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La and/or V oxide promoted Rh/SiO_2 catalysts: Effect of temperature, H_2/CO ratio, space velocity, and pressure on ethanol selectivity from syngas

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ABSTRACT

CO hydrogenation to ethanol was carried out over $Rh(1.5)/SiO_2$ promoted with La and/or V oxides. Recent results at 230 °C and 1.8 bar have shown 21% ethanol selectivity for the doubly promoted $Rh–La/V/SiO_2$. Here, we extend this work to examine the effects of reaction conditions – temperature, H_2/CO ratio, space velocity, and pressure – on the activity and selectivity of these catalysts. An ethanol selectivity of 51.8% (close to the highest literature value) at a CO conversion of 7.9% was achieved with a corresponding methane selectivity of 15.4% at 270 °C, 14 bar and $H_2/CO = 2$ over the $Rh–La/V/SiO_2$ catalyst. Combined La/V promotion reduces methane selectivity and increases C_{2+} oxygenates selectivity compared to the singly promoted catalysts by increasing the rate of CO insertion. Contrary to literature studies, higher pressures led to a dramatic increase in methane selectivity at the expense of ethanol, indicating increased CO dissociation activity at higher pressures, leaving fewer active CO molecules for insertion. The chain growth factor (α) for higher oxygenates differed significantly from that for hydrocarbons, suggesting that formation of these two types of products either proceeds by different mechanisms or on different active sites.

1. Introduction

The catalytic hydrogenation of CO is one of the most promising technologies for the synthesis of ethanol and higher alcohols from syngas, which can be derived from coal, biomass, or natural gas. Among the potential end products of coal/biomass gasification, ethanol is particularly attractive since it serves as a clean alternative fuel, a gasoline blend, and a hydrogen carrier [1].

Supported Rh-based catalysts have the highest activity and selectivity for the formation of ethanol and other C_{2+} oxygenates due to their ability to catalyze both CO dissociation and CO insertion [2–6]. For example, Hu et al. recently reported 56% selectivity to ethanol on a 6% $Rh–Mn/SiO_2$ powdered catalyst [7]. The most relevant feature of Rh is its ability to adsorb reactive CO both associatively and dissociatively, allowing it to form both hydrocarbons and oxygenates. Novel materials such as carbon nanotube-based Rh catalysts [8], Cu–Co-based nanoparticles [9], electrodeposited Cu–Zn-based nanowires [10], and Rh catalysts in microchannel reactors [7] have also been reported recently for this reaction.

The general mechanism of C_{2+} oxygenate formation from syngas has been extensively studied [2,4,11–13]. CO dissociation is believed to be the first step in the synthesis of C_{2+} oxygenates from syngas. The resulting surface carbon is then hydrogenated to form a surface hydrocarbon species, $(CH_x)_{ads}$. This $(CH_x)_{ads}$ species can then undergo: (a) CO insertion to form oxygenates, or (b) hydrogenation to form methane, or (c) chain growth to form higher hydrocarbons. In a parallel reaction sequence, associatively adsorbed CO can be hydrogenated directly to form methanol [11,14,15]. Methane is the most thermodynamically favored product but is economically undesirable. Thus, hydrocarbon formation, which typically accompanies high catalyst activity, must be suppressed kinetically to maximize the ethanol selectivity.

The influence of various promoters on the catalytic activity of Rh has been extensively studied in recent years. It is proposed that the carbon atom of a CO molecule binds to the Rh atom and the oxygen atom binds to a neighboring promoter cation (tilt-adsorbed CO species) which can either weaken the C–O bond resulting in CO dissociation or promote CO insertion [16–22]. Lanthana and vanadia promoters have been reported to enhance the formation of C_{2+} oxygenates by assisting in CO dissociation and/or insertion [23,24]. Vanadia has also been found to improve the activity and selectivity toward ethanol by enhancing the hydrogenation of acyl intermediates [25,26].

