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CO hydrogenation on lanthana and vanadia doubly promoted Rh/SiO_2 catalysts

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ABSTRACT

This paper reports on a study of the combined promoting effect of La and V oxides for ethanol formation during CO hydrogenation on silica-supported Rh catalysts. Non-promoted and La and/or V oxide promoted Rh/SiO_2 catalysts were prepared by sequential or co-impregnation methods and characterized by TEM, CO chemisorption and FT-IR. Their catalytic properties for CO hydrogenation were investigated using a differential fixed bed reactor at 230 °C and 1.8 atm. It was found that, compared to non-promoted Rh/SiO_2, the singly promoted catalysts, Rh–La/SiO_2 and Rh–V/SiO_2, showed improved reactivity (3×) and better ethanol selectivities. However, the doubly promoted Rh–La–V/SiO_2 catalysts exhibited even higher activity (9×) and selectivity for ethanol and other C_{2+} oxygenates, with the selectivity of total C_{2+} oxygenates >30% at these low pressure reaction conditions. The better performance of the Rh–La–V/SiO_2 catalysts appears to be due to a synergistic promoting effect of the combined lanthana and vanadia additions through intimate contact with Rh. Use of just more of each promoter by itself was not able to produce the enhanced catalytic performance.

1. Introduction

Catalytic synthesis of ethanol and other higher alcohols from CO hydrogenation has been a subject of significant research since the 1980s. Higher alcohols synthesized from syngas derived from natural gas, coal, or biomass can be used as additives to gasoline or as an easily transportable source of hydrogen. Ethanol is especially desirable to produce selectively. Such produced ethanol would not only decrease the demand for imported crude oil but could also have a positive environmental impact [1].

Rh-based catalysts have been shown to have high activity for the synthesis of C_{2+} oxygenates due to the unique carbon monoxide adsorption behavior on Rh [2–6]. Extensive research efforts have been devoted to study the influence of supports and additives including La_2O_3 [2–6], SiO_2 [4,5,7–10], TiO_2 [3,8–16], Al_2O_3 [8,9,11], ZrO_2 [2,11,17], CeO_2 [8,11], MgO [8,18], V_2O_3 [18–21], alkali metals [21–25], Fe [26], Mn [27–34], Ag [35] and Mo [36] on the catalytic activity of Rh for CO hydrogenation. SiO_2 has been frequently used as a support since most Rh-based catalysts supported on SiO_2 have shown moderate activity and good selectivity towards C_2 oxygenates during CO hydrogenation [37].

It is widely accepted that CO dissociation and hydrogenation to produce CH_x species is likely the first step for the synthesis of C_{2+} oxygenates from syngas on Rh-based catalysts. The CH_x species then undergoes three possible different reactions. One is to form C_2 oxygenates by CO insertion, the second is to produce CH_4 by hydrogenation, and the third is to undergo chain growth with another CH_x to produce C_{2+} hydrocarbons [37]. Many studies have suggested that C–O bond dissociation is the rate-limiting step for CO hydrogenation [16,38], although it remains unclear whether C–O bond cleavage occurs through direct breaking of this bond in an adsorbed CO species or by a process involving hydrogen. In order to optimize the activity and selectivity of a catalyst for ethanol formation, the catalyst should have the ability to adsorb CO nondissociatively, to dissociate CO, to hydrogenate moderately, and to insert CO into a Rh–CH_x bond. A simple supported Rh catalyst does not seem to meet all these requirements optimally. Typical Rh catalysts for ethanol synthesis from syngas in recent studies all contain multiple components, such as Rh–Li–Mn–Fe [39] and Rh–Zr–Ir [40].

Lanthana and other rare earth oxides have been studied by many researchers for enhancing oxygenates synthesis from syngas and have shown interesting promotion/support effects on Rh for better ethanol formation [5,17,41–48]. However, their promotion mechanism remains unclear—it is unknown whether lanthana and other rare earth oxides enhance the formation of C_2-oxygenates by affecting the dispersion of Rh [44,49], by facilitating CO dissociation or insertion [46,47], or by stabilizing reaction intermediates [17]. The same is true for vanadia promoted Rh/SiO_2 [20,50–55]. While Kip et al. suggested that V enhances reactivity and selectivity towards ethanol by enhancing CO dissociation [55], other researchers have proposed that the function of V is to boost hydrogenation [53,54,56].

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Table 1
Preparation conditions and compositions of Rh-based catalysts.[a]

Nomenclature	Composition (wt%)[b]	Molar ratio of promoter/Rh	Metal loading method
$Rh(1.5)/SiO_2$	1.5		Impregnation
$Rh(1.5)–La(2.6)/SiO_2$	1.5, 2.6	La/Rh = 1.3	Co-impregnation
$Rh(1.5)/V(1.5)/SiO_2$	1.5, 1.5	V/Rh = 2	Sequential impregnation
$Rh(1.5)–La(2.6)/V(0.7)/SiO_2$	1.5, 2.6, 0.7	La/Rh = 1.3 V/Rh = 1	Co-sequential impregnation[c]
$Rh(1.5)–La(2.6)/V(1.5)/SiO_2$	1.5, 2.6, 1.5	La/Rh = 1.3 V/Rh = 2	Co-sequential impregnation
$Rh(1.5)–La(2.6)/V(2.2)/SiO_2$	1.5, 2.6, 2.2	La/Rh = 1.3 V/Rh = 3	Co-sequential impregnation
$Rh(1.5)–La(2.6)/V(3.7)/SiO_2$	1.5, 2.6, 3.7	La/Rh = 1.3 V/Rh = 5	Co-sequential impregnation
$Rh(1.5)–La(0.5)/V(3.7)/SiO_2$	1.5, 0.5, 3.7	La/Rh = 0.3 V/Rh = 5	Co-sequential impregnation
$Rh(1.5)–La(4)/V(1.5)/SiO_2$	1.5, 2.6, 1.5	La/Rh = 2 V/Rh = 2	Co-sequential impregnation
$Rh(1.5)–La(6)/V(1.5)/SiO_2$	1.5, 6, 1.5	La/Rh = 3 V/Rh = 2	Co-sequential impregnation

[a] All catalysts were calcined at 500 °C after each impregnation step.

