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# Unveiling the Structure Sensitivity for Direct Conversion of Syngas to C2-Oxygenates with a Multicomponent-Promoted Rh Catalyst

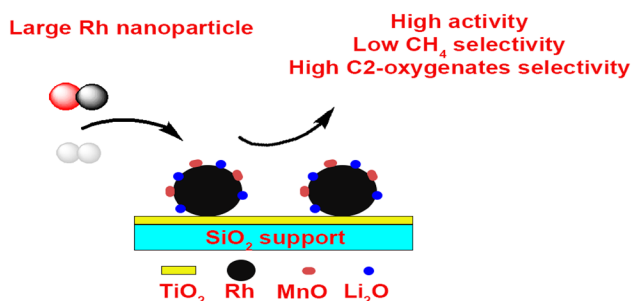
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## Abstract

Mn and Li promoted Rh catalysts supported on SiO<sub>2</sub> with a thin TiO<sub>2</sub> layer were synthesized by stepwise incipient wetness impregnation approach. The thin TiO<sub>2</sub> layer on the surface of SiO<sub>2</sub> was proved to stabilize those small Rh nanoparticles and hinder their agglomeration. The reducibility of Rh on these catalysts depends on Rh particle size as well as the position of manganese oxide, and large Rh nanoparticles with MnO on Rh nanoparticles can be only reduced at an elevated temperature. Catalyst with large Rh particles exhibits a higher CO conversion and higher products selectivity towards long chain hydrocarbons and C2-oxygenates at the expense of decreasing methane formation than a similar catalyst with smaller Rh particles. This was attributed to the synergistic effect of Mn and Li promotion and molar ratio between Rh<sup>0</sup> and Rh<sup>δ+</sup> sites on the surface of Rh nanoparticles. Moreover, Rh nanoparticles on MnO are proved to be more efficient in promoting hydrogenation of acetaldehyde to ethanol than its counterpart with MnO on Rh nanoparticles. Finally, in order to target high C2-oxygenates selectivity, low reaction temperature together with a low H<sub>2</sub>/CO ratio in the feed is recommended.

## Graphic Abstract



**Keywords** Ethanol · Acetaldehyde · Rh · Mn · Particle size

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## 1 Introduction

The synthesis of renewable fuels such as ethanol has received extensive attention in recent years for its application both as a fuel additive and an energy carrier [1–3]. Nowadays, ethanol is produced mainly by fermentation of biomass-derived sugars [4]. Catalytic conversion of syngas (mixture of H<sub>2</sub> and CO obtained from natural gas, coal or biomass) to oxygenated compounds (ethanol, acetaldehyde and acetic acid), followed by a subsequent hydrogenation of acetaldehyde and acetic acid provides an alternative route

to produce ethanol at large scales. Several catalytic systems, including rhodium- and/or molybdenum sulfide-based catalysts, and modified Fischer–Tropsch and/or methanol synthesis catalysts have been studied for this purpose [5–8]. Slow kinetics and poor oxygenates selectivity in this process remain, however, the major obstacles. Hence, exploring catalysts with new structure and compositions for C2-oxygenates synthesis with high activities and oxygenated compounds selectivity still remains a big challenge.

Several transition metals in Group VIII of the Periodic Table have been investigated in CO hydrogenation, and products were found to clearly depend on the property of metals. Metals (e.g. Ir and Pd) that hardly dissociate CO, favor methanol production [9, 10], while cobalt and iron preferably produce long chain hydrocarbons owing to their high capability in CO dissociation [11–14]. Importantly, rhodium, that is located at an intermediate position in the periodic table, and possesses a unique CO adsorption behavior, has been proved highly efficient in the synthesis of C2-oxygenated compounds from CO hydrogenation [15–17]. Generally stating, CO hydrogenation to C2-oxygenates occurs on the surface of rhodium particles. Therefore, the number of active sites, namely the activity is a function of rhodium dispersion [15]. In order to achieve an uniform rhodium distribution, the intrinsic feature of supports and catalyst preparation conditions are supposed to be considered during a catalyst design [18–20]. For instance, silica with large surface area favors the dispersion of rhodium precursors. However, during a follow-up high-temperature thermal treatment, rhodium oxides nanoparticles suffer severe agglomeration owing to a weak rhodium-silica interaction [21]. TiO<sub>2</sub> with a strong interaction strengthens the stability of rhodium nanoparticles, while the low surface area leads to a poor metal dispersion [22–24]. Thus, a rational design strategy that can optimize the particle distribution and stability of supported rhodium nanoparticles is highly attractive.