Here, a series of La and/or V oxide promoted Rh/SiO_2 catalysts were tested for CO hydrogenation in a fixed bed microreactor system at various conditions. This present research is an extension of the work of Gao et al. [27] on these Rh/SiO_2 catalysts. The focus of

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the present study was to investigate the impact of temperature, pressure, H_2/CO ratio, and space velocity on the activity and selectivity of these lanthanum and/or vanadium oxide-promoted Rh/SiO_2 catalysts.

2. Experimental

2.1. Catalyst synthesis

A series of La and/or V oxide-promoted Rh/SiO_2 catalysts were synthesized using co-sequential impregnation techniques [27]. Four catalysts, namely unpromoted Rh(1.5)/SiO_2, singly promoted Rh(1.5)/V(1.5)/SiO_2 and Rh(1.5)–La(2.6)/SiO_2, and doubly promoted Rh(1.5)–La(2.6)/V(1.5)/SiO_2 were synthesized. The numbers in the parenthesis indicate the weight percentage relative to the initial weight of the support material. For V-containing catalysts, sequential impregnation was chosen in order to be consistent with the literature for comparison purposes [28–30]. For lanthana-promoted Rh catalysts, co-impregnation of the La additive with Rh was adopted since it is believed that this method forms well-dispersed Rh particles without being fully covered by La_2O_3 [27].

2.2. CO hydrogenation reaction

CO hydrogenation was performed in a fixed bed microreactor. The catalyst was loaded between quartz wool and axially centered in the reactor tube, with the temperature monitored by a thermocouple. Prior to reaction, the catalyst was reduced at 500 °C in flowing 75% H_2/He for 1 h at atmospheric pressure. Then, gas flow was switched to a H_2/CO mixture at the reaction temperature and pressure and the reaction started. The products were analyzed for both oxygenates and hydrocarbons in an Agilent GC 6890 equipped with MSD and TCD.

Product selectivities are reported in terms of carbon efficiencies which is defined as,

$$\text{Carbon efficiency} = n_i C_i / \Sigma(n_i C_i)$$

where n_i is the number of carbon atoms and C_i is the molar concentration of the carbon-containing products.

Calibration of the GC/MS was carried out using standard gas mixtures (Air Liquide, Houston, TX) containing certified concentrations of each product gas. Multiple calibration injections were made prior to each experiment, and the errors reported here are based on 95% confidence limits.

Carbon balances for each run were made using measured flow rates and specified concentrations of the inlet gases and measured total flow rates and concentrations of the outlet gases.

3. Results and discussion

3.1. Characterization

The characterization results of the same La–V-promoted Rh/SiO_2 catalysts studied here have been reported by Gao et al. [27] and Mo et al. [31]. In summary, the BET surface areas of all the Rh-based catalysts were roughly 245 m^2/g. XRD patterns of the as-prepared or 500 °C reduced catalysts showed no crystalline phases, indicating that Rh, lanthana, and vanadia were all highly dispersed. The XRD results were confirmed by TEM which showed evenly dispersed Rh clusters with particle sizes around 3 nm for the unpromoted Rh/SiO_2 catalyst. However, for the La- and V-promoted catalysts, no clear image of Rh clusters could be identified. CO chemisorption experiments showed that La addition to Rh increases CO adsorption, while V addition resulted in a decrease in both total and irreversible CO chemisorption [27], consistent with the literature [30,32].

FTIR results show that La enhanced total CO adsorption and created new active sites for the reaction, whereas the addition of V suppressed CO adsorption and enhanced the desorption rate and/or reactivity of CO on the catalytic surface [31]. The doubly promoted Rh–La/V/SiO_2 showed only moderate CO adsorption which may be due to the combined effects of both promoters. Also, FTIR study of CO desorption and hydrogenation on different catalysts indicated the presence of both linear Rh–CO [CO(l)] and tilted Rh–CO [CO(t)] on the more active catalysts [31].