[b] wt% relative to the initial weight of the support material.

[c] First impregnation with an NH_4VO_3 solution, followed by calcination at 500 °C; then co-impregnation with a Rh and La solution, followed again by calcination at 500 °C.

The objective of this study was to investigate the promoting mechanism of La and V, and more importantly, to explore the combined promotion effect of these two elements for CO hydrogenation on Rh/SiO_2. In this study, a series of La and/or V oxide promoted Rh/SiO_2 catalysts were prepared and characterized by TEM, CO chemisorption and FT-IR. Their catalytic activities were determined for CO hydrogenation in a fixed-bed reactor at 230 °C and 1.8 atm.

2. Experimental

2.1. Catalyst preparation

$Rh(NO_3)_3$ hydrate (Rh ~36 wt%, Fluka), $La(NO_3)_3·6H_2O$ (99.99%, Aldrich), NH_4VO_3 (99.5%, Alfa Aesar), and silica gel (99.95%, Alfa Aesar) were used in catalyst preparations. Silica gel was first ground and sieved to 30–50 mesh, washed using boiled distilled water for 3 times, and then calcined in air at 500 °C for 4 h before being used as a support (BET surface area after pretreatment was $251 \pm 2\ m^2/g$). Catalysts were prepared by sequential or co-impregnation to incipient wetness of silica gel with an aqueous solution of $Rh(NO_3)_3$ hydrate and aqueous solutions of precursors of the promoters (1 g silica gel/2 ml solution), followed by drying at 90 °C for 4 h, and then at 120 °C overnight before being calcined in air at 500 °C for 4 h.

For the catalysts referred to as $Rh/M/SiO_2$ (M = La or V promoter), silica gel was first impregnated with the aqueous solution containing the precursor of the promoter and then calcined in static air at 500 °C for 4 h, followed by impregnation of the $Rh(NO_3)_3$ aqueous solution and calcination at 500 °C for 4 h. $Rh–M/SiO_2$ represents a catalyst prepared by co-impregnation. Numbers in parentheses following the symbol for an element indicate the weight percent of that element based on the weight of the silica gel support. In the text, a singly promoted catalyst refers to a catalyst containing Rh and one promoter and a doubly promoted catalyst refers to one containing Rh and two promoters.

Table 1 gives details about the catalyst compositions and preparations. The sequential impregnation method was chosen for V-containing catalysts in order to be consistent with the literature for comparison purposes [29,54,57]. For lanthana promoted Rh catalysts supported on silica, it has been reported that the sequence of impregnation has an effect on catalytic behavior [46]. Thus, for this study co-impregnation of the La additive with Rh was adopted since it is believed that well dispersed Rh particles form without being fully covered by La_2O_3 when that method is used [47].

2.2. Catalyst characterization

BET surface area was obtained using N_2 adsorption at −196 °C in a Micromeritics ASAP 2020. Prior to N_2 adsorption, the catalyst samples were degassed under a vacuum of 10^{-3} mm Hg for 4 h at 150 °C.

High resolution field emission microscopy images were obtained using a Hitachi 9500 electron microscope with 300 kV high magnification.

A Scintag XDS 2000 θ/θ powder X-ray diffractometer (XRD) equipped with Cu $K\alpha1/K\alpha2$ ($\lambda = 1.540592$ Å and 1.544390 Å, respectively) radiation was employed for the collection of X-ray diffraction patterns with a step size of 0.03°.

The number of exposed rhodium surface atoms was determined by CO chemisorption using a Micromeritics ASAP 2010C. Catalyst samples of approximately 0.2 g were first evacuated at 110 °C for 30 min before being reduced at 500 °C in a hydrogen flow for 30 min, and then evacuated at 10^{-6} mm Hg and 500 °C for 120 min. After cooling under vacuum to 35 °C, the adsorption isotherm was recorded. The amount of chemisorbed CO was obtained by extrapolating the total adsorption isotherm to zero pressure, and the metal dispersion (Rh_s/Rh_{Tot}) was calculated subsequently assuming $CO/Rh_s = 1$.

CO adsorption was also studied using a Nicolet 6700 FTIR spectrometer equipped with a DRIFT (diffuse reflectance infrared Fourier transform) cell with CaF_2 windows. The cell, whose windows were cooled by circulating water, could collect spectra over the temperature range 25–500 °C at atmospheric pressure. For a typical measurement, about 0.05 g sample was ground and placed in the sample holder. Prior to exposure to CO, the sample was reduced *in situ* at 500 °C in a flow of H_2 (20 mL/min) for 30 min and then purged with He (48 mL/min) at this temperature for 30 min. After cooling down to the desired temperature in the He flow, a background spectrum was taken. Then, 4 v/v% CO/He (total 50 mL/min) was introduced into the cell and the infrared spectra were taken at 4 cm^{-1} resolution and consisted of 128 interferograms to obtain a satisfactory signal-to-noise ratio.

