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Activity and selectivity of Group VIII, alkali-promoted Mn-Ni, and Mo-based catalysts for C_{2+} oxygenate synthesis from the CO hydrogenation and $CO/H_2/C_2H_4$ reactions

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Abstract

Activity and selectivity of Group VIII metal catalysts, H_2S-treated Group VIII metal catalysts, alkali-promoted Mn-Ni catalysts, and Mo-based catalysts toward higher oxygenates via the CO hydrogenation and ethylene hydroformylation ($CO/H_2/C_2H_4$) reactions at 545 K and 1 MPa have been studied. The catalysts exhibited a wide range of activity and selectivity for C_2 oxygenate synthesis. The selectivity toward C_2 oxygenates is attributed to the CO insertion capability of the catalyst. All of the catalysts tested, except H_2S-treated Os, exhibited CO insertion activity in the $CO/H_2/C_2H_4$ reaction leading to C_3 oxygenate formation. Rh and Ru exhibited exceptionally high activity and selectivity for C_2 oxygenates in the CO/H_2 reaction and C_3 oxygenates in the $CO/H_2/C_2H_4$ reaction. Sulfur treatment of the catalysts poisoned CO dissociation and hydrogenation capability to various degrees for the Group VIII catalysts. Coprecipitated alkali–Mn-Ni catalysts showed low hydrogenation activity and good oxygenate selectivity. Mo-based catalysts showed the poorest activity and selectivity toward higher oxygenates at 1 MPa. Optimization of C_2 oxygenate activity and selectivity requires a proper balance between CO dissociation activity, CO insertion activity, and hydrogenation activity. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: CO hydrogenation; Fischer–Tropsch synthesis; Hydroformylation; CO insertion; Oxygenates; Alcohol; Synthetic fuel; Group VIII metals; Sulfidation; Alkali; Ni; Mo; Mn; Supported metal catalyst; Coprecipitated catalyst

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1. Introduction

The ability to develop highly active, selective, and poisoning-resistant catalysts for the production of C_{2+} oxygenates is becoming increasingly important as the roles of these oxygenates expand within the fuel and chemical industries. As a fuel alternative or additive to gasoline, C_{2+} oxygenates provide many advantages, including lower production of hydrocarbons, NO_x, and CO in the exhaust stream due to a more complete combustion to CO_2 and H_2O [1]. C_{2+} oxygenates also provide high octane numbers and volatility control [2].

Although methanol, a C_1 oxygenate, would provide some of the same advantages as higher oxygenates, there are two key disadvantages associated with the use of methanol in fuel systems. The first disadvantage is that of limited miscibility between methanol and gasoline [2]. The presence of minute amounts of water causes phase separation. Secondly, methanol is not completely compatible with the fuel systems present in most of today's vehicles. Methanol may cause corrosion of some metals, plastics, and elastomers [1,2]. These problems are absent with higher oxygenates.

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Apart from the fuel industry, C_{2+} oxygenates, especially alcohols, can be utilized in many ways:

1. as precursors for synthesizing other organic chemicals;
2. for alkylation and solubilization of coal;
3. for combined cycle peak electric power generation;
4. as a substitute for propane in liquefied petroleum gas (LPG) applications;
5. as a transportation medium for coal in slurry pipelines; and
6. as general solvents [2].

The early developments of higher oxygenate synthesis from CO and H_2 (syngas) took place in Germany. In 1913, BASF discovered that cobalt and osmium catalysts produced a mixture of oxygenates, including alcohols, aldehydes, ketones, and acids, at pressures up to 20 MPa and temperatures up to 673 K [2]. Since that time, a significant amount of work has been done to characterize the performance, i.e. activity and selectivity, of catalysts for the Fischer–Tropsch (FT) synthesis and higher oxygenate formation [3]. A summary of these catalysts and a description of their typical selectivities are given in Table 1. Although there are current successful technologies for the production of some higher oxygenates from heterogeneous catalysts [2,3], there remains much room for improvement with regard to obtaining high activity and selectivity toward a single C_{2+} oxygenate.

The objective of this study is to determine activities and selectivities of Group VIII metal catalysts, alkali-promoted Mn-Ni catalysts, and Mo-based catalysts for the formation of higher oxygenates via the CO hydrogenation and ethylene hydroformylation ($CO/H_2/C_2H_4$) reactions. The effects of sulfur poisoning on the Group VIII metal catalysts are also examined.

2. Experimental

Table 2 contains a list of catalysts used in this study, their preparation method, and particle size/surface area. The catalysts prepared by the impregnation method were allowed to dry overnight before being subjected to either calcination or reduction. For reduction, the temperature was ramped at a rate of 1 K/min to 673 K.

Catalysts I-1 through I-7, i.e. Group VIII metals, in Table 2 also underwent sulfur-poisoning treatment. After reduction, with the exception of Ni/SiO_2, half the catalyst was removed; the half that remained was subjected to 5 cm^3/min flow of H_2S in H_2 (1000 ppm) for 4 h at 673 K. The Ni catalyst was poisoned in the reactor subsequent to the initial CO hydrogenation and hydroformylation runs. In this case, poisoning was carried out for 2 h.

Mn-Ni catalysts prepared by precipitation were filtered with the help of a vacuum filter, washed with de-ionized water, and dried on a heating plate before being crushed into a fine powder. The washing was performed to rid the catalyst of excess alkali. Subsequent to crushing, the catalyst underwent calcination and/or reduction. Detailed discussions on the preparation techniques for these catalysts can be found in Ref. [4].

