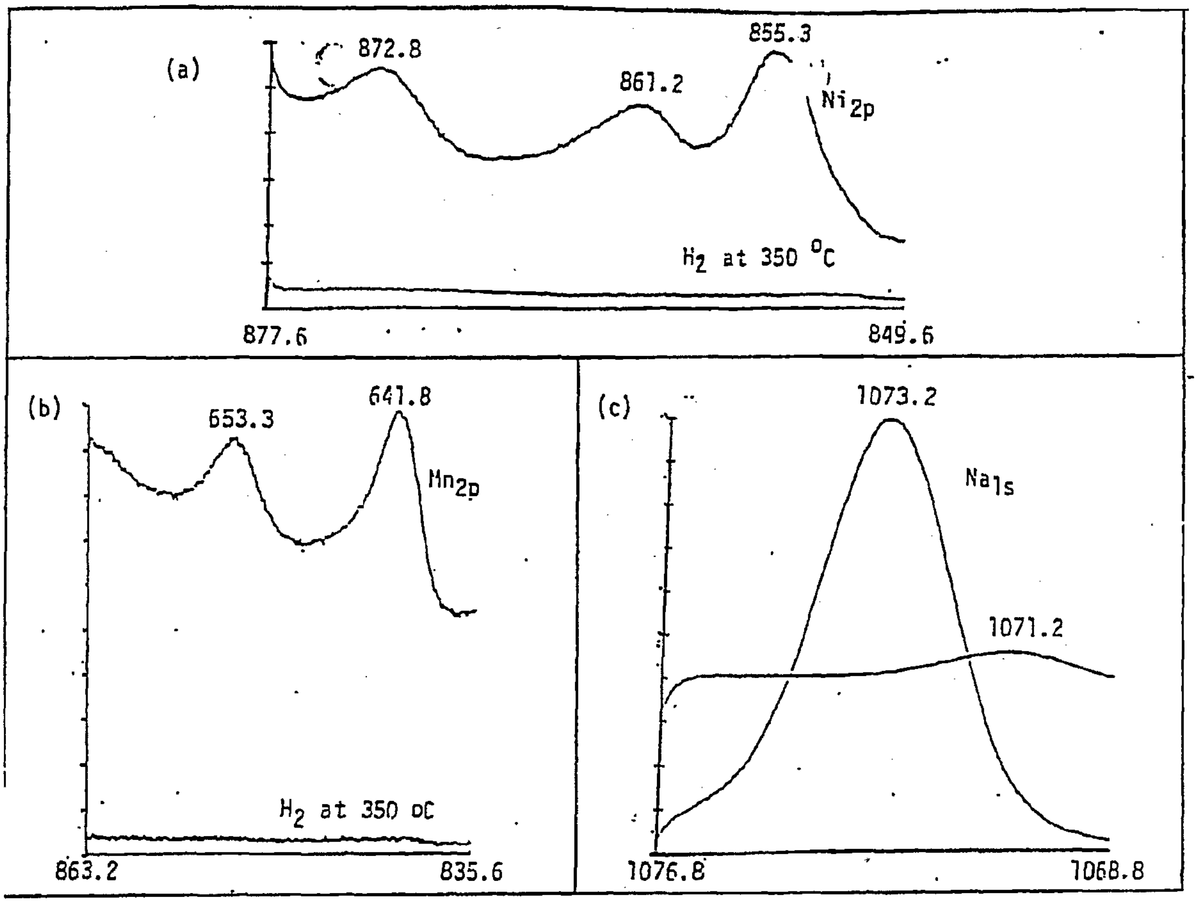

Figure 1. X-ray photoelectron spectroscopy of the Na-Mn-Ni catalyst

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