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La, V, and Fe promotion of Rh/SiO_2 for CO hydrogenation: Effect on adsorption and reaction

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ABSTRACT

This study is a continuation of the research reported recently that showed La and V doubly promoted Rh/SiO_2 catalysts to be active and selective for the synthesis of ethanol from syngas. In this work, the effect of Fe on $Rh–La–V/SiO_2$ was examined and the role of each individual promoter was further scrutinized. Several series of promoted Rh/SiO_2 catalysts were prepared by incipient wetness and characterized by BET, XRD, TEM, FTIR, TPR, and H_2-TPD. The catalytic activity was tested using a fixed-bed differential reactor at 230 °C and 1.8 atm. It was found that the addition of 0.8 wt% Fe, 2.6 wt% La, and 1.5 wt% V to 1.5 wt% Rh/SiO_2 resulted in the highest selectivity to ethanol (34.6%) and a moderate activity compared to other promoted catalysts. The investigation based on the catalytic performance and other characterizations of Rh/SiO_2 promoted by different promoters suggests that the primary promoting effects of La, V, and Fe are different. The main effects of the addition of different promoters in this study appear to be increasing CO adsorption and insertion for La, decreasing CO adsorption but enhancing CO dissociation and chain growth for V, and decreasing CO adsorption but enhancing hydrogenation for Fe. The synergistic effects of the multiple promoters indicate that the key in catalyst design for ethanol synthesis from syngas is to optimize CO dissociation, hydrogenation, and CO insertion in a balanced way.

1. Introduction

Catalytic synthesis of ethanol from coal-derived syngas provides an energy-efficient route to relieve the demand for fuel from imported crude oil [1,2]. Rh-based catalysts have been shown to have relatively high activity for the synthesis of C_2-oxygenates due to unique CO adsorption behavior on Rh [3–7]. The performances of Rh-based catalysts are highly dependent on the choice of promoter and support. As mentioned in the recent studies, typical Rh catalysts for ethanol synthesis from syngas contained multiple components, such as Rh–Mn–K [8], Rh–Ti–Fe–Ir [9], Rh–Li–Mn–Fe [10], Rh–Zr–Ir [11], and Rh–La–V [12,13]. The main challenges in heterogeneous catalytic processes for converting syngas to ethanol are low yield and poor selectivity using most known catalysts due to the complicated reaction characteristics. Another problem related to most known Rh-based catalysts is that high pressure (>40 atm) is usually required in order to achieve a higher selectivity for ethanol (>30%). For instance, CO hydrogenation was carried out at 37.5–53.3 atm in a recent study using a microchannel reactor with 34.8–56.1% ethanol selectivity [8].

In our previous studies [12,13], the effects of La and V on Rh/SiO_2 for CO hydrogenation were investigated. It was found that the addition of V or La increased the activity of Rh/SiO_2 (by 3X). On the other hand, doubly promoted Rh/SiO_2 (promoted with both La and V) exhibited an even higher activity (9X) and a moderate selectivity for ethanol (~22%) and other C_{2+} oxygenates at 230 °C, and a relatively low pressure of 1.8 atm. It was also found by IR [13] that the addition of La enhanced CO adsorption and created new reaction sites, while the addition of V decreased CO adsorption although the activities of the reaction sites increased. Since the use of just more of each promoter by itself was not able to produce the enhanced catalytic performance [12], the good performance of the $Rh–La–V/SiO_2$ catalyst appeared to be due to a synergistic promoting effect of the combined lanthana and vanadia addition through intimate contact with Rh.

The objective of this study was to investigate the effect of Fe promotion on this already doubly promoted catalyst and to further examine the role of each promoter in ethanol synthesis from syngas. Fe as a promoter for Rh-based catalysts has been studied by many researchers for CO hydrogenation and has shown interesting promoting effects on Rh for higher ethanol yield [14–24]. It has been proposed that the addition of Fe to Rh-based catalysts may boost the hydrogenation of acetaldehyde to form ethanol [17,18,20], may stabilize an acyl species (which can be efficiently converted to ethoxy species) during CO hydrogenation [21], may impede CO dissociation by suppressing the bridging carbonyl chemisorption on Rh [23], and may change the acidity of a Rh catalyst [25] (which apparently leads to a decrease in the formation rate of methane). It has also been suggested that the effect of Fe

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may be related to the oxidation state of Fe under reaction conditions [14,22].

In the present study, promotion with Fe was investigated as a means to improve the performance of the La and V doubly promoted Rh/SiO_2 catalysts for the synthesis of ethanol from CO hydrogenation. Various amounts of Fe were added to the La–V doubly promoted Rh catalysts, and these catalysts, as well as doubly and singly promoted catalysts, were investigated by BET, XRD, TEM, FTIR, TPR, H_2-TPD, and CO hydrogenation to probe the promoting effect of each promoter.

2. Experimental

2.1. Catalyst preparation

$Rh(NO_3)_3$ hydrate (Rh ~ 36 wt%, Fluka), $La(NO_3)_3 \cdot 6H_2O$ (99.99%, Aldrich), $Fe(NO_3)_3 \cdot 9H_2O$ (98.0%, Alfa Aesar), and NH_4VO_3 (99.5%, Alfa Aesar) were used without further purification. Catalysts were prepared by sequential impregnation or co-impregnation to incipient wetness of silica gel (SiO_2) (99.5%, Alfa Aesar, pre-washed [12]) with an aqueous solution of $Rh(NO_3)_3$ hydrate and aqueous solutions of promoter precursors (2 mL solution/1 g silica gel). Preparation was followed by drying at 90 °C for 4 h and then at 120 °C overnight, before being calcined in static air at 500 °C for 4 h.

2.2. Nomenclature

For the catalysts referred to as $Rh/M/SiO_2$ (M = promoter), silica gel was first impregnated with the aqueous solution containing the precursor of the promoter and then calcined at 500 °C for 4 h, followed by impregnation with the $Rh(NO_3)_3$ aqueous solution and calcination at 500 °C for an additional 4 h. $Rh–M/SiO_2$ represents a catalyst prepared by co-impregnation with a solution containing Rh and M. The promoters are denoted by their atomic symbols in this study even though they were mostly in the form of oxides in the catalysts. SiO_2 is omitted in the names of the catalysts in figures and tables for simplicity since they were all SiO_2-supported ones.

2.3. 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 vacuum at 150 °C for 4 h.

A Scintag XDS 2000 θ/θ powder X-ray diffractometer (XRD) equipped with Cu Kα1/Kα2 ($\lambda = 1.540592$ Å and 1.544390 Å, respectively) radiation was employed for the collection of X-ray diffraction patterns with a step size of 0.03° in the 2θ range of 5–65°.