Previous studies showed that supports play an essential role in the catalytic activity and products distribution for rhodium catalysts [25–28]. For example, a 2 wt% Rh/TiO<sub>2</sub> showed a CO conversion 8 times as high as the SiO<sub>2</sub> supported Rh catalyst together with an improved C2-oxygenates selectivity [27]. However, TiO<sub>2</sub> supported Rh catalysts without promoters still primarily produce methane with low C2-oxygenates yield [25–27]. In this sense, a variety of promoters (e.g. La, Mn, Fe, Li, etc.) have been investigated in order to improve C2-oxygenates selectivity by inhibiting the production of methane [26–31]. For instance, adding small amount of Fe and/or Mn into a Rh/TiO<sub>2</sub> catalyst was proven to largely promote the production of ethanol and acetaldehyde at the expense of CH<sub>4</sub> selectivity [27, 28]. Owing to the significant promotion effect, the structure and function of Mn in Rh-based catalysts have been widely studied, and MnO in close contact with Rh nanoparticles is in general

considered to be the active phase of the promoter [32–36]. The promotion functions of Mn consist of (i) increasing Rh dispersion; [15, 35] (ii) stabilizing partially oxidized Rh sites for CO insertion; [33, 37] and (iii) generating interfacial sites between Rh and MnO to accelerate CO dissociation [32, 36]. Hence, a correlation between MnO distribution and C2-oxygenates selectivity would exist in the Mn-promoted Rh catalyst. Normally, co-impregnation is the most popular strategy to prepare bimetallic catalysts [26]. However, the random deposition of Mn on the catalyst surface largely hinders the evaluation of distribution-promotion relations. In this sense, stepwise impregnation approach would be an alternative to accurately design multicomponent catalyst [32, 38].

In this study, to further investigate the relationship between the distribution and promotion functions of Mn in multicomponent-promoted Rh catalysts, a series of Rh-based catalysts were prepared by supporting Rh, Mn, and Li on a high-surface-area SiO<sub>2</sub> support with a thin layer of TiO<sub>2</sub> on the silica surface. The addition of Li in this study is attributed to the fact that Li was reported to some extent to inhibit methane formation and boost C2-oxygenates selectivity [39–41]. Catalyst synthesis is composed of several steps: (i) depositing a thin layer of TiO<sub>2</sub> on SiO<sub>2</sub>; (ii) introducing Mn on Rh or other way around by stepwise incipient-wetness-impregnation (IWI) on the prepared TiO<sub>2</sub>/SiO<sub>2</sub>; (iii) impregnating Li by a further IWI. With this strategy, we demonstrate that the thin TiO<sub>2</sub> layer on the surface of SiO<sub>2</sub> plays a crucial role in stabilizing Rh nanoparticles in right dispersion. Furthermore, Rh on MnO is more efficient in promoting the hydrogenation of acetaldehyde to ethanol compared to its counterpart with MnO on Rh. Finally, the catalytic performance of the multicomponent Rh-based catalyst also depends on Rh particle size, and catalyst with a larger Rh nanoparticle size exhibits a higher activity and C2-oxygenates selectivity, but lower methane selectivity than its counterpart with smaller Rh nanoparticles. This approach will provide new insight for the rational design of highly active and selective Rh based catalysts for C2-oxygenates production.

## 2 Experimental Section

### 2.1 Materials

Dihydroxybis(ammonium lactato)titanium(IV) (C<sub>6</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub>Ti, 50% w/w aq. soln) was purchased from Alfa Aesar, rhodium(III) chloride hydrate (RhCl<sub>3</sub>·xH<sub>2</sub>O, 40 wt% Rh) was purchased from Tanaka Kikinzoku Kogyo KK, manganese(II) chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O, > 99.9%); lithium chloride monohydrate (LiCl·H<sub>2</sub>O, > 99.9%) and citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, > 98%) were purchased from Wako Pure

Chemical Industries, Ltd. All the chemicals were used without further purification. SiO<sub>2</sub> with an average pore size of 6 nm was provided by Fuji Silysia Chemical, Ltd.

## 2.2 Catalyst Synthesis

SiO<sub>2</sub> support was washed with nitric acid (10 wt%) overnight, followed by washing with deionized water until the pH reaches neutral. The powder was further dried in air at 383 K overnight, followed by calcination at 673 K for 4.5 h, with a ramping rate of 4 K/min.

Ti/SiO<sub>2</sub>-673 was prepared by IWI of 2 g SiO<sub>2</sub> with a aqueous mixture of 0.098 g C<sub>6</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub>Ti and 1.414 g deionized water. The impregnated sample was kept in a desiccator at room temperature for 0.5 h, dried in an oven at 383 K for 3 h, and further heated to 673 K for 4.5 h in stagnant air.