2.3. Reaction

CO hydrogenation was performed in a fixed-bed differential reactor (316 stainless steel) with length ~300 mm and internal diameter ~5 mm. The catalyst (0.3 g) was diluted with inert α-alumina (3 g) to avoid channeling and hot spots. The catalyst and inert were loaded between quartz wool plugs and placed in the middle of the reactor with a thermocouple close to the catalyst bed. Prior to reaction, the catalyst was heated to 500 °C (heating rate ~6 °C/min) and reduced with hydrogen (flow rate = 30 mL/min) for 1 h. The catalyst was then cooled down to 230 °C and the reaction started as gas flow was switched to a H_2–CO mixture (molar ratio of $H_2/CO = 2$, total flow rate = 45 mL/min) at 1.8 atm total pressure. A total pressure of 1.8 atm was used since this study is part of a more extended investigation using a variety of techniques including using SSITKA (steady-state isotopic transient kinetic analysis [58]) and equivalent reaction conditions are required for comparison of all the data. This pressure would not necessarily be the optimum for obtaining the maximum selectivity to oxygenates. Flow rates were controlled using Brooks 5840E series mass flow controllers and kept at a total flow rate of 45 mL/min. The products, including hydrocarbons and oxygenates, were analyzed on-line by an FID (flame ionization detector) in a

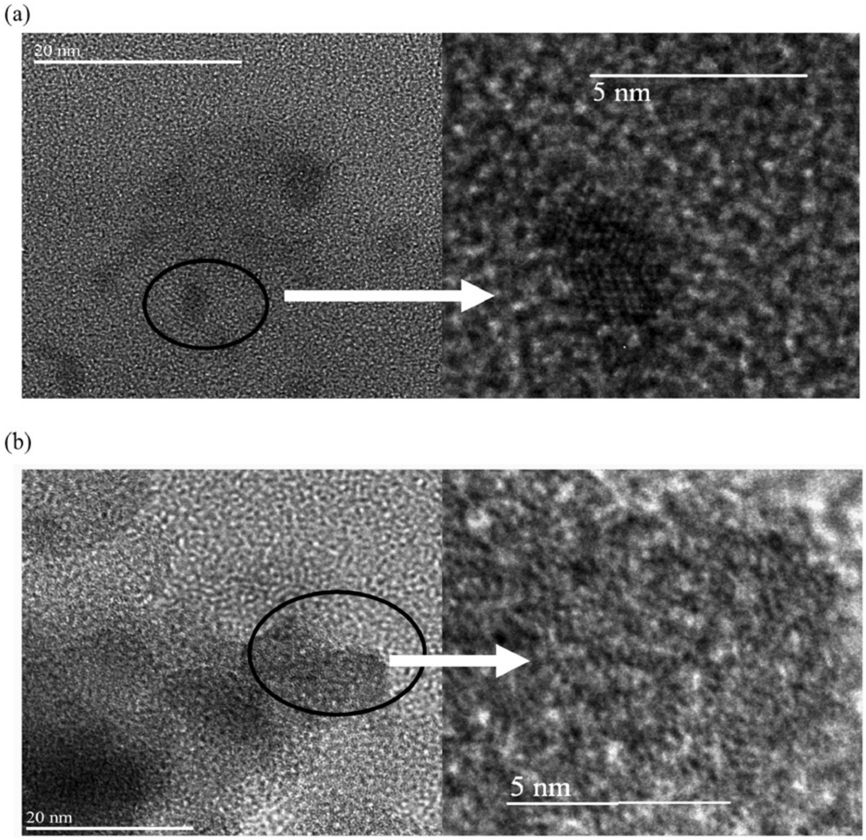


Fig. 1. TEM micrographs of (a) $Rh(1.5)/SiO_2$ and (b) $Rh(1.5)–La(2.6)/V(1.5)/SiO_2$.

gas chromatograph (Varian 3380 series) with a Restek RT-QPLOT column of I.D. 0.53 mm and length 30 m. Carbon monoxide and other inorganic gases were analyzed by a TCD (thermal conductivity detector) after separation with a Restek HayeSep® Q column of I.D. 3.18 mm and length 1.83 m. The identification and calibration of gas products were accomplished using standard gases [alkanes (C_1–C_7), alkenes (C_2–C_7), and oxygenates (methanol, ethanol, 1-propanol, 1-butanol, acetaldehyde, and acetone)] as well as liquid samples (oxygenates). For all measurements, the CO conversion was kept below 10%. The selectivity of a particular product was calculated based on carbon efficiency using the formula $n_iC_i/\sum n_iC_i$, where n_i and C_i are the carbon number and molar concentration of the ith product, respectively.

Arrhenius plots of the rates of CO conversion gave apparent activation energies of 25–27 kcal/mol for all the types of promoted catalysts; indicating no heat or mass transport limitations on the rate of reaction measurements.

3. Results and discussion

3.1. Morphology of Rh-based catalysts

As-prepared Rh-based catalysts were small dark brownish granules of 30–50 mesh. The BET surface areas of all the Rh-based catalysts were measured to be ca. 245 m^2/g. No significant difference was observed in the surface areas for the catalysts prepared using different preparation methods, probably due to the fact that the concentrations of Rh and promoters were relatively low in all the catalysts prepared in this study.