Both, the CO hydrogenation, i.e. CO/H_2, and the hydroformylation, i.e. $CO/H_2/C_2H_4$, reactions were carried out in a stainless steel tube with 3/8 in. o.d. and ≈22 in. in length. The catalyst was placed in the center of the tube and supported on both sides by glass wool. In the case of alkali-promoted and Mo-based catalysts, 0.3 g catalyst was used and the reaction was carried out at $W/F = 0.0012$ g min/cm^3, where W is the catalyst mass in grams and F the total reactant inlet flow rate in cm^3/min. In the case of the Group VIII metals, 0.5 g catalyst and $W/F = 0.002$ g min/cm^3 were used, with the exception of Rh and Ru, for which 0.3 g and $W/F = 0.0012$ g min/cm^3 were used. The tubular reactor was placed in a furnace whose temperature was controlled by an Omega CN-2010 temperature controller. A thermocouple was placed inside the tube in direct contact with the catalyst for accurate temperature measurement. Pressure was controlled by a back-pressure regulator and gas flow rates by Brooks mass flow controllers. All experiments were performed under differential conditions, i.e. under 5% conversion, at 543–548 K and 1 MPa, unless otherwise noted. For the CO hydrogenation experiments, CO and H_2 flows were each 50 cm^3/min. For the $CO/H_2/C_2H_4$ experiments, CO and H_2 flows were each 125 cm^3/min while C_2H_4 flow was 5 cm^3/min. This small amount (i.e. 2%) of ethylene was used with the CO/H_2 stream to minimize the disturbance to CO hydrogenation. The presence of ethylene in the syngas stream allows (1) the CO hydrogenation

Table 1
Typical product selectivity of various Fischer–Tropsch catalysts

Species	Selectivity
I. *Group VIII metals*	Refs.: [2,3,7–18,32]
Fe	(1) linear and branched hydrocarbons — alkanes/alkenes; and (2) oxygenates: 1-alcohols, aldehydes, esters, ketones
Co	linear hydrocarbons —alkanes/alkenes
Ni	methane and hydrocarbons
Ru	methane, hydrocarbons and polyethylene at high pressures
Rh	C_{2+} oxygenates
Pd	MeOH
Pt	MeOH
II. *Mixed oxides*	Refs.: [8,11,16,24–26,32,33]
Zn oxide	promotes MeOH and EtOH formation on Rh
Zr oxide	promotes oxygenate formation on Group VIII metals
V oxide	promotes EtOH formation on Rh
Mn oxide	promotes oxygenate formation on Group VIII metals
Alkali	promotes oxygenate formation on Group VIII metals
Th oxide	(1) hydrocarbons — branched alkanes; and (2) oxygenates —MeOH, $(CH_3)_2O$, branched alcohols
Cr oxide	MeOH and branched alcohols (C_4)
Cu/Zn oxide	MeOH
$CuCoCr_{0.8}K_{0.09}O_x$ (an IFP catalyst)	branched higher alcohols
III. *Coprecipitated Ni-based catalysts*	Refs.: [4,34]
Na-Ni	methane
Alkali-Mn-Na	methane, acetaldehyde
IV. *Mo-based catalysts*	Refs.: [35–37]
Mo	hydrocarbons
Alkali-Mo sulfide	C_1–C_5 linear, primary alcohols
Alkali-Re-W-Mo	C_1–C_4 alcohols

reaction, (2) the C_2H_4/H_2 reaction, i.e. ethylene hydrogenation, and (3) the hydroformylation reaction to occur simultaneously.

Product analysis was performed on a Hewlett–Packard (HP) 5890A gas chromatograph (GC) equipped with a flame-ionization detector (FID) and one six-foot Porapak PS column in series with a six-foot Porapak QS column. Peak areas were determined by an HP 3392A integrator.

3. Results and discussion

Reaction conditions, i.e. temperature, total pressure, reactant partial pressure, and space velocity, have a great influence on the rate of product formation and product selectivity. Reaction conditions of 545 K and 1 MPa, at which Rh-based catalysts exhibit the highest C_{2+} oxygenate selectivity [5], were chosen for comparison of C_{2+} oxygenate activity and selectivity of various catalysts. Table 3 lists the rate of product formation from CO hydrogenation at 545 K and 1 MPa. CH_3OH is a C_1 oxygenate, CH_3CHO and EtOH (i.e. C_2H_5OH) are C_2 oxygenates, and C_2H_5CHO and PrOH (i.e. C_3H_7OH) are C_3 oxygenates.

3.1. Group VIII and sulfur-poisoned group VIII metals

Table 3 shows that Rh/SiO_2, on a per mass basis, was the most active and selective catalyst toward C_2 oxygenates, followed closely in activity by Co and Ru. Ni and Ir showed no activity for C_2 oxygenates and Os exhibited only a trace. In terms of activity, Rh > Ru > Co>Os > Fe = Ni = Ir. Only Co was slightly active for C_3 oxygenates.

Various pathways have been proposed to explain the product formation from CO and H_2. These path-