2 g Ti/SiO<sub>2</sub> was impregnated with a aqueous mixture of 0.2188 g RhCl<sub>3</sub>·xH<sub>2</sub>O, 0.1064 g C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> and 1.164 g deionized water, dried at 383 K for 3 h, and calcined at 673 K for 4.5 h in stagnant air. The sample was denoted as Rh/Ti/SiO<sub>2</sub>-673.

2 g Rh/Ti/SiO<sub>2</sub>-673 was impregnated with a aqueous mixture of 0.0865 g MnCl<sub>2</sub>·4H<sub>2</sub>O, 0.112 g C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> and 1.22 g deionized water, dried at 383 K for 3 h, and calcined at 673 K for 4.5 h in stagnant air. The sample was denoted as Mn/Rh/Ti/SiO<sub>2</sub>-673.

2 g Mn/Rh/Ti/SiO<sub>2</sub>-673 was impregnated with a aqueous mixture of 0.010 g LiCl·H<sub>2</sub>O, 0.112 g C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> and 1.22 g deionized water, dried at 383 K for 3 h, and calcined at 673 K for 4.5 h in stagnant air. The sample was denoted as Li/Mn/Rh/Ti/SiO<sub>2</sub>-673, and abbreviated as CAT-I-673. For the preparation of CAT-I-773 (Li/Mn/Rh/Ti/SiO<sub>2</sub>-773), all the steps were the same as that of CAT-I-673, except changing the calcination temperature of section '2.22' to 773 K.

For the preparation of CAT-II-673 (Li/Rh/Mn/Ti/SiO<sub>2</sub>-673), all the preparation conditions were the same as that of CAT-I-673, except that the impregnation sequence of Mn and Rh was opposite.

## 2.3 Characterization

The N<sub>2</sub> adsorption–desorption measurements were performed by using Micromeritics Tristar 3020 apparatus at 77 K. Prior to measurement, samples were degassed under vacuum at 423 K overnight. The Rh, Mn, and Li contents in

the samples were measured by atomic adsorption spectroscopy (AAS) (Analyst 200, Perkin Elmer, USA).

Transmission electron microscopy (TEM) characterization was performed by using a Talos F200X microscope (FEL, Hillsboro, OR, USA) at an acceleration voltage of 200 kV.

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer equipped with a Co K $\alpha$  radiation ( $\lambda = 0.179026$  nm) in the  $2\theta$  region between 20° and 80°.

Temperature-programmed reduction in hydrogen (TPR(H<sub>2</sub>)) was performed in a homemade fixed bed reactor system connected to a thermal conductivity detector (TCD) to monitor the consumption of hydrogen by the as-prepared catalysts. 50 mg of fresh catalyst was heated in a flow of 10 vol % H<sub>2</sub>/Ar (30 ml/min) from ambient temperature to 700 K at a heating rate of 5 K/min.

In-situ DRIFTS of CO adsorption was performed in a Nicolet 6700 FT-IR (Thermo Scientific) equipped with a MCD/A detector. Samples were reduced by pure H<sub>2</sub> flow (20 cm<sup>3</sup>/min) at 673 K for 15 min (5 K/min). Afterwards, the cell was evacuated with He at 673 K for 20 min to remove the adsorbed H<sub>2</sub> molecules on the catalyst surface, followed by cooling down to 308 K under He flow (20 cm<sup>3</sup>/min). Then 1.5 vol% CO/He (20 cm<sup>3</sup>/min) was fed to the cell for 20 min at 308 K. Subsequently, the catalysts were flushed in He (20 cm<sup>3</sup>/min) for 20 min. Then the IR spectra were consecutively collected at different temperatures.

## 2.4 Catalyst Performance

Catalyst activity tests were performed in a six-flow fixed-bed microreactor (FBM) setup as previously described [42]. Prior to the operation, 100 mg fresh catalysts (50–100  $\mu$ m) mixed with SiC were activated in situ by H<sub>2</sub> at 593 K for 2.5 h at atmospheric pressure, followed by cooling to 473 K under H<sub>2</sub>. As the pressure was increased to 20 bar, feed composition was changed from H<sub>2</sub> to a mixture of H<sub>2</sub>, CO and N<sub>2</sub> in total of 40 ml/min (molar ratio: H<sub>2</sub>:CO:N<sub>2</sub> = 10:5:6) at 473 K. Then the reactor was heated to different reaction temperature with a heating rate of 2 K/min. All the reactions were run for 8 h, after which a steady state was achieved, and products were analyzed after 8 h time-on-stream (TOS) using an online GC (Trace GC-Interscience). Methanol, acetaldehyde, ethanol and C<sub>2</sub>–C<sub>3</sub> hydrocarbon were detected by a flame ionization detector (FID), while H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> were analyzed by a thermal conductivity detector (TCD). Products selectivity was calculated from each component detected via online GC using N<sub>2</sub> as an internal standard, from the total amount of CO converted.