X-ray diffraction (XRD) patterns (not shown) of these calcined 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 as shown in Fig. 1. The high resolution images of $Rh(1.5)/SiO_2$ (Fig. 1a) show evenly dispersed Rh clusters with particle sizes around 3 nm. However, for the La and V promoted catalyst $Rh(1.5)–La(2.6)/V(1.5)/SiO_2$, no clear image of Rh clusters could be identified, only some irregular-shaped patches in the range of 3–20 nm were distinguishable from the support, as shown in Fig. 1b. The singly promoted catalysts, $Rh(1.5)–La(2.6)/SiO_2$ and $Rh(1.5)/V(1.5)/SiO_2$, exhibited similar TEM images (not shown) as that of $Rh(1.5)–La(2.6)/V(1.5)/SiO_2$.

Table 2
CO chemisorption on the reduced Rh-based catalysts.

Catalyst	CO-chemisorbed[a] ($\mu mol/g_{cat}$)		Metal dispersion[b] (%)
	Total	Irrev.	
$Rh(1.5)/SiO_2$	48.1	42.9	37.2
$Rh(1.5)–La(2.6)/SiO_2$	83.2	76.5	65.4
$Rh(1.5)/V(1.5)/SiO_2$	29.6	6.9	22.9
$Rh(1.5)–La(2.6)/V(1.5)/SiO_2$	13.3	2.0	10.3

[a] Error = ±5% of the value measured.
[b] Based on total CO chemisorbed and an assumption of $CO/Rh_s = 1$.

3.2. CO chemisorption

Table 2 summarizes the results obtained from the volumetric CO chemisorption. La addition to Rh increases CO adsorption, which is in good agreement with the results reported by Bernal and Blanco [45]. On the contrary, the addition of V resulted in a decrease in both total and irreversible CO chemisorption, which is also consistent with the literature [57]. For the doubly promoted catalysts (La + V), the presence of V clearly diminished the CO chemisorption and especially the irreversible amount. It would appear, based on a comparison of the CO chemisorption results with these from TEM, that metal dispersion based on CO chemisorption for the V-promoted catalysts is probably under estimated.

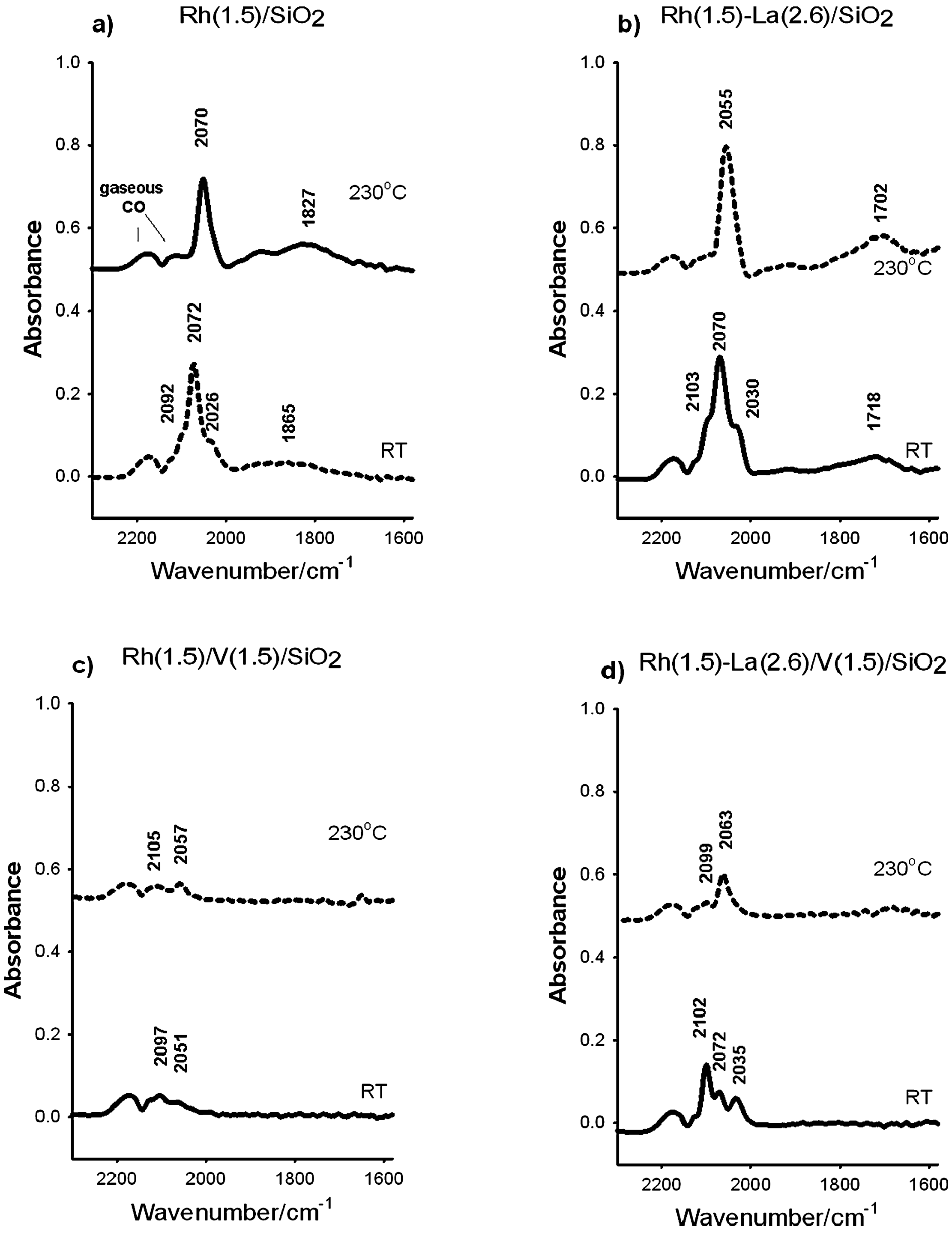


Fig. 2. The infrared spectra of chemisorbed CO at room temperature and at 230 °C on (a) Rh(1.5)/SiO_2; (b) Rh(1.5)–La(2.6)/SiO_2; (c) Rh(1.5)/V(1.5)/SiO_2; (d) Rh(1.5)–La(2.6)/V(1.5)/SiO_2 after exposing the reduced catalysts to 4 v/v% CO/He (total 50 mL/min) for 30 min.