2.4. FTIR

A Nicolet 6700 FTIR spectrometer equipped with a Harrick DRIFT (diffuse reflectance infrared Fourier transform) cell as described elsewhere [13] was employed for the IR studies. 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 study were purified by molecular sieve traps (Alltech), and He was further purified by an Oxytrap (Alltech). Prior to the exposure to 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 a He (50 mL/min) flush at 500 °C for 0.5 h. After cooling down to the desired temperature in He flow, a background spectrum was taken. Then 4 v/v% CO/He (total 50 mL/min) was flowed through the cell, and the infrared spectra were taken at 4 cm^{-1} resolution. One hundred and twenty eight interferograms were added to obtain a satisfactory signal-to-noise ratio.

2.5. Reaction

CO hydrogenation was performed in a fixed-bed differential reactor as described elsewhere [12]. The catalyst (0.3 g) was diluted with α-alumina (3 g) and loaded between quartz wool plugs in the middle of the reactor with a thermocouple close to the catalyst bed. Ultrahigh-purity H_2 and CO (99.999%, National Welders) used in the reaction studies were purified by molecular sieve traps (Alltech) and CO was further purified by a CO purifier (Swagelok). The catalyst was activated *in situ* in hydrogen (flow rate = 30 mL/min) at 500 °C for 1 h, then cooled down to 230 °C in hydrogen. The reaction started as gas flow was switched to H_2 (30 mL/min) + CO (15 mL/min) at 1.8 atm total pressure. A Varian 3380 GC was used to analyze the effluent gas on-line. Hydrocarbons and oxygenates were separated by a Restek RT-QPLOT column of ID 0.53 mm and length 30 m, and were analyzed by an FID. CO and other inorganic gases were analyzed by a TCD after separation with a Restek HayeSep® Q column of ID 3.18 mm and length 1.83 m. The identification and calibration of gas products were accomplished using standard gases and liquids. In all reaction studies, the CO conversion was kept below 5%. The selectivity of a certain 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.

2.6. TPR/TPD

TPR/TPD was carried out using the reaction system except that the effluent gas was analyzed by a Pfeiffer mass spectrometer, and an Omega temperature logger was used to monitor the temperature of the sample. For TPR measurements, 0.3 g of the as-prepared sample was pretreated at 300 °C in He for 1 h prior to a TPR measurement. During a TPR experiment, 5 v/v% H_2/Ar was used at 30 mL/min and the temperature was ramped from room temperature to 500 °C at 10 °C/min while the effluent gas was analyzed. The calculation of H_2 consumption was based on a calibration using the reduction of Ag_2O powder. For H_2-TPD measurements, two sets of experiments were carried out: from room temperature and from 180 °C. For TPD from room temperature, 0.3 g of the as-prepared sample was first reduced by flowing 5 v/v% H_2/Ar from room temperature to 500 °C at 10 °C/min, and was held at 500 °C for 10 min before cooling down to room temperature in H_2/Ar. Following a purge with a He flow of 30 mL/min for 30 min, TPD was carried out to 400 °C in He at 10 °C/min. For TPD from 180 °C, the reduction procedure was the same as that for TPD from room temperature, but after reduction the catalyst was purged with He at 500 °C for 30 min to remove adsorbed H_2, then cooled down to 180 °C in He, followed by supplying H_2/Ar for 30 min to saturate the surface with chemisorbed hydrogen at that temperature. After purging with He for 10 min at 180 °C, TPD was carried out using a flow of He at 10 °C/min. Since the main purpose of TPR/TPD here was to investigate the oxidation state and desorption characteristics of the catalysts around the reaction temperature (230 °C), the temperature ranges for TPR/TPD were chosen to not be above 500 °C.

3. Results

3.1. Preparation and characterization of catalysts

As shown in Table 1, non-promoted and promoted Rh-based catalysts were prepared using incipient impregnation. As-prepared

Table 1
Compositions, preparation conditions, and BET surface areas of Rh-based catalysts.

Catalyst	Composition (wt%)[a]	Molar ratio of promoter/Rh	Metal loading method[b]	BET surface area (m^2/g)[d]
Rh	1.5		Impregnation	244
Rh–La*	1.5:2.6	La/Rh = 1.33	Co-impregnation	238
Rh/V*	1.5:1.5	V/Rh = 2	Sequential impregnation	243
Rh–Fe	1.5:0.8	Fe/Rh = 1	Co-impregnation	251
Rh–Fe–La	1.5:2.6:0.8	La/Rh = 1.33 Fe/Rh = 1	Co-impreganaton	243
Rh–Fe/V	1.5:0.8:1.5	Fe/Rh = 1 V/Rh = 2	Co-sequential impregnation[c]	243
Rh–La/V*	1.5:2.6:1.5	La/Rh = 1.33 V/Rh = 2	Co-sequential impregnation	240
Rh–La/V(3.7)	1.5:2.6:3.7	La/Rh = 1.33 V/Rh = 5	Co-sequential impregnation	228
Rh–La(6.0)/V	1.5:6.0:1.5	La/Rh = 3 V/Rh = 2	Co-sequential impregnation	242
Rh–La–Fe(0.2)/V	1.5:2.6:0.2:1.5	La/Rh = 1.33 V/Rh = 2 Fe/Rh = 0.25	Co-sequential impregnation	237
Rh–La–Fe(0.4)/V	1.5:2.6:0.4:1.5	La/Rh = 1.33 V/Rh = 2 Fe/Rh = 0.5	Co-sequential impregnation	230
Rh–La–Fe/V	1.5:2.6:0.8:1.5	La/Rh = 1.33 V/Rh = 2 Fe/Rh = 1	Co-sequential impregnation	235
Rh–La–Fe(1.6)/V	1.5:2.6:1.6:1.5	La/Rh = 1.33 V/Rh = 2 Fe/Rh = 2	Co-sequential impregnation	245
Rh–La–Fe(2.4)/V	1.5:2.6:2.4:1.5	La/Rh = 1.33 V/Rh = 2 Fe/Rh = 3	Co-sequential impregnation	244
Rh–La–Fe(4.0)/V	1.5:2.6:4.0:1.5	La/Rh = 1.33 V/Rh = 2 Fe/Rh = 5	Co-sequential impregnation	229

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

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

[c] Co-sequential impregnation was the 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.

[d] Max error = ±5%

[*] It was found in our previous study [12] that the molar ratios of La/Rh of 1.33 and V/Rh of 2 led to the best catalytic performance of the La and V doubly promoted Rh/SiO_2 catalysts for ethanol synthesis. Thus, in this study, only Rh–La/SiO_2 (La/Rh = 1.33) and Rh/V/SiO_2 (V/Rh = 2) were chosen as La and V singly promoted catalysts for comparison purposes.

Rh-based catalysts were small dark brownish granules of 30–50 mesh. The BET surface areas of the silica gel-supported Rh catalysts were all around 240 m^2/g.