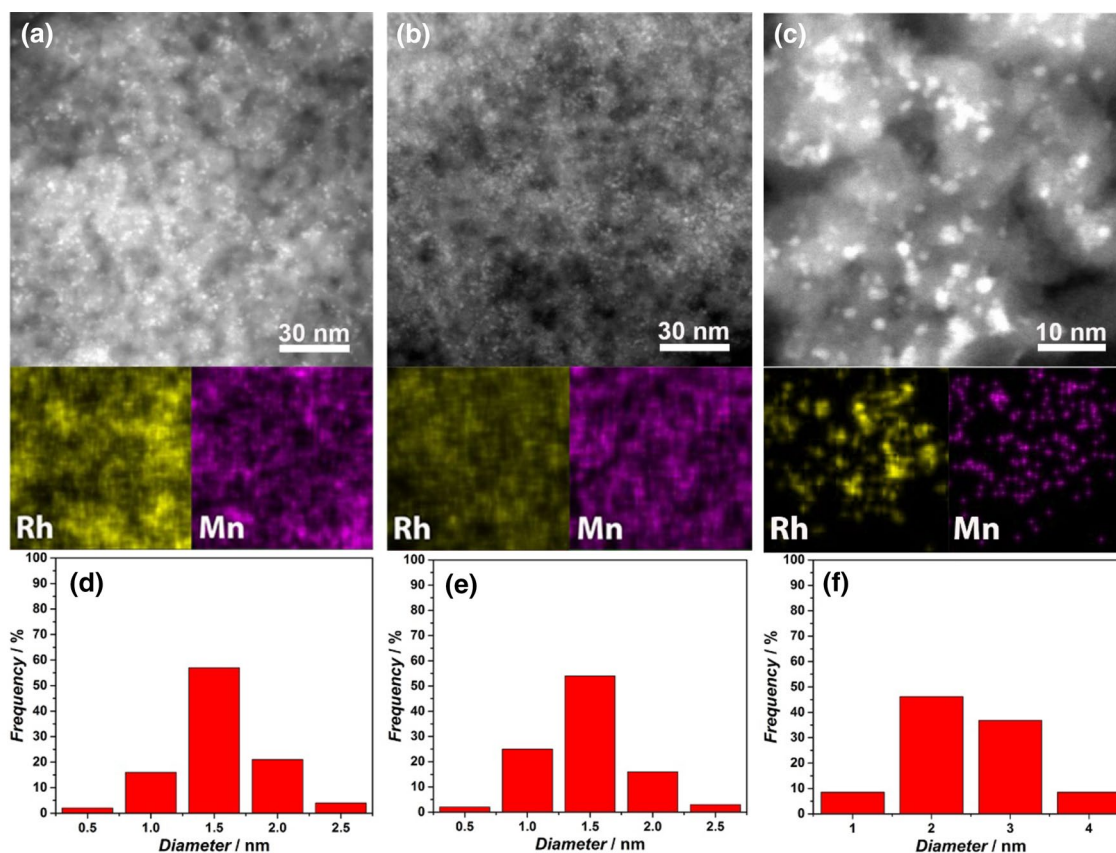
### 3 Results and Discussion

#### 3.1 Characterization of the As-Synthesized Catalysts

The textural properties of SiO<sub>2</sub> support and as-synthesized supported Rh catalysts were determined by N<sub>2</sub> sorption method (Fig. S1). The SiO<sub>2</sub> support exhibits a mesoporous structure, as proved by the type IV curve with type H<sub>2</sub> hysteresis that closes at  $P/P_0 \approx 0.4$  in the N<sub>2</sub> adsorption–desorption isotherms, demonstrating the presence of ink-bottle shape of pores. After stepwise impregnation and calcination treatments, the shape of isotherms did not change, while the BET surface area (*S*) and pore volume (*V*) of catalysts slightly decreased compared to the original SiO<sub>2</sub> (Table S1). The small differences can be probably due to the blockage of pores by nanoparticles and/or collapse of pore structure during high temperature treatment. Elemental analysis confirms a similar content of rhodium, manganese, and lithium in these as-synthesized supported rhodium catalysts (Table S1).