3.3. FTIR study

Infrared spectroscopy provides an alternate and powerful tool to study the interaction of CO with catalysts. Four representative Rh catalysts in this study were chosen for IR study—the bench mark non-promoted Rh(1.5)/SiO_2, 2 singly promoted catalysts Rh(1.5)–La(2.6)/SiO_2 and Rh(1.5)/V(1.5)/SiO_2, and a doubly promoted catalyst Rh(1.5)–La(2.6)/V(1.5)/SiO_2. A series of spectra acquired for these catalysts (after reduction at 500 °C and desorption of H_2 followed by contact with CO at room temperature or 230 °C, respectively for 30 min) is given in Fig. 2. In all the spectra, the bands centered around 2180 and 2125 cm^{-1} can be attributed to gaseous CO [59]. The IR spectrum of Rh(1.5)/SiO_2 interacting with CO at room temperature (Fig. 2a) exhibited a strong band at 2072 cm^{-1}, which can be attributed to linear adsorbed CO [CO(l)]; a doublet at 2092 and 2026 cm^{-1}, which can be assigned to the symmetric and asymmetric carbonyl stretching frequencies of gem-dicarbonyl Rh(I)$(CO)_2$; and a weak broad peak at 1865 cm^{-1}, which is assigned to bridge-bonded CO [CO(b)] [60]. The formation of the dicarbonyl species could be an indication of highly dispersed Rh since it is widely accepted that the dicarbonyl species can only be formed on highly dispersed rhodium [61,62]. The IR spectrum

Table 3
Catalytic activities of Rh-based catalysts.[a]

Catalyst	SS[b] rate (μmol/(g s))	SS selectivity (%)[c]						$C_2^=/C_2$	$C_3^=/C_3$[d]
		CH_4	C_{2+}HC[e]	MeOH	Acetaldehyde	EtOH	Other C_{2+} oxy.[f]		
Rh(1.5)/SiO_2	0.03	48.1	28.7	1.2	6.5	15.6	–	1.8	12.0
Rh(1.5)–La(2.6)/SiO_2	0.09	35.3	32.0	3.2	5.8	23.6	–	1.2	3.3
Rh(1.5)/V(1.5)/SiO_2	0.09	12.5	66.8	5.0	2.1	12.5	1.3	4.8	10.3
Rh(1.5)–La(2.6)/V(1.5)/SiO_2	0.29	16.2	50.8	1.8	5.4	20.8	4.9	3.3	12.1

[a] Catalyst: 0.3 g; inert: α-alumina 3 g; pretreatment: 500 °C in H_2; reaction conditions: $T = 230\,^{\circ}\mathrm{C}$, $P = 1.8$ atm, flow rate = 45 mL/min ($H_2/CO = 2$). Data taken at 15 h TOS after steady state reached. Error = ±5% of all the values measured except for Rh(1.5)/SiO_2 which was ±10% due to low activity.

[b] Steady state.

[c] Carbon selectivity $= n_i C_i / \sum n_i C_i$.

[d] $C_n^=/C_n$ is the ratio of C_n olefin selectivity to C_n paraffin selectivity ($n = 2, 3$).

[e] Hydrocarbons with 2 or more carbons.

[f] Oxygenates with 2 or more carbons, not indicating acetaldehyde and ethanol.

of CO adsorbed on the lanthana promoted catalyst looks identical to that of CO adsorbed on the non-promoted catalyst except that the peak of the bridge bonded CO shifted to a lower frequency, which is consistent with the literature and may be related to a tilted CO adsorption mode [CO(t)] [43]. The IR-spectra taken after exposing Rh(1.5)/V(1.5)/SiO_2 and Rh(1.5)–La(2.6)/V(1.5)/SiO_2 to CO (Figs. 2c and 2d) showed much lower intensities of CO(l) band and no CO(b) was observed. The suppression of CO absorption by the addition of vanadia to Rh/SiO_2 catalysts has previously been reported by several research groups [53,57] and is also in agreement with the quantitative CO chemisorption results reported here. Two features related to CO adsorption on the doubly promoted Rh(1.5)–La(2.6)/V(1.5)/SiO_2 at room temperature are worthy noting here: first, as shown in Fig. 2d, the gem-dicarbonyl Rh(I)$(CO)_2$ dominates the IR spectrum; second, though the overall intensities of the adsorbed CO bands are lower than those of non-promoted and the lanthana promoted Rh/SiO_2, they are significantly greater than those of the vanadia promoted Rh/SiO_2. These features indicated high dispersion of Rh and moderate CO adsorption strength of the doubly promoted catalyst at room temperature.

