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Role of promoters on Rh/SiO_2 in CO hydrogenation: A comparison using DRIFTS

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ABSTRACT

La, V, Zn, Cu, Fe, Li and Ag promoted Rh/SiO_2 catalysts were investigated for the synthesis of ethanol during CO hydrogenation at 230 °C and 1.8 atm. As is well known, the activity and selectivity depend heavily on the choice of promoter. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to probe the effects of La, V, Zn and Cu on CO adsorption and hydrogenation. From the IR study, it was found that the behavior of CO adsorbed on the differently promoted catalysts was very different. While La enhanced total CO adsorption, the addition of V, Zn and Cu suppressed CO adsorption to different extents. The doubly promoted $Rh-La/V/SiO_2$ showed only moderate CO adsorption. Results from DRIFTS suggest that the higher catalytic activity (compared to the non-promoted catalyst) observed for the La singly promoted Rh/SiO_2 catalyst may primarily be caused by an increase in the concentration of the adsorbed CO species in the presence of H_2, possibly due to the formation of new active sites at the LaO_x-Rh interface. The higher catalytic activity of the V singly promoted Rh/SiO_2 catalyst could be ascribed to an increased desorption rate/reactivity of the adsorbed CO species. The La and V doubly promoted catalyst showed both new adsorbed CO species and increased desorption rate/reactivity of the adsorbed species during CO hydrogenation due to a synergistic promoting effect of La and V. The addition of Zn or Cu promoters significantly reduced the desorption rate/reactivity of the adsorbed CO species on Rh/SiO_2, leading apparently to the much reduced activities for CO hydrogenation observed.

1. Introduction

The syntheses of ethanol and other higher alcohols from syngas derived from coal or biomass are of great research interest since such produced alcohols could decrease the demand for imported crude oil and could also have a positive environmental impact [1]. Rh-based catalysts have been shown to have good selectivity for the synthesis of C_2-oxygenates during CO hydrogenation due to unique carbon monoxide adsorption behavior on Rh [2–8]. It is well known that supports and additives affect the activities and selectivities of Rh-based catalysts for CO hydrogenation. According to the review by Chuang et al. [3], the influences of supports and promoters on Rh-based catalysts for C_{2+} oxygenate synthesis include enhancing the hydrogenation of adsorbed CO to form methanol (e.g., ZnO, MgO), enhancing CO dissociation (e.g., Mn, V, Na, La), enhancing hydrogenation of C species on the catalytic surface (e.g., Fe, Ir, P), and enhancing CO insertion (e.g., Ag, Zn, La, V).

Extensive research efforts have been devoted to study reaction mechanisms and the effects of supports and promoters on Rh-based catalysts using various characterization techniques. Among *in situ* techniques, IR has been employed widely for the study of Rh-based catalysts since the pioneering work carried out by Yang and Garland in 1957 [9]. CO adsorbed on Rh-based catalysts has been investigated most extensively and at least 9 adsorbed CO species have been identified: linear Rh-CO (2000–2070 cm^{-1}) (denoted as [CO(l)]), tilted CO (1650–1775 cm^{-1}, denoted as [CO(t)]), bridged Rh_2(CO) (1800–1900 cm^{-1}, denoted as [CO(b)]), bridged $Rh_2(CO)_3$ dimer (1905–1925 cm^{-1}, denoted as [CO(bd)]), gem-dicarbonyl $Rh^+(CO)_2$ (2031, 2101 cm^{-1}, denoted as [CO(gdc)]), Rh^+(CO) (2090–2110 cm^{-1}), Rh^{2+}(CO) (~2120 cm^{-1}), $Rh^{2+}(CO)_2$ (2176, 2142 cm^{-1}), and Rh^{3+}(CO) (2125 – 2135 cm^{-1}) [3,10–12].

Numerous studies have also been carried out to investigate CO adsorption and hydrogenation on Rh-based catalysts using IR spectroscopy under reaction conditions. Thus far, some agreements have been reached related to the interaction of CO on Rh-based catalysts. For instance, it is widely accepted that the gem-dicarbonyl [CO(gdc)] is produced on isolated Rh^+ and $Rh^+(CO)_2$ undergoes reaction to form Rh_x^0(CO) species at high temperature [9,10,13–17]. IR has also been employed to study the influence of promoters/supports on CO interaction with catalysts and on CO hydrogenation. Examples of supports studied include SiO_2, Al_2O_3 [13,14], TiO_2 [18,19], NaY [20], ZrO_2 [21] and CeO_2 [22]. Examples of promoters on Rh-based catalysts studied by IR include Fe [23–26], Zn [27], Mn [23,28], La [29,30], Ce [31], Nb, Ta [32] and V [32,33]. The influence of different supports and promoters on IR

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spectra of CO adsorption or/and CO hydrogenation on Rh-based catalysts is quite different. For instance, the addition of highly oxophilic promoters including Mn, Ti, Zr, Nb [34], Ce [22] and La [35] resulted in the formation of CO(*t*), which has been suggested to contribute to the increased catalytic activity for CO hydrogenation.

Giving a detailed review on IR studies on Rh-based catalysts for CO hydrogenation is beyond the scope of this paper. However, there have been many contradictory results and proposed correlations based on IR studies from different research groups. One controversy concerns the formation of a monocarbonyl hydride species (H-Rh-CO). Solymosi and co-workers proposed that a new band near 2040 cm^{-1}, formed during CO hydrogenation, could be a precursor of reaction [36]. While this suggestion was supported by Worley et al. [18,37], Basu et al. did not find the existence of this species during their IR study of CO hydrogenation on 0.2 wt% Rh/Al_2O_3 [14]. Another example of a controversy is the correlation between the ratio of CO(*l*)/CO(*b*) and the CO hydrogenation activities of Rh-based catalysts. Arakawa et al. [38] proposed that the ratio of bridged CO to linear CO could be correlated with the activity of Rh/SiO_2 for CO hydrogenation, but this assumption has been questioned by other researchers [22,39]. Moreover, even for CO adsorption on Rh-based catalysts under similar conditions, different research groups have obtained contradictory results. For instance, the IR spectrum of CO adsorbed at 100 °C on 3.4 wt% Rh/SiO_2 reported by Fisher and Bell [40] showed mainly CO(*l*) and CO(*b*), but the IR spectrum of CO adsorbed on 3 wt% Rh/SiO_2 at the same temperature reported by Bernal et al. [29] showed mainly CO(*gdc*). The difference observed may be due to different catalyst preparation methods, pretreatments, or even purities of materials used (catalysts and gases). Given the differences seen for studies on just Rh/SiO_2, it is not surprising that few IR studies have been done on the impact of different promoters on CO adsorption on Rh under the same reaction conditions. It would be meaningful and useful if an extensive IR study were done on an extensive set of promoters for a Rh catalyst such that most of other variables were held constant.