3.2. Effect of reaction temperature

Because methane is the thermodynamically favored product at all temperatures [1], methanation must be kinetically limited in order to increase the ethanol yield and selectivity. The reaction temperature has a significant effect on the rate and selectivity of ethanol formation. Table 1(a) and (b) summarizes the effects of temperature (230 °C and 270 °C) on the product selectivities of the unpromoted and La and/or V oxide-promoted Rh/SiO_2 catalysts at 20 bar with a space velocity of 18,000 scc/(h gcat) and H_2/CO = 2.

The two singly promoted catalysts showed increased CO conversion rates and selectivity to methanol and decreased methane selectivity compared to the unpromoted Rh/SiO_2 catalyst at both temperatures. However, vanadium suppressed methane formation to a greater extent than lanthanum at both temperatures. Lanthanum increased the selectivity to ethanol at both temperatures, whereas ethanol selectivity decreased with vanadium promotion at 230 °C but increased at 270 °C. The increased selectivity toward ethanol is perhaps due to the fact that La and V enhance both CO dissociation and CO insertion [2,33]. Winslow and Bell have demonstrated that CO dissociation does not occur readily over unpromoted Rh catalyst, even at elevated temperatures [34]. This accounts for the lower activity of unpromoted Rh and explains the higher ethanol selectivity for the La- and V-promoted catalysts, which may be due to an enhancement in the CO dissociation rate for the promoted catalysts [4,35].

At the conditions reported in Table 1, the doubly promoted Rh–La/V/SiO_2 catalyst showed the highest ethanol selectivity (39%) and CO hydrogenation rate (about six times higher than that of Rh/SiO_2) compared to the unpromoted and singly promoted catalysts, making it the most active/selective catalyst for ethanol formation among the four catalysts tested at these conditions. This same catalyst was found to exhibit the highest activity and selectivity at low pressure (1.8 bar) and 230 °C as well [27]. At 270 °C, Rh–La/V/SiO_2 has an ethanol selectivity $\sim$3.6 times higher than that for methane. This may be attributed to the combined effects of both promoters. At 270 °C, both La and V promoters also suppress the formation of acetaldehyde and enhance the formation of ethanol, which is in agreement with various literature reports that suggest that acetaldehyde is a precursor of ethanol [36–38]. Hence, La and V promoters, when coupled together, enhance the rate of hydrogenation of acetaldehyde and of non-dissociated CO to a greater extent than the CO dissociation rate, thus leading to higher ethanol and methanol selectivities.

3.3. Effect of reaction conditions on CO hydrogenation over Rh–La/V/SiO_2

It is obvious from the effect of reaction temperature that the addition of La and/or V oxide promoters to Rh/SiO_2 can significantly change the activity and selectivity for CO hydrogenation. At 270 °C, the doubly promoted Rh–La/V/SiO_2 catalyst showed the highest ethanol selectivity. The remaining work reported here focuses on exploring the effects of H_2/CO ratio, space velocity, and

Table 1
Effect of temperature on the steady-state product selectivities of Rh/SiO_2-based catalysts.

Catalyst[a]	Rate of CO conversion (μmoles/gcat/s)	Selectivity (% C)[c]					
		CO_2	CH_4	MeOH	EtOH	C_{2+} Oxy[d]	C_{2+} HC[e]
(a) Product selectivities of Rh/SiO_2-based catalysts at 230 °C[b]							
Rh(1.5)/SiO_2	0.03	13.3	56.0	9.2	7.9	10.4	3.3
Rh(1.5)/V(1.5)/SiO_2	0.06	9.7	42.0	30.0	2.5	15.2	0.6
Rh(1.5)–La(2.6)/SiO_2	0.29	1.5	50.2	33.2	8.1	5.0	1.9
Rh(1.5)–La(2.6)/V(1.5)/SiO_2	0.13	8.8	22.5	44.0	18.6	5.4	0.7
(b) Product selectivities of Rh/SiO_2-based catalysts at 270 °C[b]							
Rh(1.5)/SiO_2	0.12	3.7	45.5	7.9	16.7	25.7	0.6
Rh(1.5)/V(1.5)/SiO_2	0.32	4.3	17.9	32.0	25.6	19.4	0.9
Rh(1.5)–La(2.6)/SiO_2	0.59	2.1	24.5	27.5	31.8	14.1	0.05
Rh(1.5)–La(2.6)/V(1.5)/SiO_2	0.69	7.1	10.8	30.0	39.0	10.3	3.0