For IR spectra recorded at the reaction temperature of 230 °C, the relative intensity of the dicarbonyl species decreased compared to the spectra recorded at room temperature for all the catalysts. The attenuation of the dicarbonyl species is likely due to the reduction of $Rh^I(CO)_2$ to form CO_2 and $Rh_x^0(CO)$ species at high temperatures [63,64]. For the non-promoted Rh(1.5)/SiO_2 and the lanthana promoted Rh(1.5)–La(2.6)/SiO_2, the intensities of the bridge-bonded CO(b) or CO(t) increased. However, at this temperature, there was still no CO(b) evident in the IR spectra for the V-containing catalysts. With regards to the adsorbed CO, that on Rh(1.5)–La(2.6)/SiO_2 had the highest intensity. Results may be attributed to the fact that lanthana can interact directly with CO [43]. However, in the present study, exposing 2.6 wt% La_2O_3 supported on SiO_2 to CO did not produce any significant IR bands for adsorbed CO species at room temperature or 230 °C, suggesting that new sites available for CO adsorption might be at the Rh–LaO_x interface/surface. The IR spectrum of the vanadia promoted Rh catalyst, Rh(1.5)/V(1.5)/SiO_2, at 230 °C exhibited similar features to the spectrum recorded at room temperature except that the peaks were even weaker when compared to the other catalysts, indicating a likely stronger suppression of CO adsorption at higher temperature. One possible explanation is that at higher temperature, more Rh might be covered with vanadia. As shown in Fig. 2d, the IR spectrum taken at 230 °C of the doubly promoted catalyst exhibited weak gem-dicarbonyl Rh(I)$(CO)_2$ species besides CO(l) with moderate intensity, suggesting that high dispersion of Rh and moderate CO adsorption strength were conserved at high temperature for this catalyst. A more detailed discussion related to the IR study will be reported elsewhere [65].

3.4. Catalytic activities

Table 3 compares the catalytic activities of the non-promoted and La and/or V promoted Rh/SiO_2 catalysts for CO hydrogenation at 230 °C. Negligible amounts of CO_2 were formed for all the catalysts under the reaction conditions used in this study, thus, all the reaction rates and selectivities were calculated without including CO_2. The results presented here confirm that both La and V affect the catalytic activity of Rh/SiO_2 for CO hydrogenation [41,55]. It can be seen that all the promoted catalysts exhibited higher CO conversion rates than that of the non-promoted one. For the singly La promoted catalyst Rh(1.5)–La(2.6)/SiO_2, the selectivity towards the formation of ethanol was enhanced while the selectivity towards acetaldehyde decreased a little compared to non-promoted Rh/SiO_2. Methanol selectivity was also increased somewhat, but methane selectivity was less. Hydrocarbons still made up the majority of the total products although somewhat less than for the non-promoted catalyst. The higher total reactivity and higher C_2 oxygenate selectivity indicate that La may enhance both CO dissociation (assuming that C–O bond dissociation is the rate-limiting step for CO hydrogenation [16,38]) and insertion by increasing CO adsorption and affecting CO interaction with the catalyst at the reaction temperature, as suggested by the IR study.

Compared to the La promoted catalyst, the V promoted Rh catalyst showed significant suppression of the formation of methane, an undesired low-value product, but the selectivity for ethanol was lower than that for the La promoted Rh/SiO_2 catalyst. The formation of higher hydrocarbon dominated with a selectivity of 66.8%. It has been proposed by Luo et al. [56,66] that vanadium ions of lower valence have a good capacity for hydrogen storage, enhancing the hydrogenation ability. However, Kip et al. [57] studied ethylene-addition and found no significant difference in the amount of ethane formed on non-promoted and V_2O_3 promoted Rh/SiO_2, leading to a suggestion that the low activity of Rh/SiO_2 cannot be due simply to low hydrogenation activity. Judging from the low selectivity of CH_4 and the high fraction of olefins in the products in our study using Rh(1.5)/V(1.5)/SiO_2, our results indicate it is also unlikely that vanadium oxide boosts hydrogenation for the formation of hydrocarbons. On the other hand, the shift in selectivity from acetaldehyde to ethanol does suggest an increase in the hydrogenation function of the catalyst. This seeming contradiction may be due to different hydrogenation pathways for the formation of paraffins from olefins and alcohols from aldehydes. Based on the results of our CO chemisorption and IR studies, the addition of vanadium oxide suppresses CO adsorption, which may lead to increased H coverage on the Rh surface. It is possible that this also happens at reaction temperature and influences product selectivity. As suggested by Beutel et al. [53], it is more likely that increased capacity of hydrogen storage may assist CO dissociation by forming COH species easier first on the V promoted Rh catalyst, leading to increased formation of longer chain

Table 4
Effect of V/Rh and La/Rh ratio on catalytic activities of doubly promoted Rh catalysts.[a]

Catalyst	La/Rh molar ratio	V/Rh molar ratio	SS rate (μmol/(g s))	SS selectivity (%)[b]					
				CH_4	C_{2+}HC[c]	MeOH	Acetaldehyde	EtOH	Other C_{2+} oxy.[d]
Rh(1.5)–La(2.6)/V(0.75)/SiO_2	1.3	1	0.27	19.1	50.3	1.9	9.3	16.7	1.3
Rh(1.5)–La(2.6)/V(1.5)/SiO_2	1.3	2	0.29	16.2	50.8	1.8	5.4	20.8	4.9
Rh(1.5)–La(2.6)/V(2.2)/SiO_2	1.3	3	0.32	14.0	53.2	2.8	5.5	20.5	4.0
Rh(1.5)–La(2.6)/V(3.7)/SiO_2	1.3	5	0.29	14.8	52.2	2.7	5.2	21.1	4.0
Rh(1.5)–La(0.5)/V(1.5)/SiO_2	0.3	2	0.17	10.5	60.6	4.6	3.8	17.8	2.8
Rh(1.5)–La(4)/V(1.5)/SiO_2	2	2	0.19	16.6	47.3	2.3	8.9	22.2	2.7
Rh(1.5)–La(6)/V(1.5)/SiO_2	3	2	0.17	21.8	42.4	1.4	11.5	18.3	4.6