Table 2
Catalyst preparation method and characterization

Catalyst compositions	Preparation method	Crystallite size [nm]
I. *Group VIII metals*		
I-1. 10 wt.% Fe/SiO_2	precipitation of $FeCl_3·6H_2O$	0–16.5 nm[a]
I-2. 5 wt.% Co/SiO_2	impregnation of $Co(NO_3)_2·6H_2O$	–
I-4. 15 wt.% Ni/SiO_2	impregnation of $Ni(NO_3)_2·6H_2O$	9.2 nm[b]
I-5. 3 wt.% Ru/SiO_2	impregnation of $RuCl_3·2H_2O$	8 nm[b]
I-6. 3 wt.% Rh/SiO_2	impregnation of $RhCl_3·3H_2O$	13 nm[b]
I-7. 3 wt.% Os/SiO_2	impregnation of $H_2OsCl_6·6H_2O$	10 nm[b]
I-8. 3 wt.% Ir/SiO_2	impregnation of $IrCl_3·6H_2O$	9.8 nm[a]
II. *Sulfided group VIII metals*		Sulfur-to-metal molar ratio by EDS
II-1. sulfided 10 wt.% Fe/SiO_2	catalyst subjected to 1000 ppm H_2S in H_2 at 673 K	0.21
II-2. sulfided 5 wt.% Co/SiO_2	catalyst subjected to 1000 ppm H_2S in H_2 at 673 K	0.3
II-3. sulfided 15 wt.% Ni/SiO_2	catalyst subjected to 1000 ppm H_2S in H_2 at 673 K	0.46
II-4. sulfided 3 wt.% Ru/SiO_2	catalyst subjected to 1000 ppm H_2S in H_2 at 673 K	0.12
II-5. sulfided 3 wt.% Rh/SiO_2	catalyst subjected to 1000 ppm H_2S in H_2 at 673 K	0.14
II-6. sulfided 10 wt.% Os/SiO_2	catalyst subjected to 1000 ppm H_2S in H_2 at 673 K	0.11
II-7. sulfided 10 wt.% Fe/SiO_2	catalyst subjected to 1000 ppm H_2S in H_2 at 673 K	0.12
III. *Alkali/Ni coprecipitated catalysts*		BET Surface area [m^2/g]
III-1. Na-Ni	coprecipitation of Na_2CO_3 and $Ni(NO_3)_2·6H_2O$	7.22 m^2/g
III-2. Na-Mn-Ni	coprecipitation of Na_2CO_3, $Ni(NO_3)_2·6H_2O$, and $Mn(NO_3)2·4H_2O$	16.32 m^2/g
III-3. Li-Mn-Ni (? : 0.85 : 1)[c]	coprecipitation of Li_2CO_3, $Ni(NO_3)_2·6H_2O$, and $Mn(NO_3)_2·4H_2O$	12.93 m^2/g
III-4. K-Mn-Ni (0.12 : 0.59 : 1)[c]	coprecipitation of K_2CO_3, $Ni(NO_3)_2·6H_2O$, and $Mn(NO_3)_2·4H_2O$	25.7 m^2/g
III-5. Cs-Mn-Ni (0.0037 : 0.59 : 1)[c]	coprecipitation of Cs_2CO_3, $Ni(NO_3)_2·6H_2O$, and $Mn(NO_3)_2·4H_2O$	26.3 m^2/g
IV. *Mo-based catalysts*		BET Surface area [m^2/g]
IV-1. Ni-Mo/SiO_2 (7.5 : 1.8 : 100)[c]	coimpregnation of $(NH_4)6Mo_7O_{24}·4H_2O$ and $Ni(NO_3)_2·6H_2O$	274.38 m^2/g
IV-2. Ni-K-Mo/SiO_2 (7.1 : 6.5 : 1.5 : 100)[c]	coimpregnation of KCl and $(NH_4)_6Mo_7O_{24}·4H_2O$ followed by $Ni(NO_3)_2·6H_2O$	256.33 m^2/g
IV-3. S-Ni-K-Mo/SiO_2 (30.4 : 7.3 : 8 : 1.2 : 100)[c]	coimpregnation of KCl and $(NH_4)_6Mo_7O_{24}·4H_2O$ followed by $Ni(NO_3)_2·6H_2O$ and $(NH_4)_2S$	221.58 m^2/g
IV-4. K-Co-Mo/SiO_2 (6.2 : 6.2 : 2 : 100)[c]	coimpregnation of $Co(NO_3)_2·6H_2O$ and $(NH_4)6Mo_7O_{24}·4H_2O$ followed by K_2CO_3	–
IV-5. Mo-Co-S (1 : 1.3 : 18.6)[c]	coprecipitation of $(NH_4)_6Mo_7O_{24}·4H_2O$, $(NH_4)_2S$, & Co acetate	–
IV-6. Mo-Fe-S (1 : 1.6 : 6.1)[c]	coprecipitation of $(NH_4)_6Mo_7O_{24}·4H_2O$, $FeSO_4$, & $(NH_4)_2S$	–

[a] Determined by TEM.
[b] Determined by XRD.
[c] Molar ratio of species determined by XRF.

ways have been summarized and linked together in a network form as shown in Fig. 1(a) [6]. The absence of C_1 oxygenates, but presence of C_2 oxygenates in the product stream indicates that C_2 oxygenate formation did not involve C_1 oxygenate species. Thus, the most probable pathway toward C_2 oxygenates over Group VIII metal catalysts is via CO dissociation, hydrogenation, and CO insertion, which is illustrated in Fig. 1(b). The pathway in Fig. 1(b) shows that $^*CH_x$ is a common precursor for either hydrogenation to form CH_4 or CO insertion/hydrogenation to form CH_3CHO, i.e. C_2 oxygenates. Thus, the selectivity of C_{2+} oxygenates can be defined

$$S_{C_2OX} = \frac{C_2 \text{ oxygenate rate of production}}{CH_4 \text{ rate of production}}$$

and

$$S_{C_3OX} = \frac{C_3 \text{ oxygenate rate of production}}{C_2H_6 \text{ rate of production}}$$

Table 3
Product rates of formation (mol/kg h) and CO conversion for CO hydrogenation on all catalysts at ca. 545 K and 1 MPa