Freshly prepared supported rhodium catalysts were further studied by transmission electron microscopy

(TEM) combined with energy-dispersive X-ray spectroscopy (EDX). After the deposition of Ti precursor followed by a thermal treatment, uniformly dispersed TiO<sub>2</sub> on SiO<sub>2</sub> surface is observed (Fig. S2). Since TiO<sub>2</sub> is known to contain a large number of surface hydroxyl groups, these hydroxyl groups can provide anchors for rhodium precursors, stabilize rhodium nanoparticles, and impede their growth and agglomeration during the subsequent thermal treatment [26]. Indeed, the presence of a thin layer of TiO<sub>2</sub> on the surface of SiO<sub>2</sub> to a large extent improve the dispersion of Rh<sub>2</sub>O<sub>3</sub> nanoparticles compared to that in a similar Rh/SiO<sub>2</sub> catalyst (Fig. S3a, b). In the multicomponent promoted Rh catalysts, the Rh particle size and distribution largely depend on the calcination temperature. CAT-I-673 and CAT-II-673 show a homogenous distribution of Rh<sub>2</sub>O<sub>3</sub> nanoparticles with an average Rh nanoparticle size around ~1.5 nm (Fig. 1a, b). Further raising the calcination temperature to 773 K leads to an increase of Rh nanoparticle size to 2.8 nm, with some large clusters consisting of small Rh<sub>2</sub>O<sub>3</sub> crystals (Fig. 1c). EDX analysis displays overlapping signals of Rh and Mn on TiO<sub>2</sub>/SiO<sub>2</sub>, and a close interaction between Rh and Mn can be expected. The small size of rhodium oxide nanoparticles is



**Fig. 1** Dark field TEM images and Rh particle size distribution of **a, d**; CAT-I-673; **b, e** CAT-II-673; and **c, f** CAT-I-773 catalysts, with element distribution of Rh and Mn

further supported by the powder XRD analysis. As shown in Fig. 2a, the characteristic diffraction peaks for  $\text{Rh}_2\text{O}_3$  (104) and (110) planes at  $2\theta$  value of  $\sim 38$  and  $\sim 41^\circ$  are broad and small, confirming the high dispersion. At the same time, the absence of diffraction peaks for Mn and Li species can be ascribed to their highly dispersed states and low loadings in these samples.

The reducibility of Rh species in all these as-synthesized samples was studied by temperature-programmed reduction in  $\text{H}_2$  [TPR( $\text{H}_2$ )]. As present in Fig. 2b, only one reduction peak is observed in all these Rh-based catalysts, attributed to the reduction of rhodium oxide to its metallic phase [43, 44]. The reduction profiles of Rh depend on the impregnation sequence of Mn and Rh precursors and the calcination temperature. CAT-I-673 and CAT-II-673 exhibit a sharp reduction peak, suggesting that supported  $\text{Rh}_2\text{O}_3$  nanoparticles in each sample have similar properties, supporting the narrow Rh particle size distribution. CAT-I-673 exhibits a higher temperature for Rh reduction than that of CAT-II-673, indicative for a stronger interaction between Mn and Rh in CAT-I-673. Moreover, further raising calcination temperature to 773 K shifts the reduction peak to a high temperature, and leads to a much broader peak than that in CAT-I-673, supporting the heterogeneity of Rh particle size distribution.

FTIR spectroscopy of adsorbed CO has been widely employed to study the nature of surface sites in most transition metal based catalysts due to the sensitivity of the CO stretching frequency to the electronic state of the adsorption sites [11]. Figure 3 together with Fig. S4 show the results obtained applying this CO adsorption technique on all these as-synthesized catalysts. No obvious CO adsorption bands can be observed from  $\text{SiO}_2$  support itself (Fig. S4a). The rhodium-based catalysts exhibit similar features, as shown in Figs. 3a–d and S4b–d. Two regions at  $2150\text{--}1950\text{ cm}^{-1}$  and  $1950\text{--}1650\text{ cm}^{-1}$  are clearly observed in the spectra of

pre-adsorbed CO. In the region of  $2150\text{--}1950\text{ cm}^{-1}$ , the band centered at  $\sim 2070\text{ cm}^{-1}$  is attributed to the linearly adsorbed CO on  $\text{Rh}^0$  sites [CO(l)], and the doublet at  $\sim 2102\text{ cm}^{-1}$  and  $\sim 2038\text{ cm}^{-1}$  can be assigned to the symmetric and asymmetric stretching vibration of a gemdicarbonyl  $\text{Rh}^+(\text{CO})_2$ , [CO(gdc)] [45]. No bands around  $2145\text{ cm}^{-1}$  and  $2135\text{ cm}^{-1}$  are detected, indicative of the absence of  $\text{Rh}^{3+}$  and  $\text{Rh}^{2+}$  species in these samples [45].