[a] Catalyst: 0.3 g; inert: α-alumina 3 g; pretreatment 500 °C; reaction conditions: $T = 230\,^\circ\mathrm{C}$, $P = 1.8$ atm, flow rate = 45 mL/min ($H_2/CO = 2$). Data taken at 15 h after steady state reached. Error = ±5% of the value measured.

[b] Carbon selectivity $= n_iC_i / \sum n_iC_i$.

[c] Hydrocarbons with 2 or more carbons.

[d] Oxygenates with 2 or more carbons, not including acetaldehyde or ethanol.

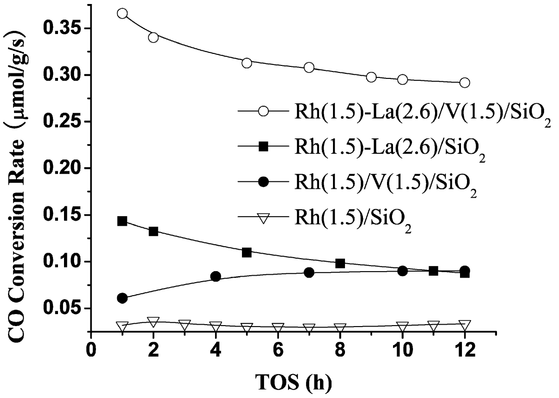


Fig. 3. CO conversion rate vs TOS for Rh(1.5)/SiO_2, Rh(1.5)–La(2.6)/SiO_2 and Rh(1.5)–La(2.6)/V(1.5)/SiO_2.

hydrocarbons and oxygenates. Certainly, if there were increased H coverage, it did not appear to have a positive effect on CH_4 synthesis.

As shown in Table 3, compared to Rh/SiO_2 promoted only by La or by V, the doubly promoted catalyst Rh(1.5)–La(2.6)/SiO_2 combined the positive promoting effects of both La and V, resulting in the highest CO hydrogenation rate (about 9 times higher than Rh/SiO_2), high ethanol and other C_{2+} oxygenates selectivities, and low selectivities for methane and methanol. These results may be related to the intimate contact of Rh with both V and La, resulting in modified CO and H_2 adsorption as suggested by CO chemisorption and IR studies, which leads to faster CO dissociation, insertion and hydrogenation.

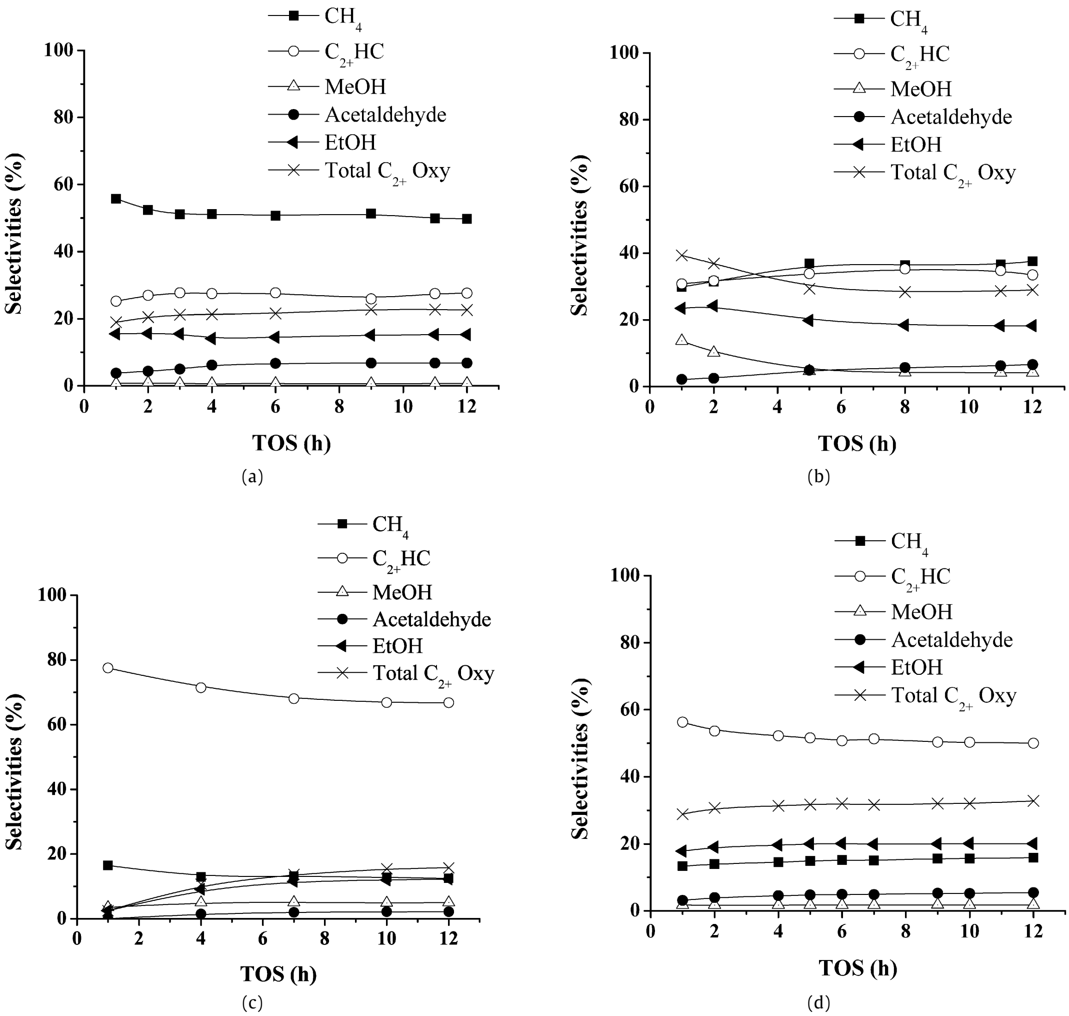
Table 4 presents the effects on CO hydrogenation of La/Rh and V/Rh ratios in the doubly promoted Rh/SiO_2 catalysts. It can be concluded that a V/Rh ratio ranging from 1 to 5 had little impact on the total activity for CO hydrogenation. However, as V/Rh changed from 1 to 2, both total oxygenate and ethanol selectivities increased while those for acetaldehyde and methane decreased. This suggests that the main effect of V was to enhance chain growth, probably by accelerating CO dissociation and hydrogenation. When the La/Rh ratio was increased from 0.3 to 3, methane selectivity appeared to increase while the activity shows a peak at 1.3. La appears to affect V–Rh effects but excess La shows negative results. Since varying the La/Rh and V/Rh ratios showed different effects, it is safe to conclude that the better performance of the doubly promoted (La + V) catalyst is not because of a simple additive effect but rather a synergistic one. Use of just more of each promoter by itself is not able to produce the enhanced catalytic performance.