	CO Conv.	CH_4	C_2H_4	C_2H_6	C_{3+} HC	CH_3OH	CH_3CHO	EtOH	C_2H_5CHO	PrOH
Group VIII metals										
Fe/SiO_2	0.26	0.10	0.02	0.01	0.025	0.020	0	0	0	0
Co/SiO_2	8.1	1.9	0.19	0.11	1.3	0.030	0.08	0	0.013	0
Ni/SiO_2	37.2	33	0.02	1.35	0.59	0	0	0	0	0
Ru/SiO_2	3.1	0.70	0.078	0.024	0.39	0	0.090	0.011	0	0
Rh/SiO_2	0.69	0.24	0.018	0.0080	0.015	0	0.16	0.016	0	0
Os/SiO_2	0.062	0.03	0.002	0.001	0.003	0	0.008	0	0	0
Ir/SiO_2	0.10	0.102	0.0003	0	0	0	0	0	0	0
Fe/SiO_2 (H_2S treated)	0.022	0.013	0.0002	0	0.0003	0	0.004	0	0	0
Co/SiO_2 (H_2S treated)	0.018	0.016	0.001	0	0	0	0	0	0	0
Ni/SiO_2 (H_2S treated)	0.036	0.036	0	0	0	0	0	0	0	0
Ru/SiO_2 (H_2S treated)	0.038	0.036	0.00046	0	0	0	0	0	0	0
Rh/SiO_2 (H_2S treated)	0.014	0.014	0	0	0	0	0	0	0	0
Os/SiO_2 (H_2S treated)	0.03	0.02	0.004	0.0003	0.0004	0	0	0	0	0
Ir/SiO_2[a] (H_2S treated)	0.13	0.12	0.003	0.0004	0.002	0	0	0	0	0
Alkali/Ni coprecipitated catalysts										
Na-Ni	0.42	0.31	0.04	0.004	0.0022	0	0.0054	0	0	0
Li-Mn-Ni	11.5	7.4	0.05	0.95	0.55	0	0.09	0.04	0.006	0
Na-Mn-Ni	0.73	0.61	0.01	0.008	0.0066	0	0.03	0	0	0
K-Mn-Ni	0.44	0.29	0.01	0.0023	0.0036	0	0.04	0	0.01	0
Cs-Mn-Ni	0.61	0.32	0.04	0.04	0.035	0	0.0052	0.0028	0	0
Mo-based catalysts										
$Ni-Mo/SiO_2$[a]	1.7	0.95	0.06	0.13	0.11	0.07	0	0	0	0
$Ni-K-Mo/SiO_2$[b]	0.55	0.19	0.04	0.02	0.056	0	0	0	0.0062	0
$S-Ni-K-Mo/SiO_2$[b]	0.12	0.06	0.01	0.0067	0.0099	0	0	0	0	0
$K-Co-Mo/SiO_2$[c]	2.7	1.6	0.12	0.24	0.13	0	0	0	0	0
Mo-Co-S	0.28	0.14	0.02	0.02	0.019	0	0	0	0	0
Mo-Fe-S	0.056	0.05	0.0027	0.0042	0	0	0	0	0	0

[a] Run at 513 K
[b] Run at 1.6 MPa.
[c] Run at 4.2 MPa.

which represent the rate ratio of CO insertion to hydrogenation. Fig. 2 shows that the selectivity to C_2 oxygenates decreases in the following order: Rh > Os > Ru > Co > Fe = Ni = Ir. The difference in the C_2 oxygenate activity and selectivity order for Os, Ru, and Co can be attributed to the high rate of formation of CH_x precursor for Ru and Co. High CH_x formation rate would increase the rate, i.e. activity, of formation of all products.

Previous studies have revealed Rh to exhibit high activity for CO insertion [7–12], which is corroborated by this study as well. Ru and Co, both of which are excellent Fischer–Tropsch catalysts, produce C_{2+} hydrocarbons as major products and C_{2+} oxygenates as minor products. Fe catalysts have shown a variety of activities and selectivities. Fe selectivity appears to be very sensitive to catalyst composition and reaction conditions — higher oxygenates at high pressure and low temperature, and hydrocarbons at higher temperatures and lower pressures [13]. Under conditions reported in this study, the activity of higher oxygenates on Fe is quite limited. However, studies have shown Fe to act as an effective promoter for higher alcohol synthesis over Rh catalysts [14,15]. Ni/SiO_2 catalyst shows the highest methanation activity due to its excellent CO dissociation and hydrogenation activity. This has been widely observed in the literature [6,16–18]. There are relatively few studies which address Os and Ir. Even though Os and Ir polynuclear carbonyls have shown to be active and selective for homogeneous oxygenate synthesis under high-pressure conditions