The purpose of this work was to investigate the effect of promoters on Rh/SiO_2 for CO hydrogenation at the atomic level using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The following elements were chosen as promoters for this study to represent different promoter groups and different reported roles in the synthesis of oxygenates over Rh-based catalysts: Li (alkali metal, suggested to enhance the selectivity towards oxygenates [24,41,42]), Fe (transition metal, suggested to enhance hydrogenation [24,43–45]), V (transition metal, suggested to enhance CO dissociation or CO insertion [32,46–51]), La (lanthanide, suggested to enhance CO dissociation or insertion [29–31,35,52–56]), and Cu, Zn, Ag (transition metals, suggested to enhance CO insertion [27,57,58]). The catalytic activities of non-promoted and promoted Rh/SiO_2 catalysts for CO hydrogenation were compared and the effects of some of the above promoters showing significantly different promoting effects on the activity of Rh/SiO_2 for CO hydrogenation were studied in detail using DRIFTS. For comparison purposes, the promoting effects of some doubly promoted catalysts were also studied.

2. Experimental

2.1. Catalyst preparation and characterization

$Rh(NO_3)_3$ hydrate (Rh ~36 wt%, Fluka), $La(NO_3)_3 \cdot 6H_2O$ (99.99%, Aldrich), NH_4VO_3 (99.5%, Alfa Aesar), $LiNO_3$ (99.99%, Aldrich), $AgNO_3$ (crystal, MP Biomedicals), $Fe(NO_3)_2 \cdot 9H_2O$ (98+%, Alfa Aesar), $Zn(NO_3)_2 \cdot 6H_2O$ (99.998%, Alfa Aesar) and $Cu(NO_3)_2 \cdot 3H_2O$ (99.5%, Alfa Aesar) were used without further purification. Silica gel (99.5%, Alfa Aesar) was first ground and sieved to 30–50 mesh (0.3–0.6 mm), washed using boiled distilled water for 3 times to remove possible impurities such as Fe and Na, and then calcined in air at 500 °C for 4 h before being used as a support in catalyst preparations.

Catalyst preparation has been described in our previous paper [59] by sequential or co-impregnation of silica gel with an aqueous solution of $Rh(NO_3)_3$ hydrate and aqueous solutions of promoter precursors (2 mL aqueous solution/1 g silica gel) to incipient wetness, 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.

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.

A Scintag XDS 2000 θ/θ powder X-ray diffractometer (XRD) equipped with Cu $K\alpha1/K\alpha2$ (λ = 1.540592 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 $CO/Rh_s = 1$.

2.2. Nomenclature

For the catalysts referred to as $Rh/M/SiO_2$ (M = promoter), silica gel was first impregnated with an aqueous solution containing a promoter precursor, and then calcined 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 atomic symbol indicate the weight percent of that atom based on the weight of support silica gel. The promoters will be referred to by their atomic symbols even though they are mostly in the form of oxides in the catalysts. SiO_2 was omitted in the names of the catalysts in figures and tables to make them more readable.

2.3. Reaction

CO hydrogenation was performed in a fixed-bed differential reactor as described elsewhere [59]. The catalyst (0.3 g) was diluted with inert α-alumina (3 g) to avoid channeling and hot spots. Prior to reaction, the catalyst was heated to 500 °C (heating rate ~6 °C/min) and reduced *in situ* with hydrogen (flow rate = 30 mL/min) for 1 h. The catalyst was then cooled down to the reaction temperature in H_2 and the reaction started as gas flow was switched to H_2/CO (molar ratio of $H_2/CO = 2$, total flow rate = 45 mL/min) at 1.8 atm total pressure. Note that this study is part of a more extended investigation using a variety of techniques including SSITKA (steady-state isotopic transient kinetic analysis [60]) and equivalent reaction conditions are required for comparison of all the data. Thus, the reaction conditions were not optimized for the formation of C_{2+} oxygenates. The products, including hydrocarbons and oxygenates, were analyzed on-line by an FID (flame ionization detector) in a 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 5%. 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.

2.4. DRIFTS

A Nicolet 6700 FTIR spectrometer equipped with a Harrick DRIFT (diffuse reflectance infrared Fourier transform) cell was employed for the IR study. The cell contains a reaction chamber designed for operation from room temperature up to at least 600 °C under vacuum. The reaction chamber has a temperature-controlled sample stage, which is thermally isolated from the outer wall by a water-cooled jacket. The reaction chamber was covered during pretreatment and measurement with a removable dome containing glass observation and two CaF_2 windows. About 0.05 g sample was ground and placed into the sample cup. Ultrahigh-purity He, H_2 and CO (99.999%, National Welders) used in the IR investigations were purified by molecular sieve traps (Alltech) and He was further purified by an Oxytrap (Alltech). Prior to exposure to the reaction gas, the sample was reduced *in situ* at 500 °C in a flow of H_2 (20 mL/min) for 30 min, followed by He (50 mL/min) flushing at 500 °C for 0.5–1 h. After cooling down to the desired temperature in He, a background spectrum was taken, then the reactant gas (or gas mixture) flow was started to the cell and the infrared spectra were taken at 4 cm^{-1} resolution with 128 interferograms being added to obtain a satisfactory signal-to-noise ratio. A total flow rate of 50 mL/min was used in the IR study. Gas mixtures of CO/He (CO/He = 1/24, $P_{CO} = 0.04$ atm), CO/H_2/He (CO/H_2/He = 1/2/22, $P_{CO} = 0.04$ atm, $P_{H_2} = 0.08$ atm) and H_2/He (H_2/He = 2/23, $P_{H_2} = 0.08$ atm) were used during CO adsorption, CO hydrogenation and H_2/He flushing. One reason for using the inert diluent during the IR study is to minimize pressure fluctuations over the catalyst surface during gas switches. The IR study was not carried out using exactly the same conditions as those for reaction due to experimental limitations. The experimental conditions used, however, should not have affected greatly the nature of the adsorbed CO in the CO partial pressure range of 0.04 atm (IR) and 0.6 atm (reaction) [14].

Due to the fact that silica absorbs IR below 1300 cm^{-1} [22,61], the DRIFTS study was limited to the IR region >1400 cm^{-1} (the signal became noisy below 1400 cm^{-1}). Since the thermocouple monitoring the cell temperature was located at the bottom of the sample cup and it was not possible to place another thermocouple closer to the sample surface, the actual temperature of the sample surface exposed to the IR beam could be slightly different from the temperature recorded by the installed thermocouple. For all the catalysts, the CO adsorption bands were fully developed and stable within 20 min of exposure of the catalysts to the reactant gas or gas mixture. Unless otherwise specifically indicated, all the IR spectra of CO adsorption were taken after a sample had been exposed to the IR beam for 30 min.

3. Results

3.1. Catalyst characterization

The as-prepared Rh-based catalysts were all small dark brownish granules of 30–50 mesh. X-ray diffraction (XRD) patterns (not shown) of these as-prepared or 500 °C reduced catalysts were identical, showing no distinct peaks in the 2θ range of 5–65°, which suggests that Rh and promoters were highly dispersed after preparation and pretreatment. The BET surface areas of all the catalysts were around 250 cm^2/g.

3.2. CO hydrogenation

Table 1 lists the compositions and the catalytic activities for CO hydrogenation of the different catalysts. 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. Reactions using pure silica or silica impregnated with only promoters (except for Fe) resulted in negligible amounts of products, indicating that Rh is the active component for CO hydrogenation. The catalytic results for the CO hydrogenation over non-promoted and Rh/SiO_2 catalysts can be summarized as following:

- La, V, LaV, Fe, LaLi, LaCu and Ag promotion resulted in an increase in overall rate;
- Li, Zn and Cu promotion resulted in a decrease in overall rate;
- La, LaV, Li and LiLa promotion resulted in an increase in the selectivity for C_{2+} oxygenates (EtOH + acetaldehyde + other higher oxygenates with 2 or more carbons);

Table 1

Catalytic activities of non-promoted and promoted Rh/SiO_2 catalysts.