[a] The numbers in the parenthesis indicate the weight percentage relative to the initial weight of the support material.

[b] Catalyst: 0.2 g; reaction conditions: P = 20 bar, H_2/CO = 2, S.V. = 18,000 scc/(h gcat). 95% confidence limits (relative to the absolute values reported) on selectivities are less than ±0.4% for all values except CO_2 (within ±3%) and CH_4 (within ±6%). Product selectivities varied no more than ±5% upon repetition of the 230 °C run. Carbon balances on all runs are within 0.5%.

[c] Product selectivities are reported in terms of carbon efficiencies defined as: carbon efficiency = $n_iC_i/\Sigma(n_iC_i)$, where n_i is the number of carbon atoms and C_i is the concentration of the carbon-containing products.

[d] Oxygenates with two or more carbons except ethanol (acetaldehyde, acetone, *i*-propanol, *i*-butanol, *n*-propanol, and *n*-butanol).

[e] Hydrocarbons with two or more carbons (ethane, propane, *i*-butane, *n*-butane, *n*-hexane, and propylene).

pressure on the most active/selective catalyst (Rh–La/V/SiO_2) at T = 270 °C.

3.3.1. Effect of H_2/CO ratio

Coal-derived syngas has a H_2/CO ratio of ~0.7, which can be adjusted via the water gas shift reaction to that required for ethanol synthesis. Higher H_2/CO ratios may lead to the formation of hydrocarbons, particularly methane [1], while at lower H_2/CO ratios, higher oxygenate selectivity would be expected [39].

Table 2 shows the effect of H_2/CO ratio on the conversion and selectivity of the Rh–La/V/SiO_2 catalyst at 14 bar and 270 °C. When the H_2/CO ratio was raised from 2 to 4, the CO conversion increased and CO_2 selectivity decreased, which suggests that water gas shift reaction is not significant for higher H_2/CO ratios and thus CO_2 selectivity decreased. The increase in CO conversion was accompanied by a substantial increase in the selectivity to methane, but a sharp decline in the selectivity to higher hydrocarbons. A slight, but statistically significant, decrease in ethanol selectivity was observed when the H_2/CO ratio was increased from 2 to 4. However, the ratio of ethanol selectivity with respect to that of methane was still >1. Thus, it is clear that on Rh–La/V/SiO_2 catalyst, lower H_2/CO ratios suppress methane formation, probably by decreasing the rate of hydrogenation of CH_x-type species to form methane [39].

Table 3 shows the effect of H_2/CO ratio on the ethanol/methane point selectivity ($S = r_{\mathrm{EtOH}}/r_{\mathrm{CH_4}}$). Although the rate of formation of ethanol and methane both increase with H_2/CO ratio, consistent with the results of Egbebi and Spivey on Rh–Li–Mn/TiO_2 [40], the results here differ from [40], in that the point selectivity here decreases with H_2/CO ratio because the rate of ethanol formation increases less than that of methane with increasing H_2/CO ratio. Thus, excess H_2 does not increase the point selectivity in the case of La–V-promoted Rh/SiO_2 catalysts, which differs from previous literature findings for other Rh-based catalysts [40].

