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The EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

by

Steven S.C. Chuang

Department of Chemical Engineering

University of Akron

Akron, OH 44325 U.S.A.

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MASTER

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 third quarter of 1989, the effect of catalyst preparation methods on CO hydrogenation selectivity over the Na-Mn-Ni catalysts has been studies. The SiO_2-supported Ni and Mn-Ni catalysts prepared from impregnation exhibit high methanation and hydrocarbon selectivity. The Mn-Ni catalysts prepared from coprecipitation of Mn and Ni nitrates with Na carbonate show high selectivity for C_{2+} oxygenate synthesis

ABSTRACT

The effect of catalyst preparation methods on CO hydrogenation selectivity over the Na-Mn-Ni catalysts has been studied. The SiO_2-supported Ni and Mn-Ni catalysts prepared from impregnation exhibit high methanation and hydrocarbon synthesis selectivity. The Mn-Ni catalysts prepared from coprecipitation of Mn and Ni nitrates with Na carbonate show high selectivity for C_{2+} oxygenate synthesis. Temperature programmed desorption studies reveal that hydrogen chemisorption on the coprecipitated catalysts is highly activated and the binding energy of H-Ni is greater on the coprecipitated Ni catalysts than on the SiO_2-supported Ni catalysts. The results suggest that highly activated hydrogen chemisorption may lead to a hydrogen-deficient surface which could lead to more effective competition for CO insertion versus hydrogenation.

INTRODUCTION

Although use of Ni-based catalysts for CO hydrogenation has been a subject of study for several decades [1-5], remarkably little work has been done on their use for producing C_{2+} oxygenates since the early work of Storch et. al.[1] on the Fischer-Tropsch synthesis revealed that Ni catalysts produced small quantities of oxygenates under 150-350 $^{\circ}$C and 1-30 atm. Recent ethylene addition studies have demonstrated that Ni/SiO_2, a methanation catalyst, exhibits CO insertion activity which results in the formation of propionaldehyde from reaction of added ethylene with syngas [6]. Increases in the reaction pressure resulted in enhancement of CO insertion activity [7]. Since CO insertion is a key step to C_2 oxygenates, i.e., acetaldehyde, ethanol, and acetic acid, in CO hydrogenation, the manifestation of CO insertion activity indicates that Ni is a potential catalyst for C_2 oxygenate synthesis.

Working with coprecipated Ni-catalysts at 60 atm, 300 $^{\circ}$C and $CO/H_2 = 2$, Uchiyama and coworkers [8,9] found that Ni-MnO and $Ni-TiO_2$ exhibited high activity for C_2 oxygenate synthesis while Ni-ZnO showed high selectivity for methanol synthesis. The selectivity of coprecipated Ni catalysts is different from that of impregnated Ni catalysts. Interestingly, the effect of these oxides on the activity and selectivity of coprecipitated Ni catalysts parallels, to some extent, those reported for the supported Rh prepared by impregnation [10]. The use of Ni-based catalysts for C_{2+} oxygenate synthesis is of particular interest

because of its low cost compared to other C_{2+} oxygenate synthesis catalysts such as Rh.

The purpose of this paper is to investigate the effect of catalyst preparation methods on the selectivity and activity of Na-Mn-Ni catalysts for C_{2+} oxygenate synthesis. Mn and Na were used as promoters for this study because of their potential for enhancing CO insertion on the metal catalysts [11-13]. The effects of coprecipitation and impregnation methods, as well as Na and Mn additives on the adsorptive properties, C_{2+} oxygenate activity and selectivity, and deactivation characteristics of the catalysts were examined by temperature programmed desorption of H_2 as well as CO hydrogenation studies.