Catalyst	Composition (wt%)	molar ratio of promoter/Rh	SS* Rate [a] (μmol/g/s)	Selectivity (%)[b]					
				CH_4	C_{2+}HC[c]	MeOH	Acetaldehyde	EtOH	Other C_{2+} oxy[d]
Rh(1.5)	1.5		0.03	41.8	37.0	1.2	5.9	14.3	–
Rh(1.5)-La(2.6)	1.5, 2.6	La/Rh = 1.3	0.09	35.3	32.0	3.2	5.8	23.6	0.1
Rh(1.5)/V(1.5)	1.5, 1.5	V/Rh = 2	0.09	12.6	64.1	6.0	1.3	14.6	2.2
Rh(1.5)-La(2.6)/V(1.5)	1.5, 2.6, 1.5	La/Rh = 1.3 V/Rh = 2	0.28	14.4	51.8	2.9	7.1	21.6	2.2
Rh(1.5)-Fe(0.8)	1.5, 0.8	Fe/Rh = 1	0.12	55.3	13.7	9.5	2.2	19.4	0
Rh(1.5)/Ag(1)	1.5, 1	Ag/Rh = 0.5	0.11	51.4	19.2	7.9	4.6	15.8	1
Rh(1.5)/Li(0.07)	1.5, 0.07	Li/Rh = 1	0.02	29.6	33.9	2.6	28.3	5.8	0
Rh(2)-Li(0.043)-La(2.6)	2, 0.043, 2.6	Li/Rh = 0.5 La/Rh = 1	0.14	49.6	15.2	3.2	8.4	22.3	0
Rh(1.5)/Zn(0.5)	1.5, 0.5	Zn/Rh = 0.5	0.007	10.0	71.2	12.9	–	5.7	–
Rh(2)-Zn(0.6)-La(2.6)	2, 0.6, 2.6	Zn/Rh = 0.5 La/Rh = 1	0.05	43.1	17.2	12.7	13.1	5.3	0.1
Rh(1.5)/Cu(0.5)	1.5, 0.5	Cu/Rh = 0.5	0.002	58.0	–	25.3	–	16.7	–
Rh(2)-Cu(0.6)-La(2.6)	2, 0.6, 2.6	Cu/Rh = 0.5 La/Rh = 1	0.09	46.9	10.6	24.1	5.4	13.1	0.1

* Steady state.

[a] Catalyst: 0.3 g; Inert: α-alumina 3 g; Pretreatment 500 °C; Reaction conditions: $T = 230$ °C, $P = 1.8$ atm, flow rate = 45 mL/min (H_2/CO = 2), data taken at 15 h after steady state reached; Experimental error: ±5%.

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

[c] Hydrocarbons with 2 or more carbons.

[d] Other oxygenates besides acetaldehyde and ethanol with 2 or more carbons.

- V, LaV and Zn promotion resulted in a significant decrease in the CH_4 selectivity;
- V, Fe, Ag, Zn, Cu and CuLa significantly increased the MeOH selectivity.

The catalytic activities of singly promoted catalysts for CO hydrogenation are in agreement with the literature (V and/or La: [59]; Fe: [24,44,45]; Li: [24]; Cu: [57,62]). The only exception is the addition of Zn, which resulted in a much decreased activity. Ichikawa's group observed only slight decrease in activity when Rh(4.0 wt%)/SiO_2 was modified with Zn [34]. The inconsistence might be due to the different loadings of Rh and Zn. For the doubly promoted catalysts, only La + V showed a satisfactory overall performance with regards to both the activity and selectivity towards ethanol. It is important to also note that the La + V doubly promoted catalyst has also been found to give >50% selectivity to EtOH at a higher pressure [63].

Thus, it is obvious that the addition of different promoters to Rh/SiO_2 can change significantly the activity and selectivity of a Rh catalyst for CO hydrogenation. The probe of the promoting effect in this study will focus on the two most 'positive' promoters (V and La) and the two most 'negative' promoters (Zn and Cu) found in this study.

3.3. CO chemisorption

Table 2 compares the results obtained from volumetric CO chemisorption. It was found in previous studies that La addition to Rh increases CO adsorption while the addition of V results in a suppression in CO chemisorption [29,33,59]. The presence of Zn or Cu also reduced CO chemisorption, though not as significantly for V. Readers are cautioned that the use of chemisorption of CO or H_2 to estimate the dispersion of metal catalysts may give under/overestimations as a result of suppression/blockage of chemisorption by promoters or interaction of adsorbed molecules with the promoter at the interface of the promoter and the catalytic metal. Kip et al. [64] have also suggested that hydrogen chemisorption measurements cannot be used with total confidence to determine metal particle sizes in highly dispersed catalysts due to the uncertainty in $H/M_{surface}$ stoichiometry. The CO chemisorption results obtained in this study suggest that the addition of promoters changed the CO adsorption properties of Rh/SiO_2.

3.4. IR study

3.4.1. CO adsorption on silica and non-Rh containing catalysts

The IR spectra acquired after exposing silica and silica containing only promoters to CO/He for 30 min at 230 °C are shown in Fig. 1. In all the spectra, the bands centered around 2180 and 2125 cm^{-1} can be attributed to gaseous CO [65], which could readily be removed by flushing with He for 10 min (not shown). No bands in the range 2100–1600 cm^{-1} were apparent for these samples.

Table 2
CO chemisorption on Rh-based catalysts.

Catalyst	CO-chemisorbed (μmol/g) (total)	Metal dispersion (%)
Rh(1.5)	43.0	33.3
Rh(1.5)-La(2.6)	72.9	56.4
Rh(1.5)/V(1.5)	10.7	8.3
Rh(1.5)-La(2.6)/V(1.5)	11.2	8.7
Rh(1.5)/Cu(0.5)	37.2	28.7
Rh(1.5)/Zn(0.5)	27.3	21.1

Error = ±5% of the value measured.

3.4.2. CO adsorption on different Rh catalysts at room temperature and 230 °C

A series of spectra of the *in situ* reduced catalysts after CO adsorption at room temperature for 30 min is given in Fig. 2. The

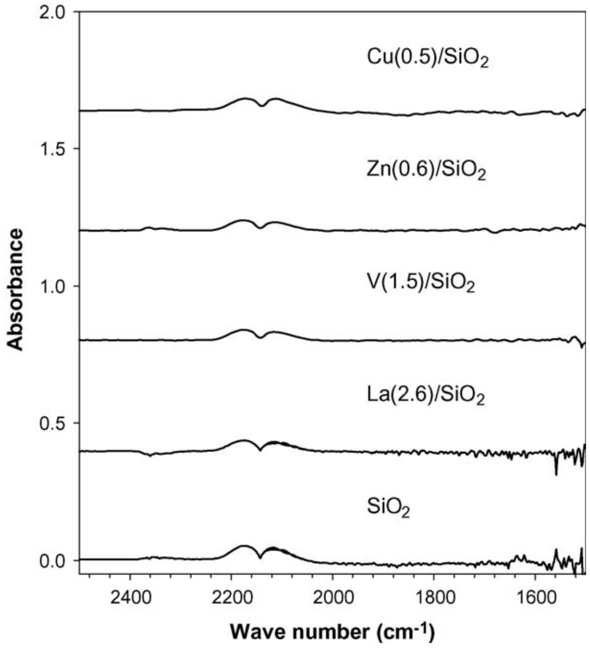

Fig. 1. The infrared spectra of CO chemisorbed at 230 °C on the SiO_2 support and on the support with various promoters without Rh.