X-ray diffraction (XRD) patterns (not shown) of silica and the as-prepared Rh catalysts studied showed no discernable peaks related to any crystalline phase, suggesting that Rh and the promoters are highly dispersed. Our previous TEM study [12] found that non-promoted Rh(1.5)/SiO_2 catalysts prepared this way had Rh particle sizes around 3 nm. However, TEM of La- and/or V-promoted Rh catalysts showed no clear images of Rh particles, but some irregular-shaped patches in the range of 3–20 nm only slightly distinguishable from the support [12]. The high resolution images (not shown) of Fe-containing catalysts prepared in this study exhibited similar TEM images for the La/V-promoted catalysts as observed in our previous study [12]. Since elemental analysis of individual nanometer patches under such high magnification is unavailable, it is not clear whether these patches contain any mixed oxides of the different metals (including promoters). Likewise, identification by other bulk techniques of small fractions of low amounts of promoters that may be in a mixed oxide form (assuming they even exist) is seldom possible.

3.2. FTIR study

FTIR was used to study CO adsorption on the surfaces of the different catalysts at room temperature and at the reaction temperature of 230 °C, but under atmospheric pressure. A detailed IR study including CO chemisorption on La- and V-promoted Rh/SiO_2 catalyst has been carried out by our group [13]. Therefore, in this paper we mainly report CO adsorption on the Fe-containing catalysts. Likewise, a discussion of La compounds that may have formed on the La-containing catalysts in the presence of CO and/or hydrogen is given in Ref. [13].

The spectra of CO adsorbed on the *in situ* reduced catalysts at room temperature for 30 min are given in Fig. 1a. In all the spectra, the bands centered around 2180 and 2125 cm^{-1} are attributed to gaseous CO [26]. As also found in our previous study [13], the IR spectra of non-promoted Rh(1.5)/SiO_2 interacting with CO at room temperature exhibited a band around 2070 cm^{-1} and a doublet at 2092 and 2026 cm^{-1}. The 2070 cm^{-1} band can be attributed to linear adsorbed CO [CO(l)] and the doublet can be assigned to the symmetric and asymmetric carbonyl stretching of gem-dicarbonyl $Rh^+(CO)_2$ [CO(gdc)] [12]. The IR spectra of CO adsorbed on Rh(1.5)/SiO_2 also showed a weak broad peak assigned to bridge bonded CO [CO(b)] at 1865 cm^{-1} [27]. La promotion of Rh/SiO_2 gave spectra similar to those for the non-promoted catalyst, except for the formation of tilted CO(t) (centered around 1716 cm^{-1}) [13]. However, it is obvious that the addition of Fe and V significantly suppressed CO adsorption on Rh/SiO_2, while the doubly promoted Rh catalysts with La (Rh–La/V/SiO_2 and Rh–La–Fe/SiO_2) showed moderate CO adsorption.

For the IR spectra of CO adsorption recorded at the reaction temperature of 230 °C (but 1 atm pressure) as shown in Fig. 1b, CO(l) dominated all the spectra and the relative amount of

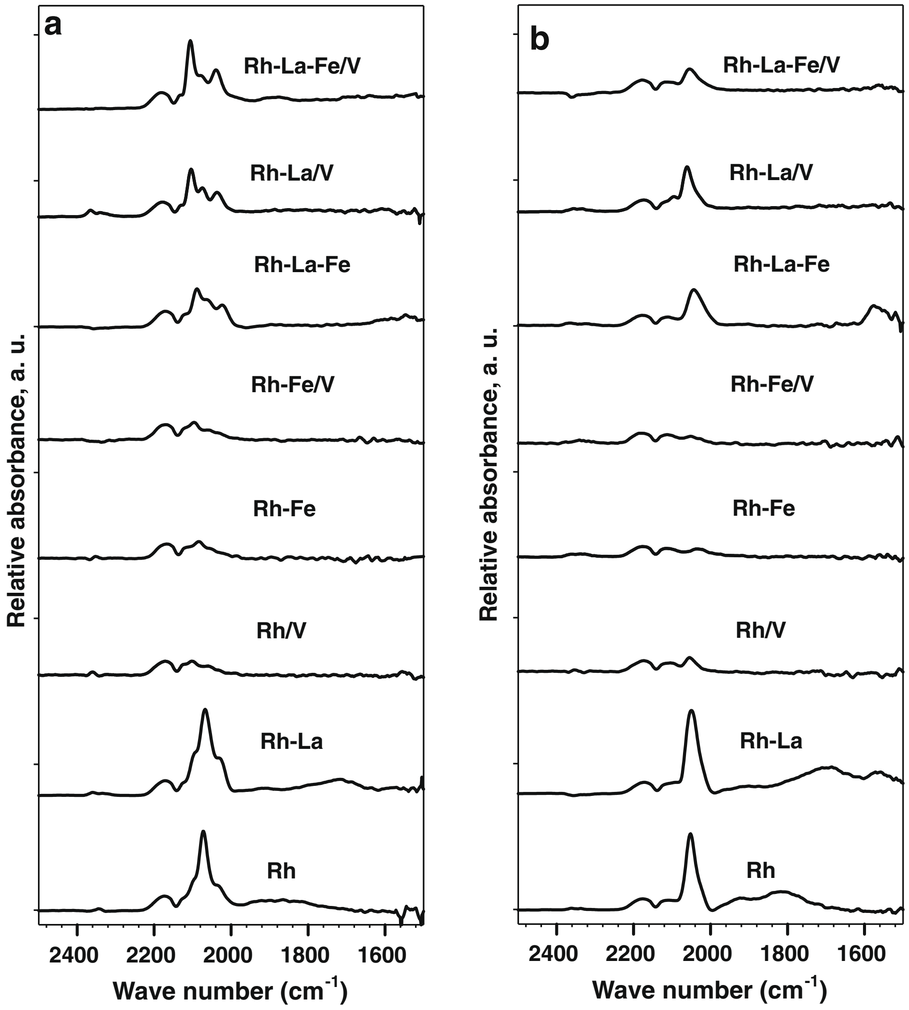

Fig. 1. FT-IR spectra of chemisorbed CO on different catalysts at (a) room temperature and (b) 230 °C.

adsorbed CO changed significantly for different catalysts. Again Fe and V appeared to cause significant suppression of CO adsorption. The triply promoted catalysts, even though containing La, also showed significant suppression of CO adsorption compared to the doubly promoted catalysts with La (Rh–La/V and Rh–La–Fe). The significant changes in CO adsorption species and in the intensities of CO adsorption peaks observed at 230 °C compared to those observed at room temperature suggest some re-structuring of the catalysts, which may be due to different interactions of the promoters and Rh.