Fig. 3 shows the time-on-stream (TOS) behavior of CO conversion on Rh(1.5)/SiO_2, the singly promoted catalysts Rh(1.5)–La(2.6)/SiO_2 and Rh(1.5)/V(1.5)/SiO_2, and one of the doubly promoted catalysts Rh(1.5)–La(2.6)/V(1.5)/SiO_2. The activity of the non-promoted Rh(1.5)/SiO_2 was relatively constant while the activities of Rh(1.5)–La(2.6)/SiO_2 and Rh(1.5)–La(2.6)/V(1.5)/SiO_2 decreased slightly during the first eight hours and then remained steady. In contrast, the CO hydrogenation activity on Rh(1.5)/V(1.5)/SiO_2 exhibited an induction period lasting for 8 h before a steady-state was reached. Not many previous studies have been reported regarding the activation and deactivation behaviors of Rh-based catalysts for CO hydrogenation. Several research groups have observed performance versus TOS for non-promoted and promoted Rh/SiO_2 catalysts [55,67–69]. It has been suggested that deactivation during the initial stages of reaction may be due to the inhibiting effect of CO since strongly adsorbed CO on Rh sites may be less likely to be hydrogenated [68,69]. The re-structuring of the Rh surface during the reaction may also be a cause for the deactivation.

Fig. 4 compares the selectivities during CO hydrogenation with TOS on these four catalysts. While not all the selectivities changed much with TOS, there were still several interesting results. The selectivity for acetaldehyde for the non-promoted and La promoted catalysts showed an opposite trend from ethanol. This is consistent with what Chuang et al. [37] proposed, namely that the ethanol selectivity improves by suppressing acetaldehyde production through hydrogenation since acetaldehyde is an intermediate to ethanol. However, no such trend was seen for the V-promoted and doubly promoted catalysts. Finally, the selectivities for Rh(1.5)–La(2.6)–V(1.5)/SiO_2 did not change with TOS as much as the singly promoted catalysts Rh(1.5)–La(2.6)/SiO_2 and Rh(1.5)/V(1.5)/SiO_2, providing additional evidence for a synergistic effect of La and V.

4. Conclusions

A series of La and/or V promoted Rh/SiO_2 catalysts was prepared using the incipient wetness impregnation method. Powder X-ray diffraction and TEM results suggested that Rh, lanthana and vanadia were all highly dispersed in the promoted Rh/SiO_2 catalysts, with no Rh particles distinguishable in TEM images. CO chemisorption and FT-IR studies indicated significantly different CO adsorption behaviors of the different catalysts. V promotion decreased CO adsorption while La promotion showed the opposite effect. Compared to the singly promoted catalysts Rh–La/SiO_2 and Rh/V/SiO_2, the doubly promoted Rh–La/V/SiO_2 catalysts exhibited higher activity and better selectivity towards ethanol formation. The catalytic performance of the Rh–La/V/SiO_2 catalyst was not affected significantly by increasing the V content beyond V/Rh = 2; however, La promotion greater than La/Rh = 2 resulted in less desirable catalytic properties. The high performance of the Rh–La/V/SiO_2 catalysts appears to be due to a synergistic promoting



(a) (b) (c) (d)

Fig. 4. Product selectivities vs TOS for (a) Rh(1.5)/SiO$_2$, (b) Rh(1.5)–La(2.6)/SiO$_2$, (c) Rh(1.5)/V(1.5)/SiO$_2$ and (d) Rh(1.5)–La(2.6)/V(1.5)/SiO$_2$.

effect of lanthana and vanadia, modifying both chemisorption and catalytic properties.

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