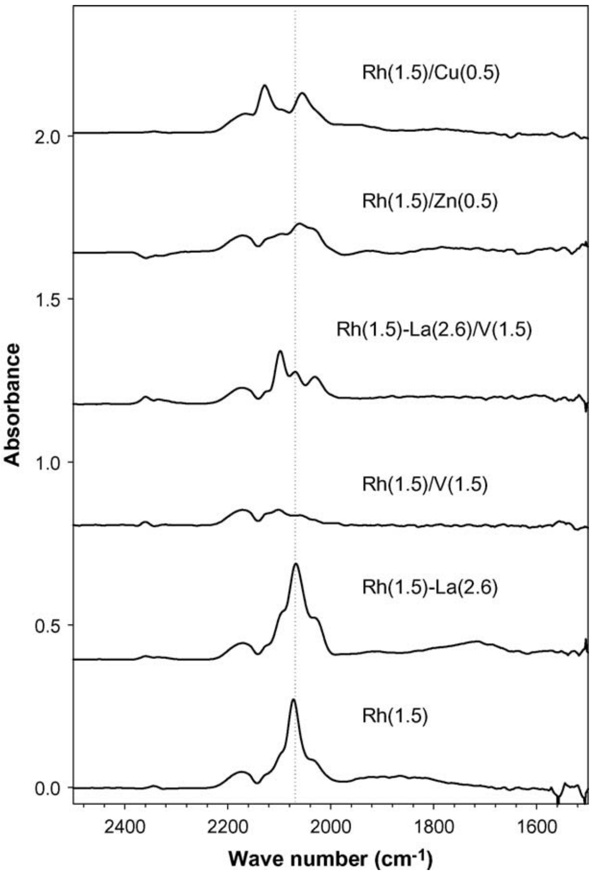

Fig. 2. The infrared spectra of CO chemisorbed on the different catalysts at room temperature.

Table 3
The positions and assignments of IR bands for different catalysts.

Catalyst	Freq. at room temperature (cm^{-1})					Freq. at 230 °C (cm^{-1})				
	CO(*gdc*)	CO(*l*)	CO(*b*)	CO(*bd*)	CO(*t*)	CO(*gdc*)	CO(*l*)	CO(*b*)	CO(*bd*)	CO(*t*)
Rh(1.5)	2095 2034	2070 (s)	1864				2054 (s)	1827	1919	
Rh(1.5)-La(2.6)	2094 2026	2068 (s)			1716		2051 (s)		1917	1716 1575
Rh(1.5)/V(1.5)	2103 (s) 2031	2060					2055			
Rh(1.5)-La(2.6)/V(1.5)	2102 (s) 2035	2069				2094	2057 (s)			
Rh(1.5)/Zn(0.5)	2097 2031	2059 (s)		1922			2034 (s)		1934	
Rh(1.5)/Cu(0.5)		2056		1946			2038 (s)		1936	

positions and assignments of bands are listed in Table 3. As described in our previous study [59], the IR spectra of non-promoted and V or/and La promoted Rh(1.5)/SiO_2 interacting with CO at room temperature all exhibited a band around 2065 cm^{-1} and a doublet at ~2100 and ~2030 cm^{-1} with different relative intensities. The 2065 cm^{-1} band can be attributed to the linear adsorbed CO [CO(*l*)] and the doublet can be assigned to the symmetric and asymmetric carbonyl stretching of the gem-dicarbonyl Rh(*I*)$(CO)_2$ [CO(*gdc*)] [59]. The IR spectrum of CO adsorbed on Rh(1.5)/SiO_2 also showed a weak broad peak assigned to bridge bonded CO [CO(*b*)] at 1864 cm^{-1} [9] and the spectrum for Rh(1.5)-La(2.6)/SiO_2 showed a weak peak at lower frequency (1716 cm^{-1}), which could be assigned as tilted CO [CO(*t*)] [35]. For Zn-promoted Rh/SiO_2, the CO(*l*) band was suppressed and there were some weak peaks in the range 1950–1600 cm^{-1}, which may be due to bridging CO species [27]. The addition of Cu to Rh/SiO_2 led to a quite different CO adsorption behavior, showing a strong band centered at 2130 cm^{-1} besides CO(*l*) (centered at 2056 cm^{-1}). The 2130 cm^{-1} band could be assigned to CO adsorbed on metallic Cu or Cu^+ [66–69], which decreases in intensity at higher temperature [69]. This could also explain why no CO adsorption was observed on Cu(0.5)/SiO_2 at 230 °C. With regards to the adsorbed CO, it is obvious that La enhanced CO chemisorption and the addition of V significantly suppressed CO adsorption on Rh/SiO_2, as was the case for Zn or Cu promoted catalysts. The amount of adsorbed CO at room temperature is consistent with the chemisorption results except for the V-containing catalysts. One likely reason is that the pretreatment (reduction) conditions for IR and chemisorption were not the same. The main difference was that the sample was evacuated at 10^{-6} mm Hg and 500 °C for 2 h after reduction by H_2 during chemisorption, while in IR study the sample was purged with flowing He for 0.5 h at 500 °C after reduction by H_2. It was well known that pretreatment conditions have significant effects on the structure and activity of vanadium oxide promoted Rh catalysts [47,50,70]. Since the pretreatment conditions used for the IR study were closer to those used in the reduction CO hydrogenation with respect to the pressure and the time at 500 °C, results obtained from IR should be more meaningful in a comparison with those for reaction.

For IR spectra recorded at the reaction temperature of 230 °C as shown in Fig. 3, CO(*l*) dominated in all the spectra and CO(*gdc*) disappeared except for the doubly promoted (V + La) catalyst. The 2130 cm^{-1} band observed for the Cu promoted catalyst no longer was evident, consistent with the IR spectrum of CO adsorption on Cu(0.5)/SiO_2 at 230 °C. Except for the V-containing catalysts, a band centered around 1930 cm^{-1} became distinct for all the catalysts. This band may be assigned to the bridged $Rh_2(CO)_3$ dimer, CO(*bd*) [9,10,40]. For the non-promoted and La or Cu promoted Rh(1.5)/SiO_2 catalysts, the intensities of CO(*b*) increased. The La singly promoted catalyst Rh(1.5)-La(2.6)/SiO_2 exhibited the highest intensities of CO adsorption bands and the intensity of CO(*t*) band centered around 1716 cm^{-1} substantially increased compared to the IR spectrum recorded at room temperature. In addition, a weak peak around 1575 cm^{-1} was observed. The assignment of this new peak is unclear and will be discussed in a later section. It is also interesting to note (1) for the V-containing catalysts, no CO(*b*) was observed in the IR spectra; (2) as shown in Table 3, compared to IR spectra taken at room temperature, the position of CO(*l*) shifted to a lower frequency for all the catalysts; (3) the positions of CO(*l*) for the Cu- and Zn-promoted catalysts were about 20 cm^{-1} lower than for other catalysts.