The feature of these CO adsorption bands varies with an increase of temperature, especially in the range of  $2150\text{--}1950\text{ cm}^{-1}$ . Taking the ‘-773’ samples for instance, the band of linearly adsorbed CO gradually becomes weaker together with an obvious shift of the intensity maximum to a lower wavenumber as the temperature increases, owing to a weaker dipolar coupling between CO molecules at a lower CO surface coverage. Although the intensity of gemdicarbonyl  $\text{Rh}^+(\text{CO})_2$  signals decreases with temperature as well, the bands stay at the identical position. The development of these dicarbonyl complex bands demonstrates that these adsorption sites are spatially isolated, since close proximity of adsorbed CO molecules is supposed to lead to dipole–dipole interaction and, therefore, a shift to lower wavenumbers as surface coverage should decrease [45]. Furthermore, the representative signals of  $\text{Rh}^+(\text{CO})_2$  gradually decrease with an increase of temperature, indicative of a weak adsorption energy of CO molecules on these rhodium sites. The feature of these CO adsorption bands varies with the composition in the catalysts as well. Rh–Ti/ $\text{SiO}_2$ -773 exhibits a higher fraction of CO(gdc) species than that of Mn–Rh–Ti/ $\text{SiO}_2$ -773 and CAT-I-773. The presence of Li in CAT-I-773 improves the adsorption strength of the CO(gdc) species, as proven by the presence of CO adsorption band at  $\sim 2102\text{ cm}^{-1}$  at 423 K.

In the region of  $1950\text{--}1650\text{ cm}^{-1}$ , a broad shoulder with a tail is present, suggesting the existence of several kinds of

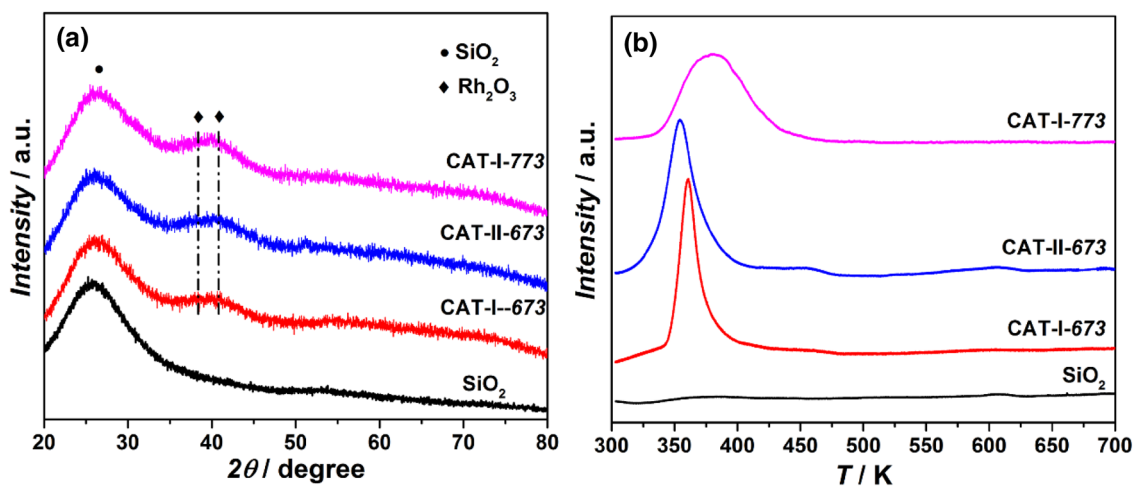
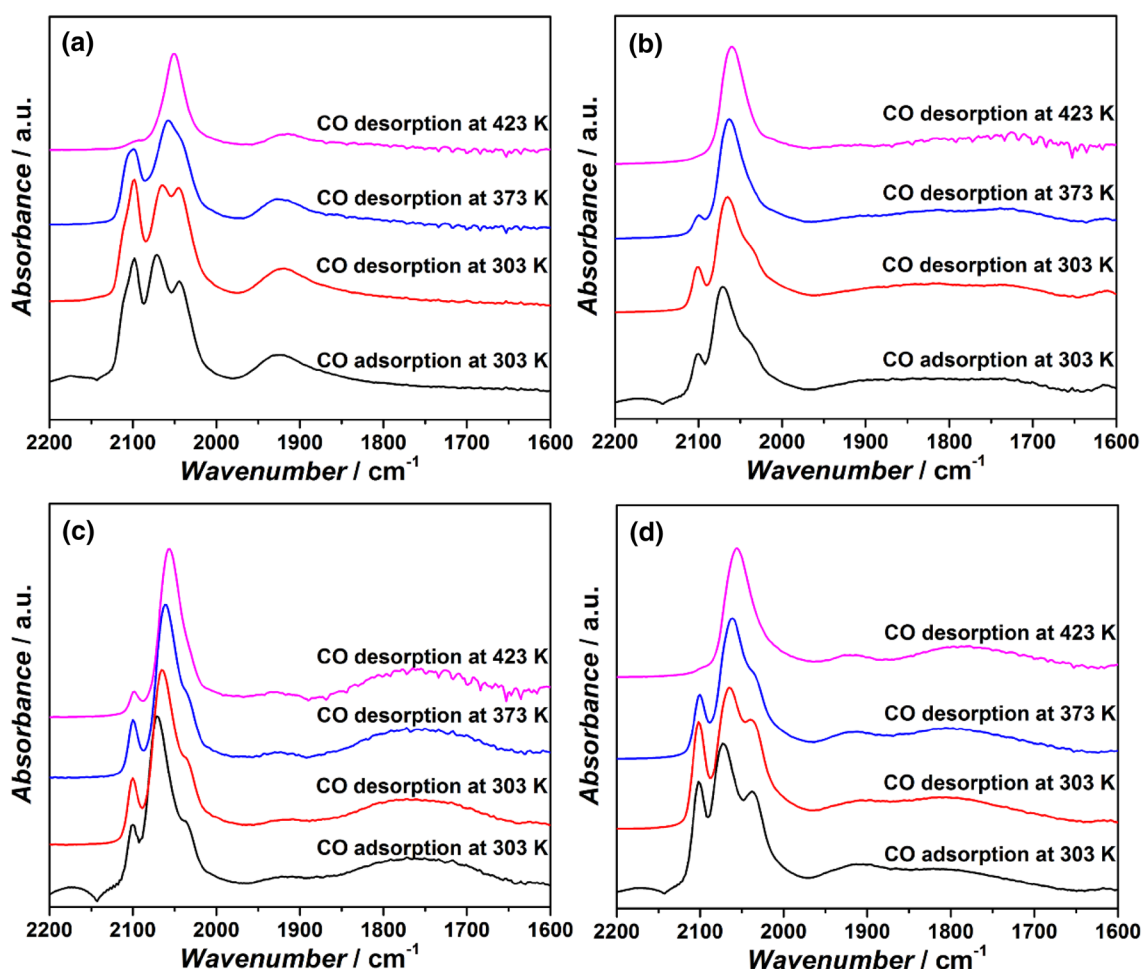