EXPERIMENTAL

Catalyst Preparation

15 wt% Ni/SiO$_2$ was prepared by impregnation of large pore SiO$_2$ (Strem Chemicals) using Ni nitrate (Alfa Chemicals). Mn-Ni/SiO$_2$ (the molar ratio of Mn to Ni = 0.5 : 1) containing 5 wt% Ni was prepared by coimpregnation using Mn and Ni nitrates; Na-Mn-Ni/SiO$_2$ (molar ratio of Na:Mn:Ni=0.2:0.5:1) containing 5 wt% Ni was prepared by coimpregnation using Na, Mn, and Ni nitrates. After impregnation, the sample was dried overnight in air at 30 ^{O}C, then reduced in flowing hydrogen at 400 ^{O}C for 16 hours. Coprecipitated catalysts were prepared by precipitating Mn and Ni nitrates with Na carbonate at room temperature followed by washing off Na carbonate. The resulting precipitate consists

of Na, Mn, Ni which has molar ratio of Na:Mn:Ni=0.005:0.5:1.
High Na content of Na-Mn-Ni (molar ratio of Na:Mn:Ni=0.05:0.5:1)
catalysts were prepared by impregnation of the washed catalyst
with Na nitrates. Then the catalysts were calcined at 350 ^{O}C for
3 hours and reduced at 350 ^{O}C for 7 hours. The overall surface
area of the catalysts was measured by BET method. The
crystallite size of the Mn and Ni metals was determined by X-ray
diffraction line-broadening technique.

Temperature Programmed Desorption

   Temperature programmed desorption (TPD) of hydrogen was
conducted in an automated temperature programmed desorption
system (Altrmira) with an IBM personal computer for controlling
the experiment and for data analysis. A catalyst sample (0.2g)
was reduced in flowing hydrogen for 90 min. at 400 ^{O}C prior to
introducing the adsorbing gas. Adsorption of hydrogen on the
catalysts was carried out in two manners: (i) flowing hydrogen
during cooling down of the reactor from 400 ^{O}C to 30 ^{O}C and (ii)
pulsing hydrogen in Ar carrier gas at 30 ^{O}C. Gorte's criteria
were used to set the desorption conditions so that the mass
transfer effects can be minimized [14]. TPD experiments were
carried out in Ar from 30 ^{O}C to 400 ^{O}C at 20 ^{O}C/min. and
maintained at 400 ^{O}C for 15 min.

Reaction Studies

CO hydrogenation ($CO/H_2 = 1:1$) was performed over the catalysts in a (1/4'ID) differential reactor system under 200 – 300 $^\circ$C and 10 atm. Space velocities of 2,100 to 11,000 hr^{-1} were used to keep CO conversion below 5% in order to minimize heat and mass transfer effects and secondary reactions. Product distribution was determined by using an HP-5890A gas chromatograph (GC) with a 6 ft Porapak PS in series with a 6 ft Porapak QS column. The combination of these two GC columns permits a good on-line separation of all C_1-C_6 hydrocarbons as well as C_1-C_4 alcohols and aldehydes.

RESULTS

BET Studies

Table 1 shows the results of BET study on the nickel catalysts. The silica supported catalysts have a higher BET surface area as compared to the coprecipitated catalysts. For the supported catalyst, coimpregnation of nickel and manganese on silica decreased its surface area by about 15 percent. The addition of sodium in coimpregnation further reduced it by 17 percent. The coprecipitated Na-Mn-Ni (0.005:0.5:1) catalyst has a specific surface area of 6.7 m^2/gm. The specific surface area decreases with the addition of sodium. The decrease in the BET area appears to be due to pore blockage by sodium, most of which was introduced to the coprecipitated catalyst by impregnation with Na nitrates.

Hydrogen Temperature Programmed Desorption (TPD)

Figure 1 shows the TPD spectra obtained for hydrogen following exposure of the catalysts to flowing hydrogen during cooling of the reduced catalysts from 400 ^{O}C to 30 ^{O}C. There are distinct differences in TPD spectra among these catalysts. For impregnated catalysts, hydrogen desorbed from Ni/SiO_2 as a broad peak centered at 70 ^{O}C followed by a wide shoulder ranging from 90 ^{O}C to 180 ^{O}C. Coimpregnation of Mn and Ni resulted in a sharp peak at 50 ^{O}C and appearance of a broad peak centered at 320 ^{O}C. Addition of both Na and Mn led to the shift of the low temperature peaks from 50 ^{O}C to 100 ^{O}C and the suppression of high temperature peaks.