Fig. 4 shows the IR spectra of adsorbed species on different catalysts after the CO/He flow was switched to pure He at 230 °C. For all the catalysts, gaseous CO disappeared within the first 5 min. The intensities and wavenumbers of CO(*l*) decreased with time, ascribable to a decrease in dipole coupling with desorption and the

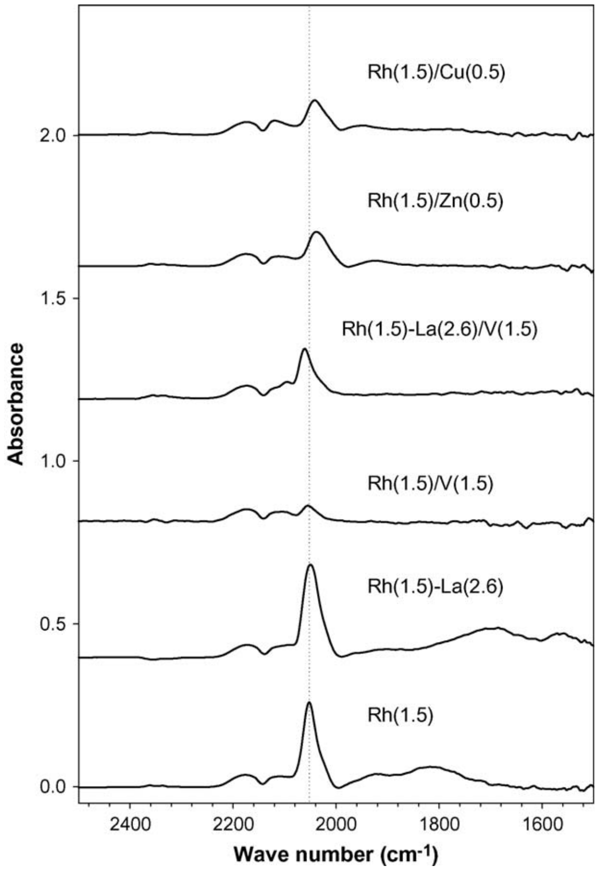

Fig. 3. The infrared spectra of CO chemisorbed on the different catalysts at 230 °C.

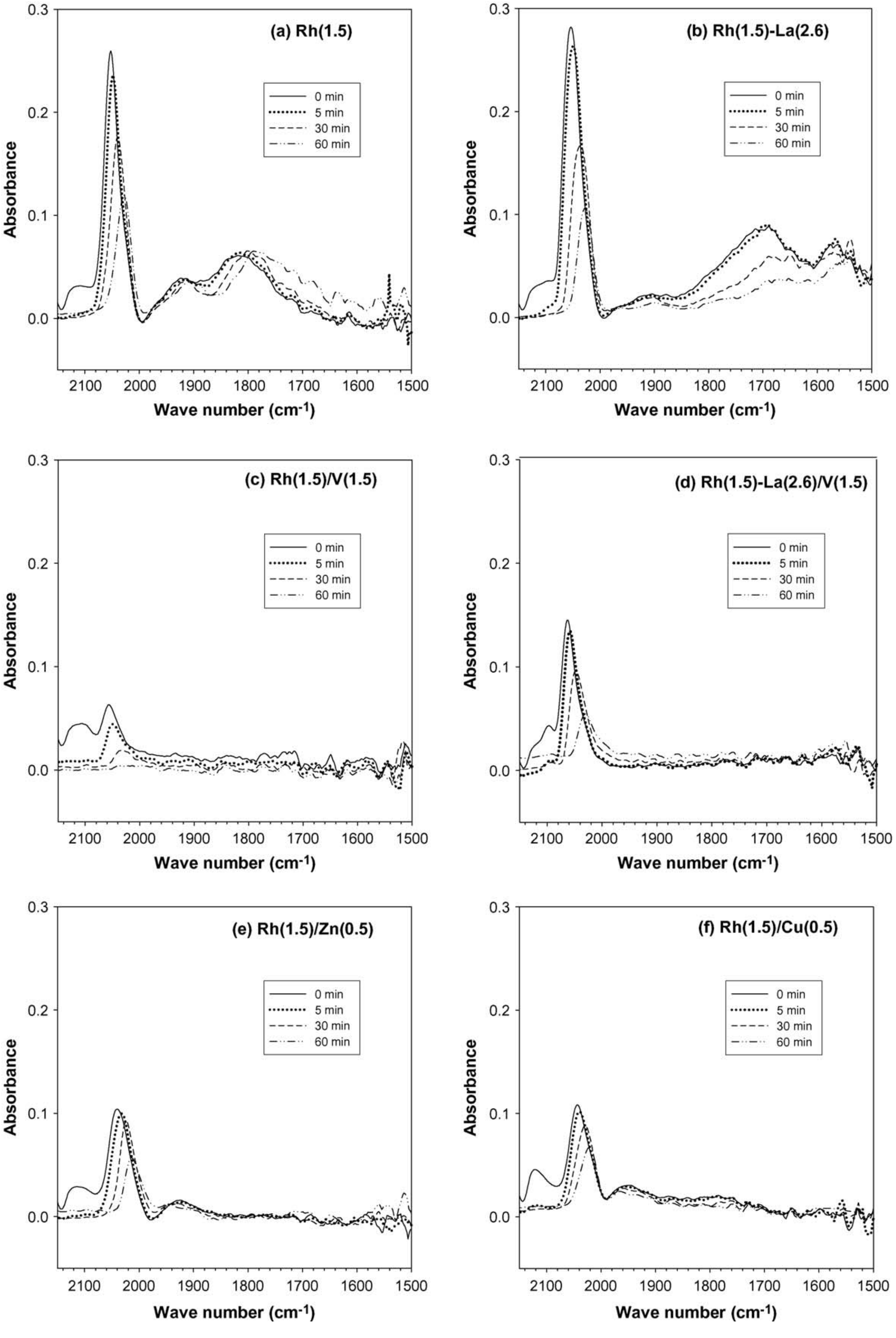

Fig. 4. The infrared spectra of CO chemisorbed at 230 °C for 30 min followed by flushing with pure He (time = 0, start of He flushing): (a) Rh(1.5), (b) Rh(1.5)-La(2.6), (c) Rh(1.5)/V(1.5), (d) Rh(1.5)-La(2.6)/V(1.5), (e) Rh(1.5)/Zn(0.5) and (f) Rh(1.5)/Cu(0.5).