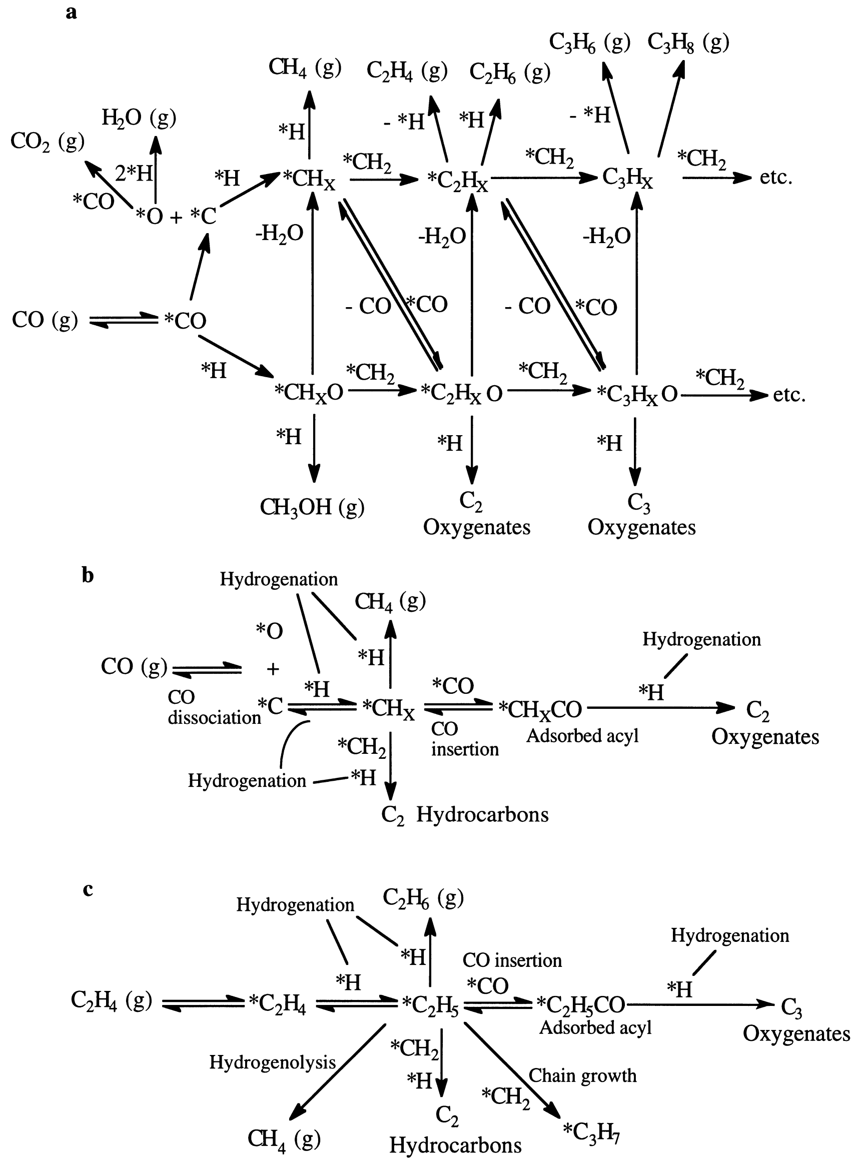

Fig. 1. (a) Proposed reaction network for production of hydrocarbons and oxygenates from the CO hydrogenation reaction. (b) Reaction pathway to C_2 oxygenates from the CO hydrogenation reaction. (c) Reaction pathway to C_3 oxygenates from the $CO/H_2/C_2H_4$ reaction.

[19], their heterogeneous counterparts are primarily inactive.

H_2S-treated catalysts showed little activity for CO hydrogenation. Previous studies have shown sulfur to hinder CO dissociation on the catalyst surface [20]. The electronegative sulfur is thought to make the neighboring atom more electropositive, shifting linearly adsorbed CO to a higher wave number, thus increasing the CO bond order and strengthening the C–O bond [21,22]. It also blocks CO dissociation and hydrogenation sites. Since CO dissociation is the first step of the CO hydrogenation sequence, blocking CO dissociation should stop the entire reaction sequence for product formation.

Table 4 lists the rate of product formation for the $CO/H_2/C_2H_4$ reaction at 545 K and 1 MPa. A

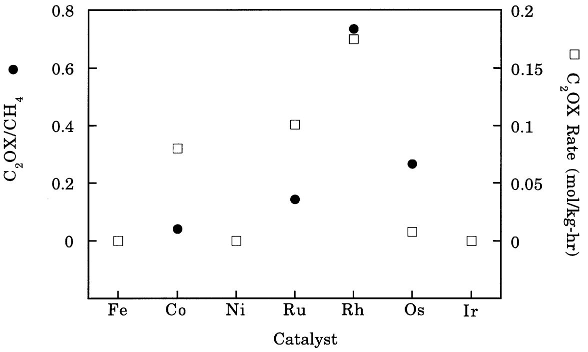

Fig. 2. Activity and selectivity toward C_2 oxygenates from the CO hydrogenation reaction over Group VIII metal catalysts.

comparison of the rates of product formation from $CO/H_2/C_2H_4$ and those from CO/H_2 over Group VIII metals from Table 3 reveals that the addition of ethylene to CO/H_2 caused increases in the rates of ethane and propionaldehyde formation for all the catalysts, as well as increases in methane and C_{3+} hydrocarbon formation for a number of catalysts. Increases in the product formation rates from the ethylene added to CO/H_2 can be explained by participation of ethylene in the following reactions:

1. hydrogenation leading to C_2H_6;
2. CO insertion producing propionaldehyde;
3. hydrogenolysis to CH_4; and
4. chain growth as shown in Fig. 1(c).

Significant increases in the rate of formation of ethane and propionaldehyde suggest that an abundance of sites are available for hydrogenation and CO insertion of ethylene during CO hydrogenation. A slight change in the rate of C_{2+} hydrocarbon formation suggests that the FT chain growth was only slightly disturbed. Thus, addition of ethylene to the reactant stream acts as an effective probe for CO insertion and hydrogenation activities.

Table 4
Product rates of formation (mol/kg-h) and CO conversion for the $CO/H_2/C_2H_4$ reaction on all catalysts at ca. 545 K and 1 MPa

	CO Conv.	CH_4	C_2H_4	C_2H_6	C_{3+}HC	CH_3OH	CH_3CHO	EtOH	C_2H_5CHO	PrOH
Group VIII metals										
Fe/SiO_2	0.15	0.068	0	0.52	0.042	0	0	0	0.019	0
Co/SiO_2	7.4	2.6	0	5.2	2.0	0	0	0	0.32	0.1
Ni/SiO_2	3.5	2.4	0	27	0.33	0	0	0	0.74	0.07
Ru/SiO_2	7.7	2.7	0	7.5	1.9	0	0.32	0.021	1.7	0.23
Rh/SiO_2	4.2	0.58	0	10	0.061	0	0.29	0.042	2.6	0.62
Os/SiO_2	0.072	0.054	0	0.55	0.004	0	0	0	0.017	0
Ir/SiO_2	0.37	0.34	0	0.24	0.001	0	0	0	0.038	0
Fe/SiO_2 (H_2S treated)	0.053	0.034	0	0	0.002	0	0	0	0.017	0
Co/SiO_2 (H_2S treated)	0.28	0.036	0	1.5	0.003	0	0	0	0.24	0
Ni/SiO_2 (H_2S treated)	1.88	0.092	0	2.8	0.0022	0	0	0	1.7	0.066
Ru/SiO_2 (H_2S treated)	0.113	0.095	0	0.12	0	0	0	0	0.018	0
Rh/SiO_2 (H_2S treated)	1.9	0.073	0	2.2	0	0	0	0	1.8	0.085
Os/SiO_2 (H_2S treated)	0.055	0.052	0	0.14	0.003	0	0	0	0	0
Ir/SiO_2 (H_2S treated)	0.37	0.32	0	0.22	0	0	0	0	0.04	0
Alkali/Ni coprecipitated catalysts										
Na-Ni	0.67	0.64	0	0.73	0.0024	0	0.01	0	0.02	0
Li-Mn-Ni	3.74	2.7	0	18	0.29	0.15	0	0	0.61	0
Na-Mn-Ni	1.6	1.1	0	4.7	0.034	0	0.06	0	0.46	0
K-Mn-Ni	0.83	0.69	0	0.22	0	0	0	0.09	0.05	0
Cs-Mn-Ni	0.95	0.58	0	0.25	0.31	0	0.04	0	0.1	0
Mo-based catalysts										
$Ni-Mo/SiO_2$[a]	1.4	0.92	0	18	0.32	0	0.04	0	0.21	0
$Ni-K-Mo/SiO_2$[a]	2.9	0.23	0	4.2	0.6	0.0071	0.46	0.28	0.24	1.12
$S-Ni-K-Mo/SiO_2$[a]	0.5	0.14	0	4.3	0.31	0	0	0	0.09	0
$K-Co-Mo/SiO_2$[b]	0.4	0.22	0	1.13	0.16	0.0054	0.01	0	0.0072	0