3.3. TPR study

Fig. 2 presents the TPR profiles obtained for the non-promoted, La-promoted, V-promoted, Fe-promoted, V–La-doubly promoted, and Fe–V–La-triply promoted Rh/SiO_2 catalysts. It can be seen that Rh in the non-promoted catalyst was reduced starting at room temperature, while after the addition of La, V, or Fe, higher temperatures were required for the reduction of Rh, in agreement with the literature [14,15,28–31]. Regarding the doubly and triply promoted Rh/SiO_2 catalyst, the addition of the second promoter or the third promoter further hindered the reduction of Rh. Judging from the H_2 consumption, La most likely stayed at a high oxidation state after reduction up to 500 °C even with Rh present in the catalyst, while V^{5+} and Fe^{3+} were partially reduced before 200 °C. These results are also consistent with the literature [14,22,28,29,32,33]. The TPR profile of the V singly promoted Rh/SiO_2 catalyst only showed one sharp peak, indicating that V^{5+} was partially reduced simultaneously with Rh^{3+}. The reduction peak for the Fe singly promoted catalyst was quite broad, suggesting that the reduction of Fe^{3+} did not start before Rh^{3+} ions were almost totally reduced. Assuming that all Rh was present as Rh^{3+} before the reduction and was reduced to the metallic state and that La was not reduced at temperatures below 500 °C, Fe might have been present as Fe^{2+} and Fe^0, and V might have been present as V^{4+} and V^{3+} in the triply promoted catalyst judging from the hydrogen consumptions.

3.4. H_2-TPD study

The H_2-TPD profiles of the non-promoted and promoted Rh/SiO_2 catalysts after reduction at 500 °C are shown in Fig. 3. In the temperature range of 40–400 °C, the desorption of H_2 could be assigned to three different adsorbed H species: desorbing below 150 °C (H_α), desorbing between 150 and 300 °C (H_β), and desorbing afterwards (H_γ). Several conclusions can be drawn from the TPD results:

(1) The addition of La did not change the desorption dynamics of H_2 compared to that of non-promoted Rh/SiO_2, but did increase the total amount of hydrogen desorbing, which is consistent with the increased H_2 chemisorption at 298 K reported for La-promoted Rh/SiO_2, especially with the addition of small amounts of La [28,29,34,35].

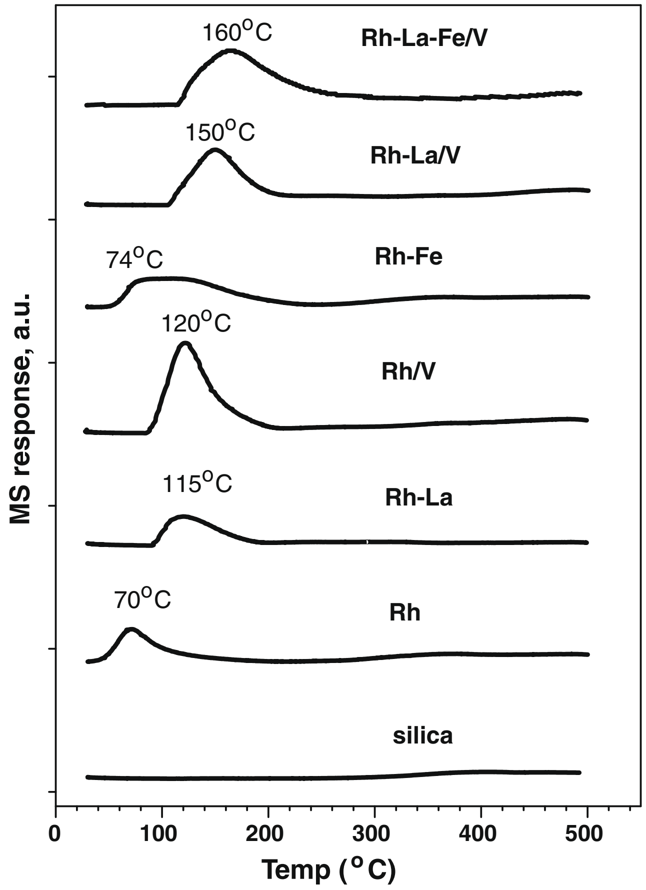

Fig. 2. TPR profiles of the non-promoted and promoted Rh/SiO_2 catalysts.

(2) The addition of V not only significantly reduced the amount of chemisorbed H_α and H_β, but also shifted the desorption peak to a higher temperature for H_β. Suppression of low temperature H_2 desorption with the addition of V compared to that of non-promoted Rh/SiO_2 has been reported by different research groups, with the amounts of H_2 desorbing at high temperature (>350 °C) increasing [30,36].

(3) The addition of Fe also reduced the amounts of H_α and H_β, but the desorption peak for H_α could still be seen and there was no significant peak position shift for H_β. This observation is consistent with the decreased H_2 chemisorption with the addition of Fe to Rh catalysts seen in other studies [22,24].

(4) For the doubly promoted catalysts, the TPD profile for the addition of La–Fe was similar to that with the addition of Fe, and the profiles for Fe–V and La–V were similar to that with the addition of V, except that the H_β peaks were larger.

(5) The triply promoted Rh/SiO_2 ($Rh–La–Fe/V/SiO_2$) showed the highest H_β desorption peak among the doubly and triply promoted catalysts, but no significant peak for H_α.

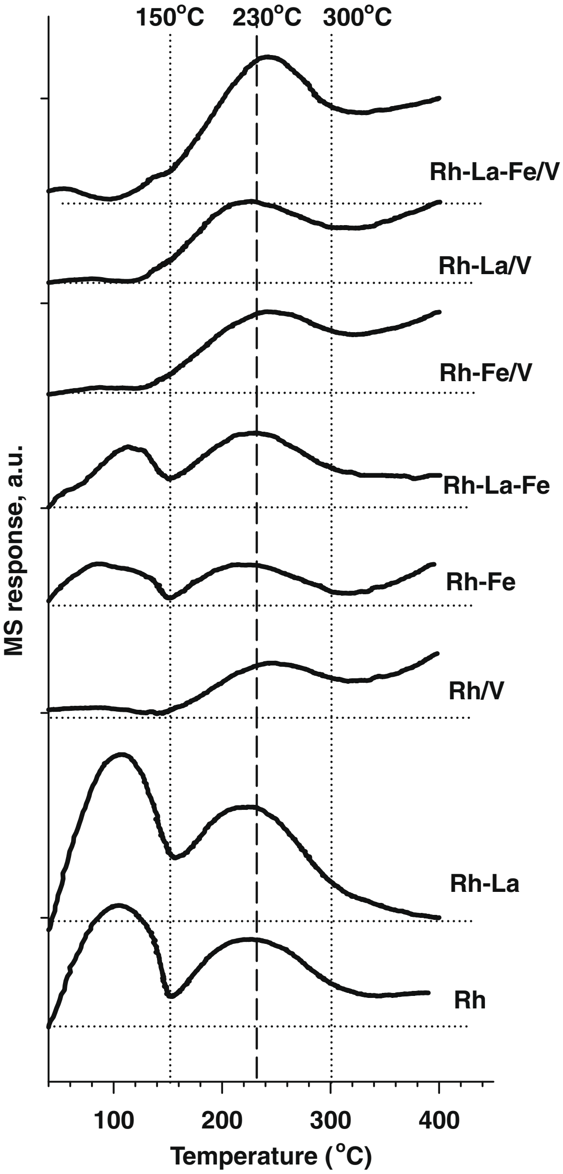

Fig. 3. H_2-TPD profiles of the non-promoted and promoted Rh/SiO_2 catalysts.