The TPD spectra for the coprecipitated Na-Mn-Ni (0.005:0.5 :1) appeared as a weak, broad band centered at 40 ^{O}C and a skew peak at 135 ^{O}C. The spectra for Na-Mn-Ni(0.05:0.5:1) consist of a peak at 150 ^{O}C with shoulders below and above 150 ^{O}C indicating existence of at least three different adsorbed states for hydrogen. It appears that the peak temperatures for hydrogen desorption on Na-Mn-Ni catalysts are higher than those for impregnated catalysts. Figure 2 illustrates the TPD spectra followed by pulsing hydrogen into Argon carrier gas at 30 ^{O}C. The hydrogen desorption peaks for $Mn-Ni/SiO_2$ are much smaller than those shown in Figure 1. No obvious desorption peaks were found for the coprecipitated Na-Mn-Ni (0.05:0.5:1) and Na-Mn-Ni/SiO_2 catalysts, indicating that little hydrogen adsorption occurs at 30 ^{O}C. The observation of significantly

more hydrogen adsorbed in cooling from 400 ^{O}C to 30 ^{O}C compared

to the quantity adsorbed at 30 ^{O}C suggests that hydrogen

adsorption on Na-Mn-Ni/SiO$_2$ and coprecipitated catalysts may be

highly activated.

The amount of hydrogen present on the catalysts
prior to TPD, determined by integrating the area under the
TPD curves (shown in Fig 1), is listed in Table 1. The values
were used to estimate the Ni surface area assuming a
stoichiometric ratio of H/Ni =1. The amount of hydrogen desorbed
during TPD has been found to be approximately the same as that of
hydrogen determined by static chemisorption for the Ni catalysts
[15]. The hydrogen TPD appears to provide a reasonable estimate
of hydrogen uptake.

CO Hydrogenation

Table 2 presents the turnover number (TON) for CO
conversion, which was calculated with the number of exposed Ni
atoms determined by hydrogen TPD, and the rate of product
formation for the reaction at 300 ^{O}C and 10 atm. Table 3 shows
the product selectivity of CO hydrogenation. Ni/SiO$_2$ produced
mainly methane with small amounts of C$_{2+}$ hydrocarbons. Addition
of Mn and Na to the catalysts decreased the turnover number and
rate of CO conversion and shifted the selectivity towards C$_{2+}$
hydrocarbons. Trace amounts of acetaldehyde and methanol were
obs.rved for Mn-Ni/SiO$_2$ and Na-Mn-Ni/SiO$_2$ catalysts. In
conc.ast, both coprecipitated catalysts exhibited high activity

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for the formation of oxygenates including methanol, acetaldehyde, ethanol, and propionaldehyde. The effect of Na is to increase the selectivity towards C_{2+} oxygenates at 300 ^{O}C.

Figure 3 shows the change in C_2 oxygenate (acetaldehyde and ethanol) selectivity with temperature. The C_2 oxygenate selectivity improves with an increase in temperature up to 300 ^{O}C. Watson and Somorjai in a CO hydrogenation study on LaRhO$_3$ found that C_2 oxygenate formation is most favored at temperatures close to 300 ^{O}C [16]. It has been suggested that C_2 oxygenate selectivity is maximized when the relative rates of CO dissociation, CO insertion and hydrogenation are optimized [16]. Pant, working with Ni-Mn-La, also found that the C_2 oxygenate selectivity increases with temperature but decreases at temperature above 300 ^{O}C [17]. It is possible that these catalysts also follow a similar temperature-selectivity curve after 300 ^{O}C.