Fig. 2 a XRD patterns and b TPR( $\text{H}_2$ ) profiles of the as-synthesized supported Rh catalysts



**Fig. 3** DRIFT spectra of CO adsorbed on **a** Rh-Ti/SiO<sub>2</sub>-773, **b** Mn-Rh-Ti/SiO<sub>2</sub>-773, **c** CAT-I-773, and **d** CAT-I-673 catalysts at different temperatures

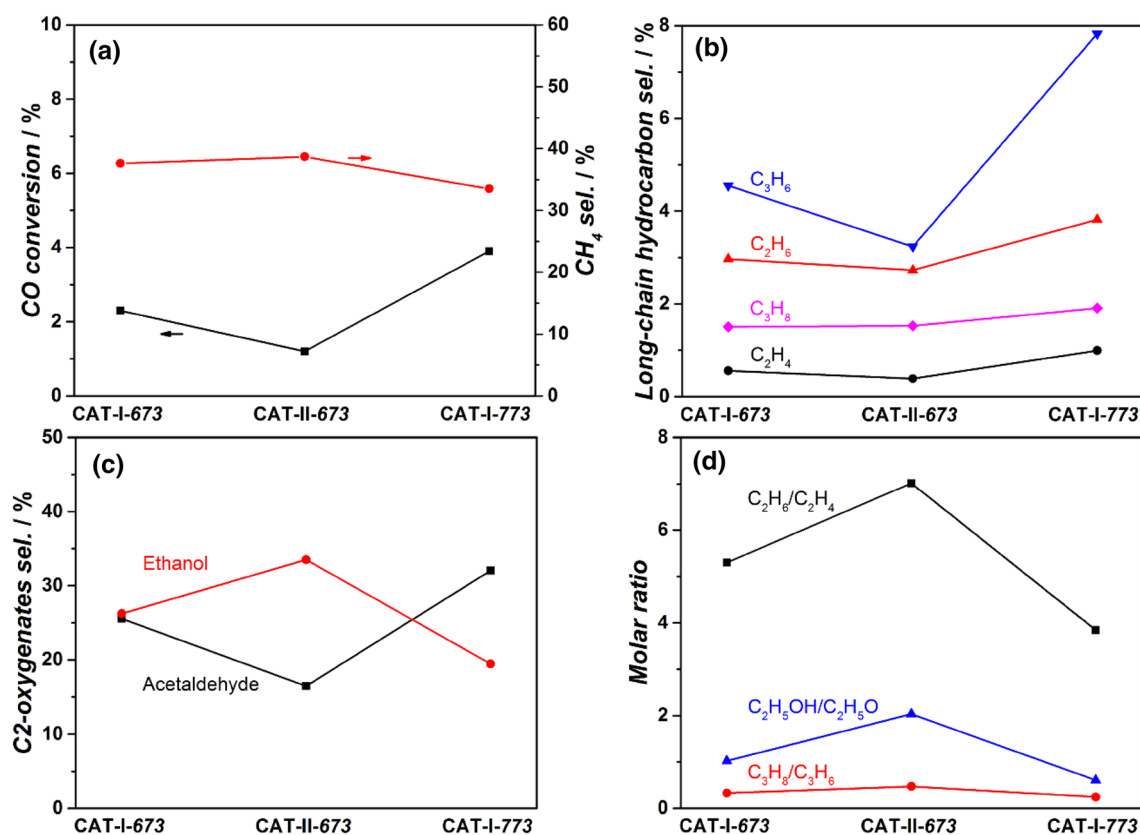
CO adsorption sites at the surface of rhodium nanoparticles. Specifically, the broad bands between 1950 and 1750 cm<sup>-1</sup> represent the existence of bridge bonded CO on Rh<sup>0</sup> [46]. The tail with a wavenumber ranging from 1750 cm<sup>-1</sup> to 1650 cm<sup>-1</sup> [CO(t)] is too low to be attributed to CO bridge-bonded to several Rh atoms via carbon atom alone. Similar bands at 1725 cm<sup>-1</sup> and 1696 cm<sup>-1</sup> were also detected by Lisitsyn et al. [21] These bridging sites have been considered as the metal/oxide interfacial sites, on which the C and O in CO molecule are bonded to metallic Rh and Mn<sup>δ+</sup> cation, respectively, namely a tilted Rh-C-O-Mn species [21, 38, 47]. Such an adsorption state should weaken the C-O bond and enhance CO dissociation.