In order to examine whether the change in the H_2 desorption profile with the addition of Fe to $Rh–La/V/SiO_2$ could be ascribed to a unique property of Fe or whether it was just a result of adding more promoter, two other $Rh–La/V/SiO_2$ catalysts with different La and V amounts were studied using TPD. As shown in Fig. 4, the TPD of the La–V doubly promoted catalysts with more V added exhibited only a H_β peak with the center shifted slightly to a higher temperature. On the other hand, the TPD of the La–V doubly promoted catalysts with more La added exhibited mainly a H_α peak with the center shifted to a higher temperature. Obviously increasing La did not lead to increased H_2 adsorption; on the contrary, the addition of more La resulted in the suppression of H_β. This result is in agreement with the literature that the addition of too much La can lead to reduced H_2 chemisorption due to the La covering the Rh surface [34]. Thus, it is clear that the effect of the addition of Fe to $Rh-La/V/SiO_2$ is not the same as just adding more La or V.

In order to further investigate the effect of the addition of Fe to $Rh–La/V/SiO_2$, TPD was also carried out to study H_2 adsorption/desorption at a higher temperature near the reaction temperature, as shown in Fig. 5. Only one desorption peak was observed in the temperature range of 180 °C and 350 °C for these two catalysts, and it is obvious that the desorption peak for the triply promoted catalyst was larger than that for the doubly promoted catalyst, which is consistent with TPD from room temperature.

3.5. Catalytic activities

Table 2 gives the catalytic activities of the non-promoted and promoted Rh/SiO_2 catalysts for CO hydrogenation at 230 °C and 1.8 atm. It can be seen that all the promoted catalysts exhibited

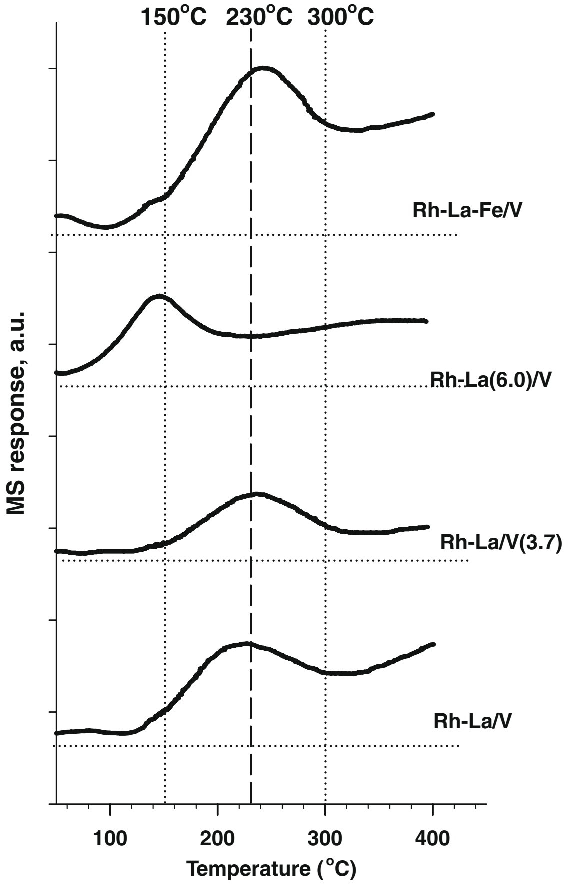

Fig. 4. H_2-TPD profiles of the doubly and triply promoted Rh/SiO_2 catalysts.

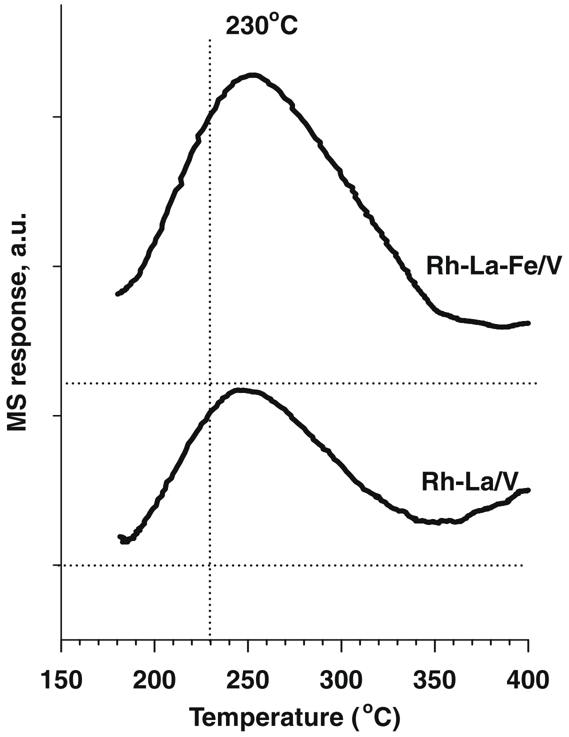

Fig. 5. H_2-TPD profiles of $Rh–La/V/SiO_2$ and $Rh–La–Fe/V/SiO_2$ for H_2 adsorption at 180 °C.

higher CO conversion rates than the non-promoted ones, with the catalysts promoted by both La and V showing the highest activity. With respect to selectivity, different promoter(s) led to significantly different product distributions, which can be summarized as follows:

- In agreement with the results reported previously [12,13], the non-promoted catalyst showed a relatively modest selectivity for ethanol (EtOH) and the formation of hydrocarbons (HC) made up the majority of the total products. The addition of V resulted in the lowest selectivity for CH_4 and the addition of La led to an increase in the selectivity for EtOH.
- The addition of Fe to Rh/SiO_2 led to higher selectivities for CH_4 and methanol (MeOH)—two unwanted by-products. However, the addition of Fe did lead to a decrease in the selectivity for higher hydrocarbons and a small improvement in EtOH selectivity.
- Fe–V promotion led to a decrease in CH_4 compared to the non-promoted catalyst, but not as great a decrease as seen for the V singly promoted Rh/SiO_2.
- Fe–La led to a higher selectivity for EtOH compared to non-promoted Rh/SiO_2, but the selectivity for CH_4 increased significantly.
- La (2.6 wt%)–V(1.5 wt%) promotion resulted in high EtOH and other C_{2+} oxygenate selectivities, and low selectivities for CH_4 and MeOH, consistent with our previous results [12].
- Fe–V–La promotion gave the highest selectivity to EtOH (34.6%) with the selectivities for CH_4 and MeOH being relatively unchanged compared to the catalysts promoted by La and V, although some activity was sacrificed.
- Compared to the La–V doubly promoted catalysts with different amounts of La and V, the addition of Fe to Rh–La/V led to a quite different catalytic performance, indicating that the effect of Fe could not be achieved by adding just more of La or V.