Table 2
Effect of H_2/CO ratio on the product selectivities of Rh–La/V/SiO_2 catalyst.[a]

Results	H_2/CO = 2	H_2/CO = 4
Rate of CO conversion (μmoles/gcat/s)	2.9	3.2
CO conversion (%)	7.9	8.5
Selectivity (% C)		
CO_2	3.1	1.9
CH_4	15.4	25.7
MeOH	5.0	6.9
EtOH	51.8	49.1
C_{2+} Oxy	19.1	15.6
C_{2+} HC	5.7	0.8

[a] Catalyst: 0.2 g; reaction conditions: T = 270 °C and P = 14 bar. 95% confidence limits (as absolute values) on selectivities are less than ±0.2% for all values except CO_2 (±1.5%) and CH_4 (±5%). Carbon balances are within 4% on all runs.

Table 3
Effect of H_2/CO ratio on the EtOH/CH_4 point selectivity for Rh–La/V/SiO_2 catalyst.[a]

Results	H_2/CO = 2	H_2/CO = 4
r_{EtOH} (μmoles/gcat/s)[b]	47.5	68.5
$r_{\mathrm{CH_4}}$ (μmoles/gcat/s)[b]	28.0	72.0
Point selectivity ($S = r_{\mathrm{EtOH}}/r_{\mathrm{CH_4}}$)	1.70	0.95

[a] Catalyst: 0.2 g; reaction conditions: T = 270 °C and P = 14 bar; molar selectivities used for calculations.

[b] The rate of formation of species i is calculated as: $r_i = \frac{(M_i * F)}{(22414*60*100*W)} \frac{\mathrm{mol}}{\mathrm{gcat\ s}}$, where M_i is the mole% selectivity of product i detected, F is the total flow rate of reactant gases in cm^3/min and w is the weight of catalyst in g.

3.3.2. Effect of space velocity

Fig. 1 shows the product selectivities (mole%) and CO conversions measured at 14 bar and 270 °C with a H_2/CO ratio of 2 for three space velocities. All selectivities are far from equilibrium values [9] and are therefore determined by kinetics. Assuming the reaction network described in the literature [1,11,41], the molar selectivities to methanol and methane would be expected to be relatively high at high space velocities since these products are formed initially in the reaction network by hydrogenation of (i) associatively adsorbed CO (forming methanol) and (ii) dissociatively adsorbed CO (forming CH_4). Fig. 1 shows this to be the case at the highest space velocity, 36,000 scc/(h gcat) (note that the selectivities in Fig. 1 are mole%, not carbon efficiencies as presented in other sections). At this space velocity, the CO conversion is 0.3%, so the selectivities measured at this condition represent essentially initial reaction conditions.

As the space velocity decreases from 36,000 to 9000 scc/(h gcat), CO conversion increases from 0.3% to 8%, while the selectivities to ethanol and C_{2+} oxygenates also increase at the expense of methanol and methane. This is consistent with the same reaction network described above, in which ethanol is formed by CO insertion into a surface CH_x intermediate that can also be hydrogenated in a parallel step to form methane. At 9000 scc/(h gcat), the increase in ethanol selectivity is apparently due to a higher relative

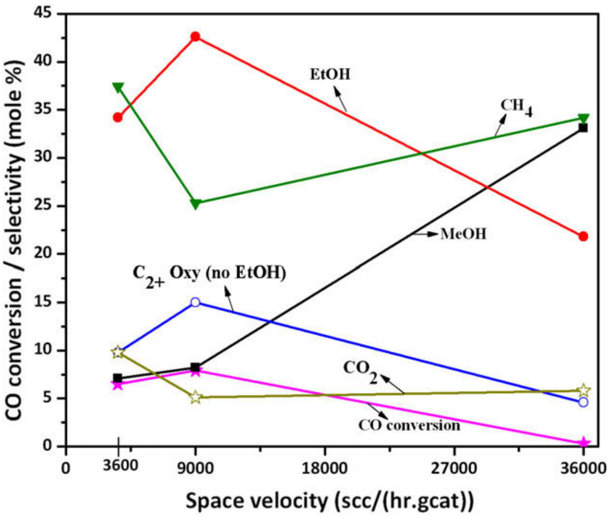

Fig. 1. Effect of space velocity on CO conversion/molar selectivity (mole%) of Rh–La/V/SiO$_2$ catalyst at 14 bar, 270 °C, and H$_2$/CO = 2. The 95% confidence limits on selectivities are less than ±0.4% for all values except CO$_2$ (within ±3%) and CH$_4$ (within ±6%).