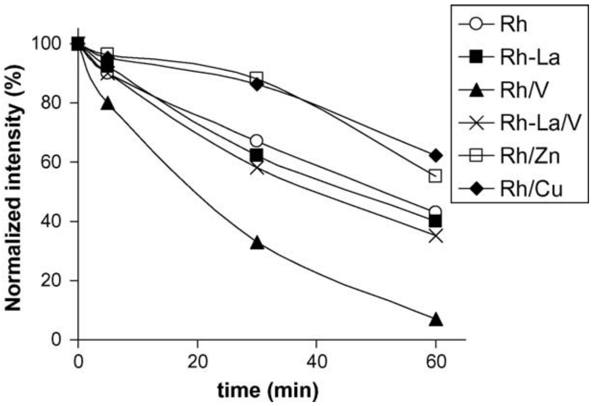

Fig. 5. Normalized IR band intensity vs time for CO(l) after switching CO /He to He. (Based on results shown in Fig. 4; Normalized intensity = 100% × I/I_{max}; Experimental error = ±10%.)

decrease in surface coverage [71]. The rates of decrease in the band for CO(l) on different catalysts were different, following the order as shown in Fig. 5: Rh(1.5)/V(1.5)/SiO$_2$ > Rh(1.5)-La(2.6)/V(1.5)/SiO$_2$ > Rh(1.5)-La(2.6)/SiO$_2$ > Rh(1.5)/SiO$_2$ > Rh(1.5)/Zn(0.5)/SiO$_2$ ~ Rh(1.5)/Cu(0.5)/SiO$_2$. With regards to the rate of decrease in different adsorbed CO species on a same catalyst, the band for CO(l) decreased much faster than those for CO(b) and CO(bd). On Rh(1.5)-La(2.6)/SiO$_2$, the rates of decrease in the band for CO(t) and the band around 1575 cm^{-1} were about the same as that for CO(l). One clear point could be drawn here is that the addition of V increased the desorption rate of the absorbed CO species while the addition of Zn or Cu had the opposite effect. The change in the desorption rate of the CO species might be due to a change in the CO-Rh bond strength after the addition of different promoters.

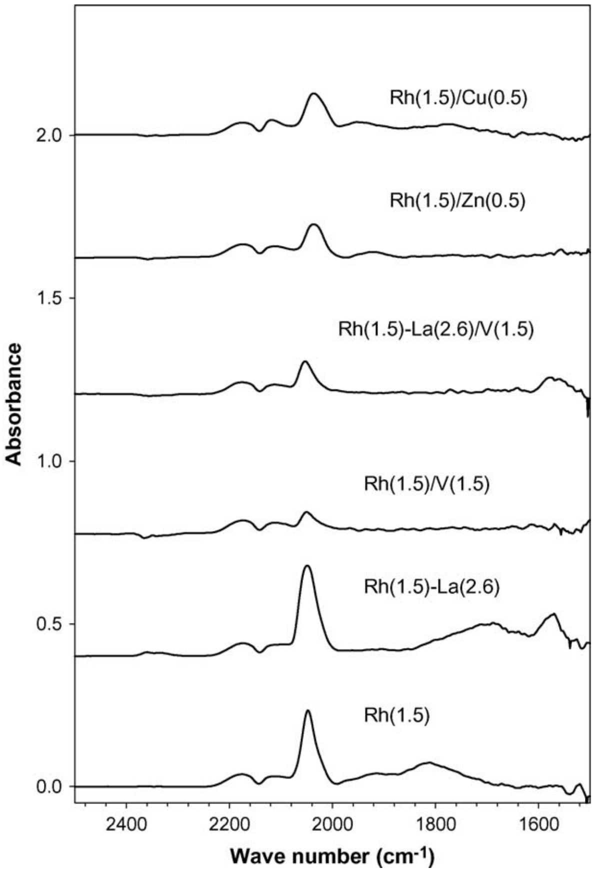

Fig. 6. The infrared spectra after CO hydrogenation on different catalysts at 230 °C for 30 min.

3.4.3. *CO reaction with H_2 on the different catalysts at 230 °C*

Fig. 6 shows the IR spectra taken after CO reaction with H$_2$ at 230 °C for 30 min on the different catalysts. The spectra look quite similar to the spectra for CO absorbed in the absence of H$_2$ on the catalytic surfaces. Two new features, however, were observed for the doubly promoted catalyst—CO(gdc) no longer existed and a weak band around 1580 cm^{-1} became distinct. At the same time, the relative intensity of the band centered around 1575 cm^{-1} for Rh(1.5)-La(2.6)/SiO$_2$ increased compared to the spectrum taken during CO adsorption alone. Since the positions of the low frequency (below 1600 cm^{-1}) bands observed on the La singly promoted catalyst and the doubly promoted catalyst were very close, they should share the same origin and will be referred to as the "1575" band in this paper. No obvious bands corresponding to C–H bonds were detected at 230 °C during CO hydrogenation in the IR region 2800–3100 cm^{-1} on any catalyst in this study, which might be due to the low concentrations of surface CH$_x$ species.

Fig. 7 shows the IR spectra after switching the CO/H$_2$/He flow to H$_2$/He and Table 4 lists the change in the intensities of individual IR bands after 30 min for different catalysts. Obviously, all the bands decreased faster compared to being flushed by pure He alone as shown in Fig. 4, suggesting that the adsorbed CO species were involved in the hydrogenation reaction, although it is unclear what fraction of the adsorbed CO simply desorbed and what fraction participated in the reaction. The rates of decrease in the band for CO(l) followed a similar order as for He flushing of the different catalysts: Rh(1.5)/V(1.5)/SiO$_2$ > Rh(1.5)-La(2.6)/V(1.5)/SiO$_2$ > Rh(1.5)-La(2.6)/SiO$_2$ > Rh(1.5)/SiO$_2$ > Rh(1.5)/Cu(0.5)/SiO$_2$ > Rh(1.5)/Zn(0.5)/SiO$_2$. With respect to the rates of decrease in the bands for different adsorbed CO species, CO(t) and the "1575" band exhibited about the same rate as that for CO(l) on La promoted Rh/SiO$_2$. On the doubly promoted catalyst, the "1575" band also decreased markedly, but with a slower rate than that for CO(l). On the non-promoted catalyst, the bands for CO(b) and CO(bd) showed much slower decreases than that of CO(l), in agreement with the literature [40,72].

Note that no effort was made to quantitatively correlate the activities with active CO sites of the catalysts based on the chemisorption results and the fraction of CO which disappeared

Table 4
Change (%) of IR band intensity after switching CO/H$_2$/He to H$_2$/He for 30 min[a].

Catalyst	CO(l)	CO(b)	CO(bd)	CO(t)	"1575" band
Rh(1.5)	35.0	3.2	11.4	–	–
Rh(1.5)-La(2.6)	47.1	–	–	55.1	53.8
Rh(1.5)/V(1.5)	90.7	–	–	–	–
Rh(1.5)-La(2.6)/V(1.5)	79.1	–	–	–	55.4
Rh(1.5)/Zn(0.5)	11.7	–	11.7	–	–
Rh(1.5)/Cu(0.5)	25.0	29.4	17.5	–	–

[a] Based on results shown in Fig. 6; Change of intensity = 100% × $(I_{max} - I_{30min})/I_{max}$; Experimental error = ±10%.