Figures 4 and 5 show the variation in the rate of product formation with time for Na-Mn-Ni catalysts. The catalysts exhibited stable activity after the first 5 hours of the reaction run. It appears that there is an initial induction period for the formation of acetaldehyde. The stability of the coprecipitated catalysts is significantly greater than that of the impregnated Ni/SiO$_2$ catalysts which showed a dramatic decline in activity for methanation under the same conditions [6].

DISCUSSION

Comparison of BET and Ni surface area (Table 1) for the coprecipitated catalysts shows that a large fraction of catalyst surface consists of Ni metal. Due to oxophilic nature of Mn, Mn is probably in the form of MnO which is inactive for hydrogen chemisorption [11]. The difference between BET and Ni surface area may be attributed to the surface area of MnO and Na species. X-ray diffraction studies revealed that MnO and Ni of the coprecipitated catalysts are in the form of large crystallites with the size between 170 and 290 $\overset{O}{A}$. For Mn-Ni/SiO$_2$, MnO and Ni are dispersed on the SiO$_2$ support with crystallite sizes less than 40 $\overset{O}{A}$. In addition, a small amount of Na$_2$CO$_3$ was present as small crystallite on the coprecipitated Ni catalyst as evidenced by X-ray diffraction.

MnO has been suggested to be a SMSI (strong-metal support interactions) support [18,19]. The typical manifestation of the SMSI behavior is : (i) a shift in product selectivity towards C$_{2+}$ hydrocarbons and an increase in CO hydrogenation activity and (ii) a suppression of hydrogen chemisorption. Comparison of reaction and TPD results show that catalysts containing Mn and Ni exhibit higher C$_{2+}$ hydrocarbon selectivity, low CO hydrogenation activity, and comparable hydrogen chemisorption activity in comparison with that of Ni/SiO$_2$. The performance of Mn-Ni catalysts does not fit into SMSI categories.

The effects of preparation methods on the properties of the Ni catalysts can be illustrated from comparison of H$_2$ TPD profile

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and CO hydrogenation selectivity over impregnated and coprecipitated catalysts. The major differences between impregnated and coprecipitated catalysts are summarized as follows:

(1) Hydrogen chemisorption process appears to be more activated on coprecipitated catalysts than on impregnated catalysts.

(2) Coprecipitated catalysts increase the binding energy of H-Ni as indicated by higher temperature desorption peak.

(3) Coprecipitated Na-Mn-Ni is more active and selective for C_{2+} oxygenate synthesis than impregnated Ni catalyst.

(4) Na slightly enhances C_{2+} oxygenate selectivity for both impregnated and coprecipitated catalysts.

The activated nature of H_2 chemisorption on the coprecipitated catalysts reflects the low activity of coprecipitated Na-Mn-Ni catalysts for reactions involved with hydrogen, such as methanation and hydrogenation. Coprecipitated Na-Mn-Ni exhibits significantly low activity and selectivity for methanation compared with that of supported Mn-Ni catalyst. Weatherbee et. al. [20] have suggested that highly activated adsorption of hydrogen could lead to hydrogen-adsorption limiting kinetics and a hydrogen-poor surface resulting in modification of product distribution in hydrogenation. A recent ethylene addition study also showed that the activity of the

coprecipitated Mn-Ni for ethylene hydrogenation is lower than that of supported Mn-Ni/SiO$_2$ [21]. Low methanation and hydrogenation activities could provide CH$_x$ (methyl and methylene species), produced from CO dissociation followed by hydrogenation, a higher chance for undergoing CO insertion for the formation of C$_{2+}$ oxygenates.