Table 4
Effect of pressure on the product selectivities of Rh–La/V/SiO$_2$ catalyst.[a]

Results	$P = 14$ bar	$P = 40$ bar
Rate of CO conversion (μmoles/gcat/s)	0.43	0.60
Selectivity (% C)		
CO$_2$	4.5	2.1
CH$_4$	26.7	42.8
MeOH	25.9	30.7
EtOH	34.1	17.4
C$_{2+}$ Oxy	8.0	6.1
C$_{2+}$ HC	0.9	0.9

[a] Catalyst: 0.5 g; reaction conditions: $T = 270$ °C, H$_2$/CO = 2 and S.V. = 36,000 scc/(h gcat). 95% confidence limits (as absolute values) on selectivities are less than ±0.3% for all values except CO$_2$ (±2%) and CH$_4$ (±5%).

rate of CO insertion versus CH$_x$ hydrogenation. Thus, the product distribution shifts toward oxygenates, mainly ethanol, thereby reducing the undesired side reactions (essentially CH$_4$ formation).

At the lowest space velocity, there is a small but statistically significant decrease in CO conversion from 8% to 6.5%, accompanied by a small but also significant increase in CO$_2$ selectivity. These results cannot be due to the shift reaction. Methanol selectivity is relatively unchanged between 9000 and 3600 scc/(h gcat), but methane selectivity increases at the expense of ethanol and C$_{2+}$ oxygenates. This may be due to a greater extent of ethanol dehydrogenation to form acetaldehyde which further decomposes into CO and CH$_4$, as proposed by Frusteri and Freni [42]. This explains the observed increase in methane selectivity at the expense of ethanol as well as a drop in apparent CO conversion due to the formation of more CO. Also, the increase in methane selectivity, decrease in C$_{2+}$ oxygenate selectivity, and small change in methanol and CO$_2$ selectivities from 9000 to 3600 scc/(h gcat) are qualitatively identical to those of Mazzocchia et al. [43] for a 1.4% Rh/ZrO$_2$ catalyst at space velocities estimated (assuming a catalyst bulk density of 0.5 g/cc) to be 1500 and 15,000 scc/(h gcat), comparable to the lower two space velocities investigated here.

Also, the selectivities of ethanol and C$_{2+}$ oxygenates followed similar trends with space velocity (Fig. 1), suggesting that they share a common intermediate, whereas methane and ethanol followed completely opposite trends, suggesting that they are formed by parallel reactions, consistent with the results reported elsewhere [11].

3.3.3. Effect of pressure

Increasing pressure increases the equilibrium concentration of ethanol from the hydrogenation of CO [11], but our results show ethanol selectivity was greater at 14 bar than at 40 bar (Table 4). Although the rate of CO conversion increased with pressure, consistent with Hu et al. [7], the selectivity to undesired methane was greater at 40 bar compared to 14 bar, while ethanol selectivity decreased at 40 bar. These results are contrary to previous literature reports [7,11]. For instance, Hu et al. [7] reported that increasing the pressure reduced methane selectivity (and increased oxygenate selectivity), while increasing the CO conversion over a Rh–Mn–V/SiO$_2$ catalyst at 270 °C (GHSV = 1700 h^{-1}, H$_2$/CO = 1).