[a] Run at 1.6 MPa.
[b] Run at 4.2 MPa.

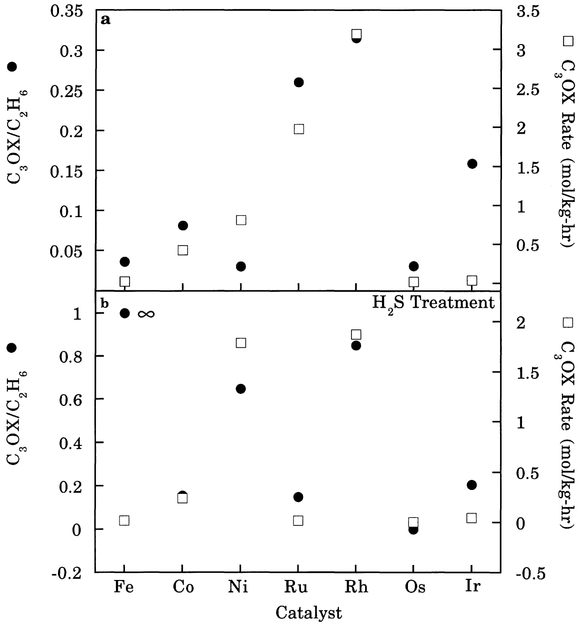

Fig. 3. (a) Activity and selectivity toward C_3 oxygenates from the $CO/H_2/C_2H_4$ reaction over Group VIII metal catalysts. (b) Activity and selectivity toward C_3 oxygenates from the $CO/H_2/C_2H_4$ reaction over H_2S-treated Group VIII metal catalysts.

Fig. 3(a) shows the activity/selectivity of C_3 oxygenates as a result of the $CO/H_2/C_2H_4$ reaction on the Group VIII catalysts. Selectivity for C_3 oxygenates decreased in the order Rh > Ru > Ir > Co > Fe > Os > Ni. The Rh catalyst is considerably more active and selective toward higher oxygenates than the other Group VIII catalysts, reflecting its high CO insertion activity. Both Ru and Co exhibit activity for C_2 oxygenate formation in the CO/H_2 reaction and C_3 oxygenate formation in the $CO/H_2/C_2H_4$ reaction. The activities of Os, Ir, and Fe catalyst are at least one order of magnitude lower than those of other Group VIII catalysts. These metals can be considered inactive for CO insertion, even though some of these metals exhibit some CO insertion selectivity.

Fig. 3(b) shows that after sulfur treatment, the activity of all catalysts dropped, with the exception of Ni. Most catalysts showed substantial improvements in oxygenate selectivity. Examination of C_3 oxygenate formation in Fig. 3(a and b) shows that H_2S treatment caused a slight decrease in C_3 oxygenate formation rate for Rh and Co, but a significant increase in C_3 oxygenate formation rate for Ni catalyst while suppressing the rate of ethane formation. Adsorbed sulfur on the H_2S-treated catalyst is known to not only block CO dissociation sites but also to poison hydrogenation sites through electronic interaction by converting reduced metal to metal cations [7,23]. A combination of these two effects of adsorbed sulfur results in a dramatic increase in C_3 oxygenate formation over Ni/SiO_2, an excellent CO dissociation and hydrogenation catalyst. Inhibition of CO dissociation and hydrogenation capability of Ni caused emergence of its CO insertion activity.

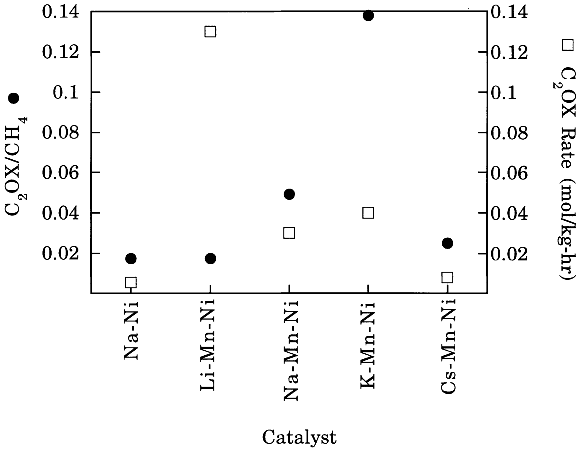

Fig. 4. Activity and selectivity toward C_2 oxygenates from the CO hydrogenation reaction over coprecipitated alkali-Mn-Ni catalysts.

Previous in situ infrared (IR) studies have demonstrated that single Rh^0 and Rh^+ sites as well as single Ni^0 sites are active for CO insertion [5,7,23]. Adsorbed sulfur blocks the pair sites for bridged CO and increases the density of single sites. Design of catalysts populated with single atom or cation sites appears to be a way for improving C_2 oxygenate activity and selectivity.