As a reminder, the reaction conditions were not optimized for the formation of EtOH in this study since this study is part of a more extended investigation using a variety of techniques including SSITKA (steady-state isotopic transient kinetic analysis [37]), and equivalent reaction conditions are required for comparison of all the data. It is expected that higher selectivity would be obtained under optimal reaction conditions, especially at higher pressure. For instance, the La–V doubly promoted catalysts have been found to give >50% selectivity to EtOH at a pressure of 14 atm [38].

Fig. 6 shows the effect of Fe loading in the Fe–La–V triply promoted catalyst on CO hydrogenation. As the Fe/Rh ratio increased to 0.5, the activity first decreased and then increased back to an activity comparable to the La–V doubly promoted catalysts for Fe/Rh = 6. Interestingly, the selectivity to higher hydrocarbons followed a somewhat similar trend and reached an approximate minimum as the molar ratio of Fe/Rh reached 1, where the selectivity to EtOH reached its maximum. With the addition of Fe, the increase of activity was primarily due to the increased selectivity for hydrocarbons, similar to what is seen for Fe catalysts for Fisher-Tropch synthesis [37]. Thus, it is obvious that when appropriate amounts of Fe are added to $Rh–La/V/SiO_2$, there is a decrease in the formation of higher hydrocarbons and an increase in the formation of EtOH.

Fig. 7 presents the catalytic performance of $Rh–La–Fe/V/SiO_2$ for CO hydrogenation versus time on stream at 230 °C and 1.8 atm. It can be seen that steady state was reached after 6 h reaction, with only ca. 15% activity being lost from the initial rate. The decrease in the total activity was mostly due to the decreased formation rate of hydrocarbons, while at the same time the selectivities for oxygenates increased. The deactivation behavior of this catalyst was similar to that of the doubly promoted $Rh–La/V/SiO_2$ catalyst

Table 2
Catalytic properties of Rh-based catalysts for CO hydrogenation.

Catalyst	SS[*] rate[a,b] (μmol/g/s)	Selectivity (%)[c]					
		CH_4	$C_{2+}HC$[d]	MeOH	Acetaldehyde	EtOH	Other C_{2+} oxy.[e]
Rh	0.03	48.1	28.7	1.2	6.5	15.6	0
Rh–La	0.08	36.8	31.7	3.1	5.8	22.5	0.1
Rh/V	0.09	12.6	63.7	5.8	1.3	14.6	2.2
Rh–Fe	0.12	55.3	13.7	9.5	2.2	19.4	0
Rh–Fe/V	0.12	23.6	55.2	4.7	2.5	13.2	0.8
Rh–La–Fe	0.19	58.2	13.3	5.0	3.9	19.4	0.1
Rh–La/V	0.27	15.0	53.1	2.7	4.2	22.8	2.2
Rh–La(6.0)/V	0.17	21.8	42.4	1.4	11.5	18.3	4.6
Rh–La/V(3.7)	0.26	14.5	51.9	2.7	6.0	20.8	3.8
Rh–Fe–La/V	0.20	18.7	33.2	5.7	4.4	34.6	3.4

[*] Steady-state.

[a] Catalyst: 0.3 g; inert: 3 g α-alumina; reduction at 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 reaching steady state.

[b] Error = ±5% of all the values measured except for Rh(1.5)/SiO_2 where the error was ±10%

[c] Molar selectivity = carbon efficiency = $n_iC_i/\sum n_iC_i$.

[d] Hydrocarbons with two or more carbons.

[e] Oxygenates with two or more carbons.

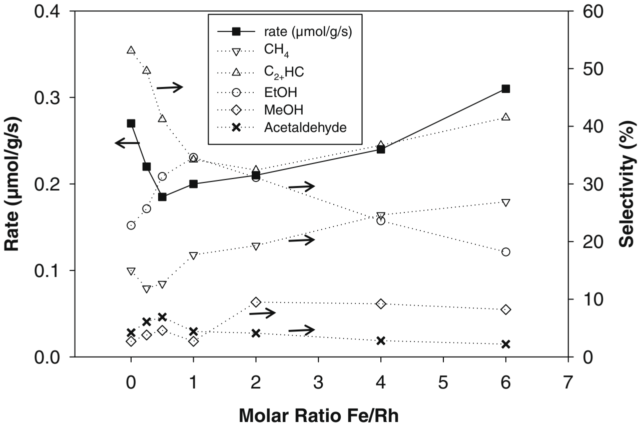

Fig. 6. The effect of Fe loading on the catalytic properties of Rh–La–Fe/V/SiO_2 (La: 2.6 wt%; V: 1.5 wt%) for CO hydrogenation.

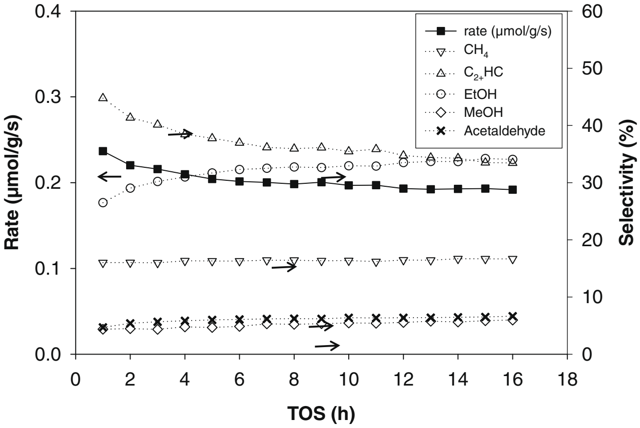

Fig. 7. Reactivity/selectivities vs. TOS for Rh–La–Fe/V/SiO_2.

[12], and this might be due to the deposition of carbon species [39,40] or re-structuring of the catalyst [41].

4. Discussion

As shown in Table 2, it is obvious that all the singly promoted Rh/SiO_2 catalysts promoted by La or V or Fe exhibited a higher activity for CO hydrogenation compared to the non-promoted one, but the product distributions were highly dependent on the choice of promoter. With respect to selectivity, La led to more oxygenates especially EtOH; V suppressed the formation of CH_4 but boosted hydrocarbon chain growth, while Fe decreased the formation of higher hydrocarbons but boosted the formation of CH_4 and MeOH. Interestingly, the combination of these three promoters seems to inherit only the advantages of each individual promoter and lead to a higher selectivity for EtOH and a lower selectivity for CH_4.