This suggests that on the Rh–La/V/SiO$_2$ catalyst, the hydrogenation rate of (CH$_x$)$_{ads}$ species to form methane, compared to the rate of CO insertion into metal–(CH$_x$)$_{ads}$ surface species to form C$_{2+}$ oxygenates, is greater at 40 bar than at 14 bar. Thus, increasing the total pressure seems to have reduced the effective concentration of activated, non-dissociated CO on the surface. This is likely due to a difference in the nature of the active sites, caused by the promoters [31]. In other words, the rate of CO dissociation appears to increase at higher pressures, leaving fewer active CO molecules for insertion. This, in turn, results in higher rate of hydrogenation of CH$_x$-type species to methane, thus decreasing the ethanol selectivity. This is consistent with the literature, which shows that ethanol formation requires a certain balance of dissociated and non-dissociated surface CO species [39].

Table 5 compares the results of recently reported Rh-based promoted catalysts [7,44] with the Rh–La/V/SiO$_2$ catalyst studied here. It can be seen that the doubly promoted Rh–La/V/SiO$_2$ catalyst led to 51.8% ethanol selectivity, which is comparable to the highest values in the literature [7]. The C$_{2+}$ oxygenate (not including ethanol) selectivity (19%) was also very high on this catalyst. The most remarkable feature is the low methane selectivity on the Rh–La/V/SiO$_2$ catalyst. The high ethanol selectivity of the Rh–La/V/SiO$_2$

Table 5
Comparison of Rh–La/V/SiO$_2$ catalyst with catalysts from literature.

Catalyst	CO conversion (%)	Selectivity (% C)					Ref.
		CO$_2$	CH$_4$	MeOH	EtOH	C$_{2+}$ Oxy	
Rh(6)–Mn(1.5)/SiO$_2$[a]	24.6	0	38.4	3.9	56.1	1.6[d]	[7]
Rh(6)–Mn(1.5)–K(3)/SiO$_2$[a]	15.6	0	27.4	27.8	44.3	0.5[d]	[7]
Rh(1.0)–Sm(0.1)–V(0.5)/SiO$_2$[b]	5.4	–	39[e]	10.6	28.9	1.7	[44]
Rh(1.5)–La(2.6)/V(1.5)/SiO$_2$[c]	7.9	3.1	15.4	5.0	51.8	19.1	[This paper]

[a] $T = 280$ °C, $P = 54$ bar, S.V. = 3750 h^{-1}, H$_2$/CO = 2.

[b] $T = 280$ °C, $P = 30$ bar, S.V. = 13,000 h^{-1}, H$_2$/CO = 2.

[c] $T = 270$ °C, $P = 14$ bar, S.V. = 9000 scc/(h gcat), H$_2$/CO = 2.

[d] C$_{2+}$ hydocarbons and oxygenates.

[e] Total hydrocarbons.

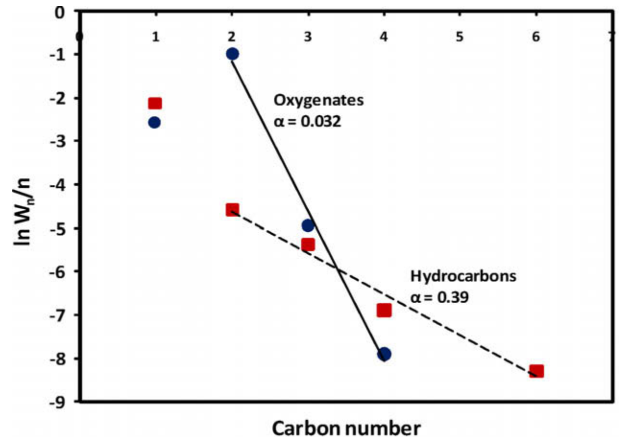

Fig. 2. ASF plot for Rh–La/V/SiO_2 catalyst at 14 bar, 270 °C, H_2/CO = 2, and S.V. = 9000 scc/(h gcat) – hydrocarbons are represented by square symbols, and oxygenates are represented by circles.

catalyst appears to be due to a synergistic promoting effect of lanthana and vanadia, modifying both chemisorption and catalytic properties [27].