3.2. Alkali-promoted Mn-Ni and Na-Ni catalysts

Figs. 4 and 5 show the activities/selectivities of C_2/C_3 oxygenates on alkali-promoted Ni catalysts for CO hydrogenation and the $CO/H_2/C_2H_4$ reaction, respectively. The most obvious effect of Na on Ni is the suppression of methanation and formation of C_2 oxygenates. Alkali coprecipitated Ni catalysts produce

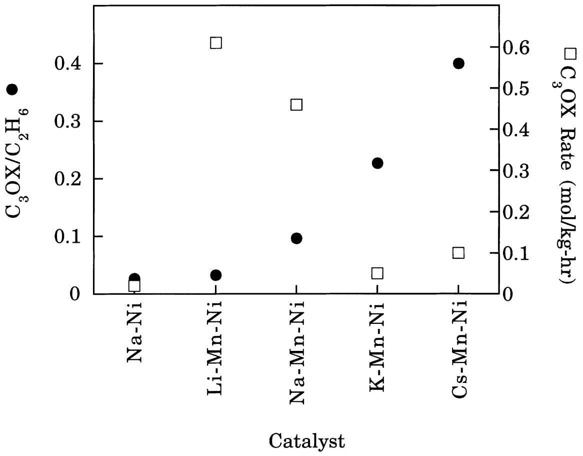

Fig. 5. Activity and selectivity toward C_3 oxygenates from the $CO/H_2/C_2H_4$ reaction over coprecipitated alkali-Mn-Ni catalysts.

more C_2 oxygenates than impregnated alkali Ni catalysts. No clear trend in the effect of various alkali species was observed. Nevertheless, a clear trend in the effect of alkali for C_3 oxygenate selectivity was observed for the $CO/H_2/C_2H_4$ reaction. The selectivity decreased in the order Ce > K > Na > Li. The lack of correlation in oxygenate selectivity between the CO/H_2 and $CO/H_2/C_2H_4$ reactions suggests that $^*CH_x$ in CO hydrogenation and $^*C_2H_5$ in the $CO/H_2/C_2H_4$ reaction do not adsorb on the same type of reaction environment.

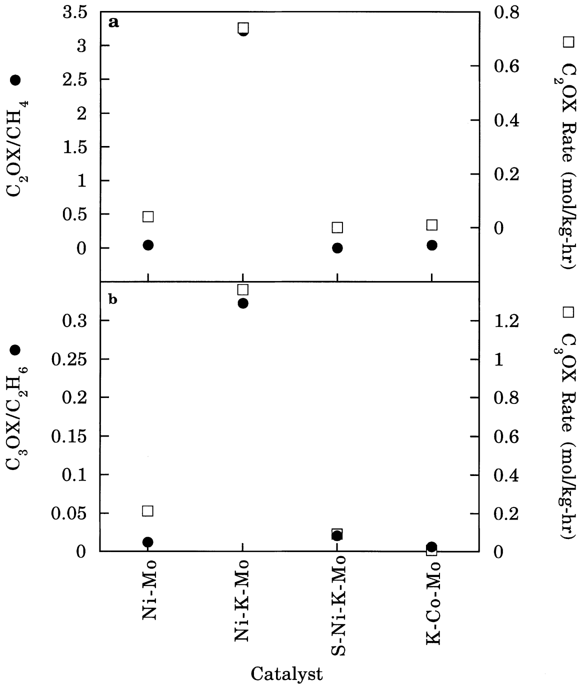

Fig. 6. (a) Activity and selectivity toward C_2 oxygenates from the $CO/H_2/C_2H_4$ reaction over Mo-based catalysts. (b) Activity and selectivity toward C_3 oxygenates from the $CO/H_2/C_2H_4$ reaction over Mo-based catalysts.

It is interesting to note the role of Mn in the reaction. Comparing the Na-Mn-Ni catalyst with the Na-Ni/SiO_2 catalyst for CO hydrogenation and $CO/H_2/C_2H_4$ reaction shows a marked increase in activity. Mn promotion on Rh has been shown to enhance oxygenate activity [11,24] and alkali has been shown to suppress hydrogenation [25]; hence, combined alkali and Mn would be expected to provide synergetic promotion of oxygenate formation. MnO has been proposed to serve as an oxophilic promoter which interacts with the oxygen end of adsorbed CO on Group VIII metal sites, facilitating CO dissociation and CO insertion [26]. The Mn-promotion of CH_x formation has been further verified by temperature-programmed reaction (TPR) [26]. In a study of hydroformylation on Mn-Rh/SiO_2, its role in CO insertion was found to be due to modification of the rate-limiting step for propionaldehyde formation [27].

3.3. Mo-based catalysts

Fig. 6 reports the activities/selectivities of Mo-based catalysts for higher oxygenates from the $CO/H_2/C_2H_4$ reaction. All Mo-based catalysts exhibited nil or nearly nil activity for higher oxygenates via CO hydrogenation; however, these catalysts showed some activity and selectivity for C_3 oxygenates in the $CO/H_2/C_2H_4$ reaction.

Although Mo-based catalysts have shown promise in commercial applications for higher oxygenate synthesis at pressures up to 18 MPa [2], the overall activity of these catalysts remained poor relative to the Group VIII and alkali-promoted Ni catalysts at 1 MPa. This is likely due to the fact that this study did not utilize pressures high enough to drive activity and selectivity toward the path of higher oxygenates.

3.4. Effect of temperature and pressure on oxygenate selectivity

The activity and selectivity of a catalyst for the CO/H_2 and $CO/H_2/C_2H_4$ reactions are a complex function of catalyst composition and reaction conditions. Our previous studies [4,28,29] showed that an increase in temperature from 543 to 573 K results in decreasing selectivity toward CO insertion, decreasing oxygenate selectivity, and increasing hydrocarbon selectivity. Decreasing total pressure from 1 MPa to 0.1 MPa decreases oxygenate selectivity. CO hydrogenation at 0.1 MPa has long been known to primarily produce hydrocarbons [3,17]. High total pressure favors CO insertion leading to C_{2+} oxygenate formation. Our previous ^{13}CO isotopic transient study found that increasing total pressure increased the rate of acyl hydrogenation, the rate-limiting step for C_3 oxygenate formation from the $CO/H_2/C_2H_4$ reaction [30].