In order to understand the promoting mechanism of each promoter, it is necessary to recall the fundamental steps during CO hydrogenation. 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 [3,4]. 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 [4]. Non-dissociated CO can also form MeOH by hydrogenation [4]. The formation of C_{2+} oxygenates requires all the basic building units in this CO hydrogenation network: dissociated CO and dissociated H_2 to form CH_x (although CH_x may be possibly formed by hydrogen-assisted CO dissociation and hydrogenation [42,43]) and non-dissociated CO for CO insertion. Thus, it is important for none of these steps to predominate; otherwise, less desired products will primarily form. For instance, an increase in the formation of CH_4 could be the result of increased CO dissociation and CH_x ($x = 0$–3) hydrogenation, while an increase in the formation of MeOH could be the result of reduced CO dissociation and enhanced hydrogenation of non-dissociated CO. And if chain growth is too fast, higher hydrocarbons may be the major products. Although there have been extensive studies on the effects of promoters on Rh-based catalysts for EtOH synthesis from CO hydrogenation, few general agreements have been reached regarding the promoting mechanisms of different promoters. In the following sections, the effects of La, V, and Fe on Rh-catalyzed CO hydrogenation will be discussed based on the results from this study and promoter effects frequently proposed in the literature.

4.1. Particle size/dispersion of Rh and the promoters

It has been suggested that the catalytic properties of Rh-based catalysts for CO hydrogenation can be correlated to the loading and particle size of Rh in catalysts since (1) high Rh loadings lead to more reaction sites and (2) Rh with different particle sizes may stabilize reaction intermediates of different sizes [34,44–47]. Borer and Prins [34] reported that, for Rh–La/SiO_2 prepared by co-impregnation, a small amount of La can improve the Rh dispersion, leading to a higher catalytic performance, but too high La_2O_3 loading is not desirable since La will cover Rh. Their suggestion is supported by the conclusion drawn by Bernal et al. [35]. However, Nonneman et al. pointed out that the different activities observed for Rh catalysts with different Rh loadings might be due to impurities contained in the precursors used during catalyst preparation [48].

In this study, XRD and TEM results suggest that Rh and the promoters were highly dispersed in all the catalysts. This is not surprising since the loadings of Rh and promoters were relatively low, and this can also explain why no significant difference was observed in the BET surface areas of the different catalysts. The high dispersion of Rh is also in agreement with the formation of gem dicarbonyl $Rh^+(CO)_2$ observed in the IR spectra of CO interaction with different catalysts at room temperature, since it is widely accepted that the dicarbonyl species can only form on highly dispersed rhodium [49,50]. Thus, the addition of different promoters in this study appeared not to result in significantly different Rh particle sizes.

The TPR results clearly indicated that the addition of promoters hindered the reduction of Rh, which may be due to the coverage of some Rh_2O_3 by promoter(s). If Rh was blocked, the adsorption of H_2 and the subsequent reduction of Rh_2O_3 would be more difficult [28]. Also, the fact that only one peak was observed for all the catalysts in the temperature range of 30–300 °C indicates that Rh was in intimate contact with the promoters.

4.2. Oxidation state

Ichikawa and co-workers [51] proposed that Rh^0 is active for CO dissociation and Rh^+ is active for CO insertion, while Rh components active for the formation of C_{2+} oxygenates have an electronic state between Rh^0 and Rh^+. The studies carried out by Ojeda et al. [52] on Mn-promoted Rh catalysts and by Yokota et al. [53] on TiO_2 and other oxide supported-Rh catalysts also suggested that the oxidation state of Rh may affect the catalytic activities of Rh catalysts. Chuang and Pien suggested that a possible presence of isolated Rh^+ sites may contribute to the increased selectivity for higher oxygenates [54]. However, Gilhooley and co-workers [40] believed that there is no obvious relationship between the oxidation state of Rh and the selectivity to oxygenated products based on their research using ESCA. In a more recent work by Munera et al. [55] using *in situ* XPS, the authors also suggested that only Rh^0 existed on the Rh/La_2O_3 catalyst during CO_2 reforming of CH_4.

In this study, even though the addition of different promoters hindered the reduction of Rh^{3+}, the Rh catalysts were still able to be fully reduced based on H_2 consumption below 230 °C, the reaction temperature, as indicated by the TPR study. Also our earlier IR results [13] indicated that CO(*gdc*) does not no exist during CO hydrogenation at 230 °C, suggesting that Rh^+ has been totally reduced. Thus, it is unlikely to have Rh with an oxidation state higher than 0 under typical reaction conditions, especially at low conversions where the concentration of H_2O is low. However, the oxidation states of Fe and V may play a role. According to Schunemann et al. [14], the promoting effect of Fe on Rh may be related to the oxidation state of Fe: Fe^0 could increase the catalytic activity while Fe^{2+} could increase the selectivity. Based on the TPR results, Fe was present as Fe^{2+} and Fe^0 in the Fe-containing catalysts, which may be responsible for both their increased activity and selectivity to EtOH. The same situation may also occur for promotion with V, although further investigation is needed in order to substantiate the hypothesis.

4.3. CO adsorption/desorption

Another important issue is related to CO adsorption/desorption on catalytic surfaces since this is the first step during CO hydrogenation. From the IR study, La not only increased CO adsorption, but also modified the interaction of CO with Rh, as evidenced by the formation of CO(t) [13]. The formation of CO(t) has been claimed to enhance CO hydrogenation [28,56,57]. It was also found in our earlier study [13] that the increased activity upon the addition of La is mainly due to an increase in the number of reaction sites, although it is unclear whether the increased selectivity to EtOH is related to the formation of CO(t) as questioned by Chuang and co-workers [58,59].

The addition of V and Fe significantly decreased CO adsorption, as seen in the IR spectra of CO adsorption on the Rh catalysts. It was suggested in our earlier IR study that the higher catalytic activity of the V singly-promoted Rh/SiO_2 catalyst may be ascribed to an increased desorption rate/reactivity of the adsorbed CO species since the addition of V appeared to reduce the total number of reaction sites [13]. Twenty years ago, Kip et al. [41] proposed that the reaction sites at Rh–V interfaces should be very active, although they had no direct evidence except for the increased overall activity using V as a promoter for Rh/SiO_2. More recently, Surnev and co-workers [60,61] studied metal-oxide boundary effects for CO oxidation on vanadium oxide–Rh(1 1 1) model catalysts using various modern techniques including variable-temperature scanning tunneling microscopy. They found that CO oxidation is promoted in the vicinity of V-oxide/Rh(1 1 1) boundaries, which could also be true for CO hydrogenation on V-promoted Rh catalysts. This suggestion could also explain the changes in selectivities when V is added to Rh/SiO_2. V suppressed CO adsorption, but it appeared to enhance the dissociation of absorbed CO, the following chain growth [the coupling/or addition of CH_x ($x = 0–2$) species], and product desorption. Thus, the selectivities for CH_4, higher saturated hydrocarbons and oxygenates were much lower compared to those for other catalysts (see Tables 2 and 3) since CO dissociation and chain growth were too fast, making hydrogenation and CO insertion more likely rate-determining steps.

Even though the addition of Fe also decreased CO adsorption as shown in the IR study, the promoting mechanism of Fe should be different from that of V since the product distribution for the Fe singly promoted catalyst was totally different from that for the V singly promoted catalyst. This hypothesis is consistent with a preliminary SSITKA study, which showed that addition of Fe did not increase the site TOF (as determined by SSITKA) of the reaction, contrary to the case for V addition [13].