3.3.4. ASF analysis

The Anderson–Schulz–Flory (ASF) product distribution for the formation of oxygenates and hydrocarbons is shown in Fig. 2. The C_1 compounds (methanol and methane) are shown in the plot but are not included in the chain growth probability calculations. The C_{2+} hydrocarbons and alcohols/oxygenates product distributions obey the ASF distribution, at least over the limited range of the data here. However, the chain growth probability factor (α) values are very different for hydrocarbons and oxygenates, suggesting that the reactions leading to these products may either proceed by different mechanisms or on different active sites.

The oxygenate distribution shows less C_1 (methanol) than would be expected by extrapolation of the ASF distribution for C_{2+} oxygenates, suggesting that methanol is not formed by the same route as ethanol and other higher oxygenates. Methanol is presumably formed by direct hydrogenation of adsorbed, activated CO that does not take part in the chain growth mechanism. On the other hand, the hydrocarbon distribution shows that more methane is produced than would be expected based on the distribution of C_{2+} hydrocarbons. This suggests that only part of the surface hydrocarbon species, $(CH_x)_{ads}$, resulting from the hydrogenation of the surface carbon formed in the CO dissociation step, participates in the ASF chain growth mechanism to form C_{2+} hydrocarbons. Most of this CH_x species undergoes further hydrogenation to form methane. In other words, methane is formed by a mechanism separate from chain growth.

The mechanism would thus appear to be one in which the dissociatively adsorbed CO is hydrogenated either completely to methane, or less than completely to CH_x species, which then proceeds via chain growth to form C_{2+} hydrocarbons. Associatively adsorbed CO is either hydrogenated directly to methanol or forms C_{2+} oxygenates via chain growth with the CH_x species and hydrogen. This mechanism has been reported by others [2], but the rate of CO insertion is greater on the doubly promoted Rh–La/V/SiO_2 catalyst than the comparable Rh-based catalysts (Table 5), leading to higher ethanol selectivity.

4. Conclusions

A series of La and/or V oxide-promoted Rh/SiO_2 catalysts were investigated for CO hydrogenation to ethanol, and the doubly promoted La–V–Rh/SiO_2 catalyst was found to be the most active/selective catalyst for ethanol formation. The formation of undesired methane can be suppressed under conditions of relatively high temperature, low pressure, and low H_2/CO ratio. For the most active Rh–La/V/SiO_2 catalyst, these conditions were found to be 270 °C, 14 bar, and H_2/CO = 2, and the highest ethanol selectivity achieved on this catalyst was 51.8%, with a corresponding methane selectivity of 15.4% at these conditions. Thus, combined La/V promotion seemed to alter the product distribution by increasing the rate of CO insertion, resulting in higher ethanol selectivities.

Ethanol and C_{2+} oxygenate selectivity followed similar trends with space velocity, suggesting that they share a common intermediate, whereas methane and ethanol followed completely opposite trends, indicating that they are formed by parallel reactions. Contrary to literature studies, higher pressures led to a dramatic increase in methane selectivity at the expense of ethanol, indicating increased CO dissociation activity at higher pressures, leaving fewer active CO molecules for insertion. The chain growth probability factors (α) for higher hydrocarbons and oxygenates were significantly different, suggesting that formation of these products could take place either due to different mechanisms or on different active sites. Less methanol was formed than would be expected by analysis of the chain growth distribution leading to C_{2+} oxygenates, suggesting that methanol formation does not follow the same route as ethanol and other higher oxygenates. At the same time, more methane was formed than expected from the same analysis, suggesting that hydrogenation of surface $(CH_x)_{ads}$ species to methane takes place at a greater rate than $(CH_x)_{ads}$ participating in the ASF chain growth mechanism to form C_{2+} hydrocarbons.

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