3.5. *Reaction pathway and catalyst activity/selectivity*

The rate-limiting step for C_2 oxygenate synthesis from CO hydrogenation may be elucidated by comparing the rate of C_2 oxygenate formation from Table 3 to the rate of C_3 oxygenate formation from Table 4. A comparison shows that the rate of C_3 oxygenate formation is, on average, much higher than the rate of C_2 oxygenate formation. C_2 and C_3 oxygenates are produced from analogous intermediates, i.e. the $^{*}CH_x$ species in Fig. 1(b) and the $^{*}C_2H_5$ species in Fig. 1(c), respectively. Both undergo CO insertion and hydrogenation to form the final product. Thus, the difference in rate of oxygenate formation must be due to the slow production of $^{*}CH_x$ precursor from CO dissociation and subsequent carbide hydrogenation, indicating that either CO dissociation or hydrogenation of the carbide species is the actual rate-limiting step. Therefore, enhancement of the rate of C_2 oxygenate formation requires (1) enhancement of CO dissociation to produce CH_x for CO insertion, and (2) enhancement of the CO insertion step.

An $Mn\text{-}Rh/SiO_2$ catalyst has been identified to be the most active for C_2 oxygenate formation of any binary catalyst [31]. Mn is thought to promote CO dissociation and CO insertion activity. Promotion of CO dissociation would increase the concentration of CH_x precursor, increasing the rate of formation of all products.

While improvement of the rate of product formation is important, enhancement of the selectivity is essential for further commercial development of a catalytic process. However, an intrinsic limitation in improving C_2 and C_3 oxygenate selectivity and selectivity is implied by the reaction pathways shown in Fig. 1(b and c). These figures suggest that improvement of oxygenate selectivities requires suppression of hydrogenation. However, suppression of hydrogenation would also decrease the rate of formation of CO insertion precursor, i.e. $^{*}CH_x$ and $^{*}C_2H_5$, and decrease the rate of hydrogenation of adsorbed acyl species, resulting in a decrease in C_2 and C_3 oxygenate formation rate.

Optimization of activity and selectivity toward C_2 oxygenates requires a proper balance of the rate of CO dissociation, CO insertion, and hydrogenation. The optimum catalyst developed thus far is an $Rh\text{-}Mn\text{-}Zr\text{-}Li/SiO_2$ catalyst. This catalyst exhibits the highest overall C_2 oxygenate selectivity of any catalyst, i.e. >80% [31]. The role of Zr is the promotion of CO dissociation and the role of alkali, in this case Li, is the suppression of hydrogenation.

Use of modified methanol synthesis catalysts favors the bottom pathway of Fig. 1(a) to produce C_2 and C_3 oxygenates:

$$^{*}CH_xO \overset{^{*}CH_2}{\rightarrow}{}^{*} C_2H_xO \overset{^{*}CH_2}{\rightarrow}{}^{*} C_3H_xO \overset{^{*}CH_2}{\rightarrow}{}^{*} etc.$$

In this pathway, though, the majority of $^{*}CH_xO$ is converted to CH_3OH, instead of participating in chain growth to form C_{2+} oxygenates. It appears that there is no single-step process for highly selective synthesis of C_2 oxygenates from synthesis gas. High selectivity toward C_2 oxygenates at present can be achieved by methanol synthesis and subsequent carbonylation of methanol. However, none of these processes allow economical production of fuel-grade C_{2+} oxygenates which can compete with non-syngas processes.

4. Conclusions

Group VIII, Ni-based, and Mo-based catalysts exhibited a wide range of activity and selectivity for C_2 oxygenate synthesis. The selectivity toward C_2 oxygenates is attributed to the CO insertion capability of the catalyst. All of the catalysts tested, except H_2S-treated Os, exhibited CO insertion activity in the $CO/H_2/C_2H_4$ reaction leading to C_3 oxygenate formation. Rh and Ru exhibited exceptionally high activity and selectivity for C_2 oxygenates in the CO/H_2 reaction and C_3 oxygenates in the $CO/H_2/C_2H_4$ reaction. Sulfur treatment of the catalysts poisoned CO dissociation and hydrogenation capability to various degrees for the Group VIII catalysts. The most dramatic effect of sulfur treatment was the increase in CO insertion activity for the Ni catalyst. H_2S-treated Ni catalysts exhibited high activity and selectivity for C_3 oxygenates in the $CO/H_2/C_2H_4$ reaction.

No clear trend in the effect of various alkali species on the coprecipitated Ni-based catalysts was observed for the production of C_2 oxygenates by CO hydrogenation. However, a clear trend in the effect of alkali for C_3 oxygenate selectivity was observed for the $CO/H_2/C_2H_4$ reaction. The selectivity decreased in the order $Ce > K > Na > Li$. Lack of correlation between C_2 oxygenate selectivity in the CO/H_2 reaction and C_3 oxygenate selectivity in the $CO/H_2/C_2H_4$ reaction suggests that $^*CH_x$ in CO hydrogenation and $^*C_2H_5$ in the $CO/H_2/C_2H_4$ reaction do not adsorb on the same type of reaction environment. Mo-based catalysts showed the poorest activity and selectivity toward higher oxygenates at 1 MPa.

The formation of CH_x is a rate-limiting step for the synthesis of C_2 oxygenates from syngas. Increase in the rate of C_2 oxygenated and hydrocarbon product formation can be achieved by enhancement of CO dissociation and hydrogenation. However, enhancement of hydrogenation would cause a decrease in C_2 oxygenate selectivity. Thus, a proper balance in the rate of CO dissociation, CO insertion, and hydrogenation is required to optimize the C_2 oxygenate activity and selectivity of a catalyst.

Acknowledgements

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