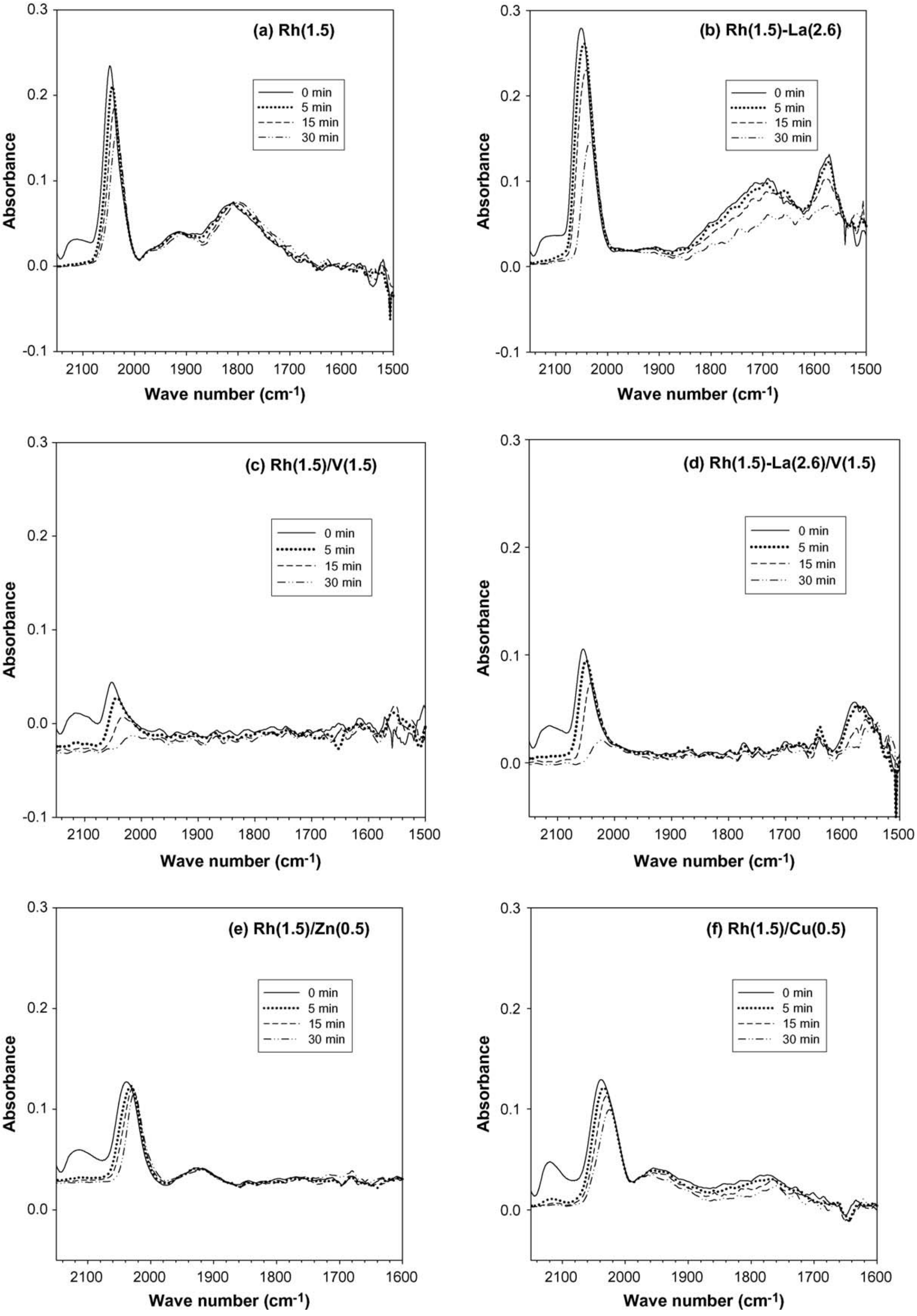

Fig. 7. The infrared spectra after CO hydrogenation at 230 °C for 30 min followed by flushing with H_2/He (time = 0, start of H_2/He flushing): (a) Rh(1.5), (b) Rh(1.5)-La(2.6), (c) Rh(1.5)/V(1.5), (d) Rh(1.5)-La(2.6)/V(1.5), (e) Rh(1.5)/Zn(0.5) and (f) Rh(1.5)/Cu(0.5).

during purging with flowing H_2/He. Using Rh dispersion obtained at room temperature may lead to questionable results in this study since (1) the IR study showed that restructuring took place for these catalysts at the reaction temperature and (2) dispersion data for a lot of differently promoted catalysts are often not perfect because chemisorption methods developed for a simple supported catalyst (e.g., Rh/SiO_2) may not apply to a promoted catalyst (e.g., Rh/V/SiO_2) because of significant changes in the chemisorption bonding and activation energy.

4. Discussion

4.1. Reactivity of adsorbed CO species on Rh-based catalysts

In this study, the characteristics of the IR spectra for only CO adsorbing (in the absence of H_2) on singly promoted Rh-based catalysts are in general agreement with results in the literature, which can be summarized as following: (1) the addition of La resulted in an increase in total adsorbed CO and the formation of CO(*t*), which may be due to new adsorption sites at the Rh-LaO_x interface/surface [35]; (2) the addition of V suppressed CO absorption, which may be due to a strong interaction of Rh and V (Rh might be covered by vanadium oxide [32,33]); (3) the addition of Zn and Cu also suppressed CO adsorption [27,34,62], although not as strongly as with the addition of V. Thus, the modification of Rh/SiO_2 with different promoters resulted in significant differences in the adsorption behavior of CO on different catalytic surfaces.

Several issues related to the adsorbed CO species deserve special note here. The first one is the formation of the gem-dicarbonyl species CO(*gdc*). Since it is widely accepted that the dicarbonyl species can only be formed on highly dispersed rhodium [13,14], the formation of CO(*gdc*) at room temperature on the non-promoted and the promoted catalysts could be an indication of highly dispersed Rh in these catalysts. The disappearance of CO(*gdc*) at reaction temperature (230 °C) for most of the catalysts in this study was likely due to the reduction of $Rh^+(CO)_2$ to form CO_2 and $Rh_x{}^0(CO)$ species [15,16]. However, CO(*gdc*) was still observed for the doubly promoted catalyst Rh(1.5)-La(2.6)/V(1.5)/SiO_2 at the reaction temperature, although with much decreased intensity. The difference in the IR spectra recorded at different temperatures suggests that some restructuring might have also occurred for all the catalysts, but perhaps with the doubly promoted catalyst conserving some of the highly dispersed Rh at the reaction temperature. It has been reported that the activities and selectivities of Rh-based catalysts can be correlated to the loadings and particle sizes of Rh in catalysts for CO hydrogenation [73–75]. Thus, the high performance of Rh(1.5)-La(2.6)/V(1.5)/SiO_2 may be related to high dispersion at the reaction temperature.