MnO has been demonstrated to be an effective promoter to enhance CO insertion on the Rh/SiO$_2$ prepared by impregnation [11,12]. The promotion effect was attributed to the oxophilic nature of Mn. Such an effect was, however, not observed in the supported Mn-Ni/SiO$_2$. Instead, the effect was found on the coprecipitated Mn-Ni catalysts. A recent study on Mn-Ni system shows that MnO blocks CO adsorption sites on Ni(111) single crystal and creates a possible site at the interface between MnO and Ni [22]. The site at the interface of MnO-Ni was thought to resemble that in Mn-Rh system which has been considered to be important in promoting CO dissociation and CO insertion. Such an interaction between Ni and Mn, which is important for C$_2$ oxygenate synthesis, may occur in the coprecipitated Ni catalysts. Further investigation is required for developing a better understanding of Mn-Ni interaction for promoting CO insertion.

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Table 1

Catalyst Characterization

Catalyst	BET Surface Area(m^2/g)	H_2 Uptake $\mu mol/g$	Ni surface Area(m^2/g)	Crystallite[a] size(Ni/MnO) ^0A
SiO_2	279.5	--	-	-
15 wt% Ni/SiO_2	-	72.5	8.5	92
Mn-Ni/SiO$_2$ (0.5 :1)	237.7	74.6	8.8	>40
Na-Mn-Ni/SiO$_2$ (0.2:0.5:1)	195.3	20.7	2.4	>40
Na-Mn-Ni (0.005:0.5:1)	6.7	35.8	2.4	170/220
Na-Mn-Ni (0.05:0.5:1)	2.7	17.0	2.0	270/290

a: Determined by X-ray diffraction line-broadening technique.

Table 2

Rates of Product Formation from CO Hydrogenation

Catalyst	CO Conversion TON (sec⁻¹)	Rate (mol/kg-hr)	CH₄	C₂₊HC Rate	CH₃OH	CH₃CHO	C₂H₅OH	C₂H₅CHO
					of Product Formation (mole/kg-hr)			
Ni/SiO$_2$	0.47	34.2	33.	1.5	–	–	–	–
Mn-Ni/SiO$_2$	0.054	4.0	1.4	0.8	–	0.04	–	0.03
Na-Mn-Ni /SiO$_2$	0.14	3.0	1.5	0.51	–	0.05	–	0.02
Na-Mn-Ni (0.005:0.5:1)	0.16	5.5	1.6	0.31	0.20	0.67	0.22	0.23
Na-Mn-Ni (0.05:0.5:1)	0.18	3.2	0.87	0.25	0.09	0.57	–	0.17

Reaction Condition: 300 $^{\circ}$C, 10 atm, CO:H$_2$= 1:1.

Table 3

Product Selectivity from CO Hydrogenation

Catalyst	CH_4	$C_{2+}HC$	CH_3OH (mol %)	CH_3CHO	C_2H_5OH	C_2H_5CHO
Ni/SiO$_2$	95.7	4.3	-	-	-	-
Mn-Ni/SiO$_2$	57.0	40.	-	1.6	-	1.4
Na-Mn-Ni/SiO$_2$	70.0	26.7	-	2.3	-	1.0
Na-Mn-Ni (0.005:0.5:1)	47.4	13.7	5.8	19.8	6.6	6.7
Na-Mn-Ni (0.05:0.5:1)	45.4	11.6	5.5	28.6	-	8.9

Reaction Condition: 300 $^{\circ}$C, 10 atm, CO:H$_2$= 1:1.

LIST OF FIGURES

Ni/SiO₂

Mn-Ni/SiO₂

Na-Mn-Ni/SiO₂

Na-Mn-Ni
(0.005:0.5:1)

Na-Mn-Ni
(0.05:0.5:1)

DESORPTION RATE, (Arbitrary Unit)

TEMPERATURE (°C)

30   100   200   300   400

Figure: Desorption rate (arbitrary unit) versus temperature (°C) showing curves for Ni/SiO₂ (X2.3), Mn-Ni/SiO₂ (X2.3), and Na-Mn-Ni (0.05:0.5:1) (X2.3).

TEMPERATURE (°C)

C₂ OXYGENATE SELECTIVITY

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