4.4. Hydrogenation

Hydrogenation ability has been viewed as an important factor affecting overall activity and selectivity since it has been suggested that the hydrogenation of dissociated CO [62,63] is the rate-determining step in the hydrogenation of CO on Rh catalysts, and many kinetic studies have obtained positive H_2 pressure dependence and negative CO pressure dependence over Rh catalysts [18,42,64,65]. Interestingly, La [29], V [31,36,66,67], and Fe [17,18,20] have all been proposed to enhance the hydrogenation ability of Rh/SiO_2. To probe the hydrogenation abilities of the different catalysts in this study, comparisons of the formation rate of acetaldehyde (AcH) with that of EtOH and of the formation rates of alkenes with those of alkanes were made as shown in Table 3. Although there have been arguments that EtOH and AcH are formed by different

Table 3
Comparison of hydrogenation ability of Rh-based catalysts.

Catalyst	Rate[a,b] (μmol/g/s)	Selectivity (%)		
		Acetaldehyde/EtOH	$C_2^=/C_2$	$C_3^=/C_3$
Rh	0.03	0.40	1.8	12.0
Rh/V	0.10	0.16	4.8	10.3
Rh–La	0.09	0.24	1.2	3.3
Rh–Fe	0.12	0.14	1.3	6.1
Rh–La–Fe	0.19	0.20	0.6	1.0
Rh–Fe/V	0.12	0.19	2.4	6.5
Rh–La/V	0.27	0.18	3.3	12.1
Rh–La(6.0)/V	0.17	0.62	4.7	18.4
Rh–La/V(3.7)	0.26	0.29	3.2	16.0
Rh–Fe–La/V	0.20	0.10	1.8	8.6
Rh–Fe(4.0)–La/V	0.29	0.12	1.5	7.4

[a] Reaction conditions same as in Table 2.
[b] Error = ±5% of all the values measured except for Rh(1.5)/SiO_2 where the error was ±10%.

routes (precursors) [63,68], more reports indicate that EtOH is formed by a secondary hydrogenation of AcH [17,69–71]. Thus, a comparison of the ratios of AcH/EtOH and alkene/alkane should provide some insights related to hydrogenation ability.

Several aspects were quite clear as indicated in Table 3. The first one is that La-, V-, and Fe-promoted catalysts all showed lower AcH/EtOH ratios compared to the non-promoted catalysts, suggesting that all these promoters boosted the hydrogenation of AcH to EtOH. This observation is consistent with the results in the literature for La [29], V [31,36,66,67], and Fe [17,18,20]. Considering that the addition of these promoters also increased the formation of MeOH to different extents as shown in Table 2, it could be true that these oxides may enhance the interaction of H with carbonyl species, leading to higher selectivities for alcohols. The second obvious feature seen from Table 3 is that what appears to promote the hydrogenation of AcH to form EtOH does not always appear to promote the hydrogenation of alkenes to alkanes. For example, considering V-promoted Rh/SiO_2 catalyst, a lower AcH/EtOH ratio did not guarantee a lower alkene/alkane ratio compared to the non-promoted catalyst. The third obvious feature is that the addition of V led to higher alkene/alkane ratios, which is in agreement with the finding of Kip et al. [41] who did not observe an increased rate for ethylene to form ethane with the addition of V to Rh/SiO_2. Also, the shift of H_2 desorption peak to higher temperature by V found in TPD study appears to be related to the low alkene/alkane ratio and low CH_4 selectivity since the availability of H was reduced with the addition of V. The fourth observation is that both La and Fe seemed to enhance hydrogenation. However, the hydrogenation ability appeared to go through a maximum with the addition of more La since the alkene/alkane ratio increased significantly when La/Rh = 3 [catalyst Rh–La(6.0)/V], which is consistent with the TPD results and results in the literature that too much La added leads to reduced H_2 chemisorption due to La covering of Rh [34]. In the case of Fe, the alkene/alkane ratio further decreased when Fe/Rh ratio reached 5 [catalyst Rh–La–Fe(4.0)/V] in the triply promoted catalysts. Also, since the AcH/EtOH ratio remained low with the addition of more Fe, Fe may indeed improve hydrogenation.

The enhanced hydrogenation ability caused by the addition of Fe seems to be in conflict with the TPD results since the amount of desorbed H_2 decreased for Fe-singly promoted Rh/SiO_2 compared to that for the non-promoted catalyst. Three possible reasons may explain this conflict. One is that the conclusions from H_2-TPD must be considered with care in interpreting H_2 storage/reactivity since most of the measurements are carried out in the absence of CO. It is well known that the adsorption of CO on Rh is very strong and affects the adsorption of H_2 [72,73]. The second possibility is that Fe does not have to serve as a H_2 reservoir to enhance hydrogenation. Instead, stabilizing reaction intermediates could also lead to more saturated hydrocarbons and alcohols as proposed by Fukushima et al. [21]. The third fact that needs to be considered is the relative surface coverage of CO and H_2 on a catalytic surface. As discussed previously, the addition of Fe or V significantly suppressed CO adsorption, especially at reaction temperature. Even though H_2 adsorption was suppressed, the hydrogenation ability of Fe-promoted catalysts might still be high since the decrease in the amount of H_2 adsorption may not have been as significant compared to the reduction in the amount of CO adsorption on the catalytic surface. Comparing Rh–La/V/SiO_2 with Rh–La–Fe/V/SiO_2, the triply promoted catalyst exhibited lower CO adsorption but higher H_2 adsorption at the reaction temperature, which may be correlated to the increased EtOH selectivity but reduced overall activity.

5. Conclusions

Non-promoted, singly, doubly and triply promoted Rh/SiO_2 catalysts containing different combinations of Fe, La, and V as promoters were prepared by incipient wetness and characterized by BET, XRD, TEM, FTIR, TPR, and H_2-TPD. It was found that Rh and promoters were highly dispersed and apparently in close contact. The addition of promoters hindered the reduction of Rh and changed CO and H_2 adsorption behaviors on the catalyst surfaces. It was also found that the addition of 0.8 wt% Fe, 2.6 wt% La, and 1.5 wt% V to 1.5 wt% Rh/SiO_2 resulted in the highest selectivity to ethanol (34.6%) and a moderate activity compared to other promoted catalysts at the reaction conditions of 230 °C and 1.8 atm. The various characterization results and the catalytic behaviors of different catalysts suggest that the main effect of La promotion was to increase CO adsorption and CO insertion, the main effect of the addition of V was to decrease CO adsorption but to enhance CO dissociation and hydrocarbon chain growth, while the main effect of the addition of Fe was to decrease CO adsorption and enhance hydrogenation. The synergistic effects of multiple promoters imply that the key to effective catalyst design for ethanol synthesis from syngas is a balance among CO dissociation, hydrogenation, and CO insertion.

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