The second issue is the formation of CO(*t*) and the "1575" band. It has been suggested that the formation of CO(*t*) due to the addition of highly oxophilic promoters including Mn, Ti, Zr, Nb [34], Ce [22], La [35] would enhance CO dissociation or insertion. However, some studies have shown that CO(*t*) is inactive for CO insertion during the reaction of C_2H_4/H_2 with preadsorbed CO on Rh-Ce/SiO_2 [76] and Rh-Mn/SiO_2 [77]. In this study, the La promoted Rh/SiO_2 catalyst did exhibit a band for CO(*t*) and an increased reactivity compared to the non-promoted catalyst, but there was no direct evidence showing that the formation of CO(*t*) led to a higher selectivity towards oxygenates. The addition of La also led to another new band centered around 1575 cm^{-1} during CO adsorption on the catalyst, and this band seemed to grow when H_2 was added. Based on previous publications, this IR band could be due to the vibration of carbonate groups formed by the reaction of CO with LaO_x [35,78,79] or to adsorbed acetate groups or to formate species formed during the CO hydrogenation on Rh catalysts [19,21,23,30,75]. If this band belongs to acetate groups, it should be removed more slowly than all the other bands after switching the feed to the infrared cell from CO/H_2 to H_2 alone [30]. If this band belongs to a carbonate species and is a reaction intermediate, it should convert to an adsorbed formate species during CO hydrogenation [21]. In this study, it was found that: (1) no such band formed during the exposure of La supported on silica to CO at 230 °C; (2) almost no CO_2 was observed from reaction; (3) during CO hydrogenation, this band grew on both La-containing catalysts and no new bands formed, suggesting that its corresponding species should contain H; and (4) this band decreased with about the same rate as that for CO(*l*) on the La singly promoted catalyst. Thus, it is unlikely to be due to acetate or carbonate groups. Instead, this band may due to a formyl species (HCO) formed on LaO_x patches covering the Rh particles that may constitute active sites for the reaction.

Third, the correlation between the adsorbed CO species and the activity for CO hydrogenation is still unclear. Among the catalysts in this study, it is interesting to note that no CO(*b*) was observed on more active catalysts (both V and La-containing catalysts). On the other hand, the Zn-promoted catalyst which exhibited poor activity showed primarily CO(*l*) after CO adsorption. Thus, simply relating the catalytic activity to the ratio of CO(*l*)/CO(*b*) is not appropriate. At the reaction temperature of 230 °C, the band for CO(*gdc*) observed during CO adsorption no longer existed during CO hydrogenation on the doubly promoted catalyst, but this was more likely due to the reduction of Rh^+ to Rh^0 by H_2, leading to the disappearance of $Rh^+(CO)_2$ [13,14] instead of it being involved in CO hydrogenation. CO(*t*) and the "1575" band were quite unique for the La-containing catalysts. Hindemann proposed that the tilted adsorption mode is probably a key one in determine selectivity and activity [2]. This study did show that CO(*l*) and CO(*t*) appeared to be more active for CO hydrogenation and CO(*b*) and CO(*bd*) less active. However, the V singly promoted catalyst also had a much enhanced CO hydrogenation activity, but the IR spectrum of CO adsorbed on this catalyst did not show any bands for CO(*t*) or CO(*b*). These results suggest that the formation of CO(*t*) and/or other new CO adsorption species is not the only way to enhance the activity of Rh-based catalysts and the promoting mechanism for V should be different than that for La.

The reason behind the difficulty to understand promoter action solely using IR is that IR studies of CO hydrogenation provide only 'macroscopic' information about the behavior of reactants, which may be limited or even misleading since only a small fraction of the adsorbed CO participates in reaction [80]. Another problem related to the IR technique is that only the vibrations of bonds normal to the surface are infrared active.

4.2. The intrinsic promoting nature of different promoters

Based on this IR study, it is conceivable that the higher catalyst activity observed for the La singly promoted Rh catalyst was primarily the result of an increase in the concentration of active surface intermediates, which could be related to the enhanced total CO adsorption and the formation of new adsorbed CO species at the LaO_x-Rh interface. On the other hand, V partially suppressed total CO adsorption, perhaps due to SMSI [50,81], but it significantly enhanced the desorption rate and/or reactivity of these adsorbed CO species judging from the rate of decrease in the band for CO(*l*) following a switch to a He or H_2/He flow without CO for the V singly promoted catalyst. The reduced CO adsorption could lead to an increase of hydrogen mobility between V and Rh, which might enhance CO dissociation and hydrogenation as suggested by other researchers using other techniques such as TPD [32,50,82,83]. The effect of V promotion of Rh/SiO_2 for CO hydrogenation is similar to that of Ce. Chuang et al. reported that the addition of Ce to Rh/SiO_2 decreased the residence time of intermediates leading to C_2H_5CHO

during ethylene hydroformylation [76]. Interestingly, an IR study carried out by Lavalley et al. showed that the addition of Ce to Rh/SiO increased the reactivity of absorbed CO on the catalytic surface [22].

With regards to the doubly promoted catalyst Rh-La/V/SiO_2, IR study showed both new adsorbed CO species and increased desorption rate/reactivity of the adsorbed species during CO hydrogenation. Preliminary SSITKA (steady-state isotopic transient kinetic analysis) results suggest that the addition of both La and V lead to both an increased activity and an increase in the concentration of active surface intermediates compared to the non-promoted catalyst. In other words, the high activity of the doubly promoted catalyst is indeed due to a synergistic promoting effect of the combined additions.

As for the Zn or the Cu promoted catalyst, the much lowered catalytic activities were due to the low desorption rate/reactivity of the adsorbed CO species. One could conclude that most of the observed CO species on these catalysts might not be involved in the reaction. One possible consequence of this strong adsorption of CO is a suppression of hydrogen chemisorption and reactivity during CO hydrogenation as proposed by Chuang for Cu-Rh/SiO_2 [57]. It is uncertain yet whether the lower catalytic activity can be correlated to the shifted CO(*l*) band, as shown in Fig. 3.

5. Conclusions

Rh-based catalysts promoted by La, V, Fe, Li, Zn, Cu, and Ag were prepared by sequential or co-impregnation followed by calcination and reduction before being used for CO hydrogenation in a fixed-bed reactor at 230 °C and 1.8 atm. The activities and selectivities were measured after 15 h TOS at a H_2/CO ratio of 2. It was found that the doubly promoted Rh/SiO_2 catalyst promoted by both La and V exhibited the highest reaction activity and a good selectivity towards ethanol and other C_{2+} oxygenates. On the contrary, the addition of Zn and Cu dramatically reduced the reaction activity of Rh/SiO_2 for CO hydrogenation.

The effects of La, V, Zn and Cu on Rh/SiO_2 catalyst for CO hydrogenation were investigated using DRIFTS at atmospheric pressure. From the IR study, it was found that the behavior of CO adsorbed on different catalysts was different. While La enhanced total CO adsorption, the addition of V, Zn and Cu suppressed the CO adsorption to different extents. The doubly promoted Rh-La/V/SiO_2 showed only moderate CO adsorption. The infrared study of CO desorption and hydrogenation on different catalysts indicated that the linear Rh-CO [CO(*l*)] and the tilted Rh-CO [CO(*t*)] might be more active while the bridged Rh_2CO [CO(*b*)] and $Rh_2(CO)_3$ [CO(*bd*)] might be less active for the reaction. The addition of V appeared to enhance the desorption rate and/or reactivity of CO on the catalytic surface, while the addition of La may have created new active sites for the reaction. For the doubly promoted catalyst Rh-La/V/SiO_2, it appeared to have more active sites to adsorb CO than the V singly promoted catalyst and the adsorbed CO species appeared to be more active than those on the La singly promoted catalyst. On the contrary, the addition of Zn or Cu significantly reduced the desorption rate and/or reactivity of CO on the catalytic surface, resulting in poor performances for CO hydrogenation.

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