Finally, the intensity ratio between CO(l) and CO(gdc) bands varies between catalysts prepared at different temperatures. The ‘-673’ samples show a similar CO(l)/CO(gdc) value but lower than that of the ‘-773’ sample (Figs. 3c, d and S4d). Since the dicarbonyl Rh<sup>+</sup> species are predominantly formed on highly dispersed rhodium nanoparticles,

the relatively higher intensity of the dicarbonyl bands in the ‘-673’ samples further supports the smaller rhodium size than that in the ‘-773’ sample [19, 29]. In contrast, the intensity ratio between CO(l) and CO(t) for the ‘-673’ samples is higher than that in the ‘-773’ sample, indicative of a higher fraction of tilted Rh-C-O-Mn species on the ‘-773’ surface.

### 3.2 Roles of Rh Particle Size and Promoters on Hydrogenation Activity and Products Selectivity

CO conversions over these supported Rh catalysts after 8 h time-on-stream (TOS) (after which CO conversion becomes stable) at 533 K, 20 bar, H<sub>2</sub>/CO molar ratio of 2 are presented in Fig. 4a. The catalytic performance of these Rh-based catalysts displays different CO conversion levels. CAT-I-773 shows a higher CO conversion (3.9%) than that of the CAT-I-673 (2.3%) and CAT-II-673 (1.2%). In



**Fig. 4** **a** CO conversion and CH<sub>4</sub> selectivity; **b** long-chain hydrocarbon selectivity; **c** C2-oxygenates selectivity and **d** products molar ratio for CAT-I-673, CAT-II-673, and CAT-I-773 catalysts after 8 h TOS at 533 K, 20 bar total pressure, and feed composition H<sub>2</sub>/CO = 2

principle, small Rh nanoparticles in CAT-I-673 exhibit a much stronger interaction with the thin TiO<sub>2</sub> layer on SiO<sub>2</sub> support compared to the large ones in CAT-I-773 [11, 20]. The strong Rh-TiO<sub>2</sub> interaction generates a large number of electron-deficient Rh atoms on the surface, which results in poor electron back-donation to the unoccupied 2π\* antibonding orbital of CO, thereby impeding CO dissociation and further hydrogenation. Moreover, MnO promoter has also been reported to improve the hydrogenation activity of supported Rh catalysts [32, 48]. For instance, Wang et al. found that adding 1.1 wt% Mn to a carbon nanotubes(CNTs) supported 4.5 wt% Rh catalyst led to a CO conversion two times as high as that of 4.5 wt% Rh/CNTs [48]. Schwartz et al. also reported a similar trend after introducing 0.5 wt% Mn into 1 wt% Rh/TiO<sub>2</sub> [26]. In general, hydrogenation of CO to formyl species intermediate is considered as the rate limiting step on Rh-based catalyst [30, 49]. The introduction of Mn species can generate Rh-MnO interfacial sites on the surface of Rh nanoparticles. CO molecules adsorb on these sites in a tilted Rh-C-O-Mn mode, which shows a high CO dissociation activity [38, 47]. Obviously, the larger Rh nanoparticle size and the higher fraction of tilted Rh-C-O-Mn species in CAT-I-773 than the ‘-673’ samples lead to a higher hydrogenation activity.

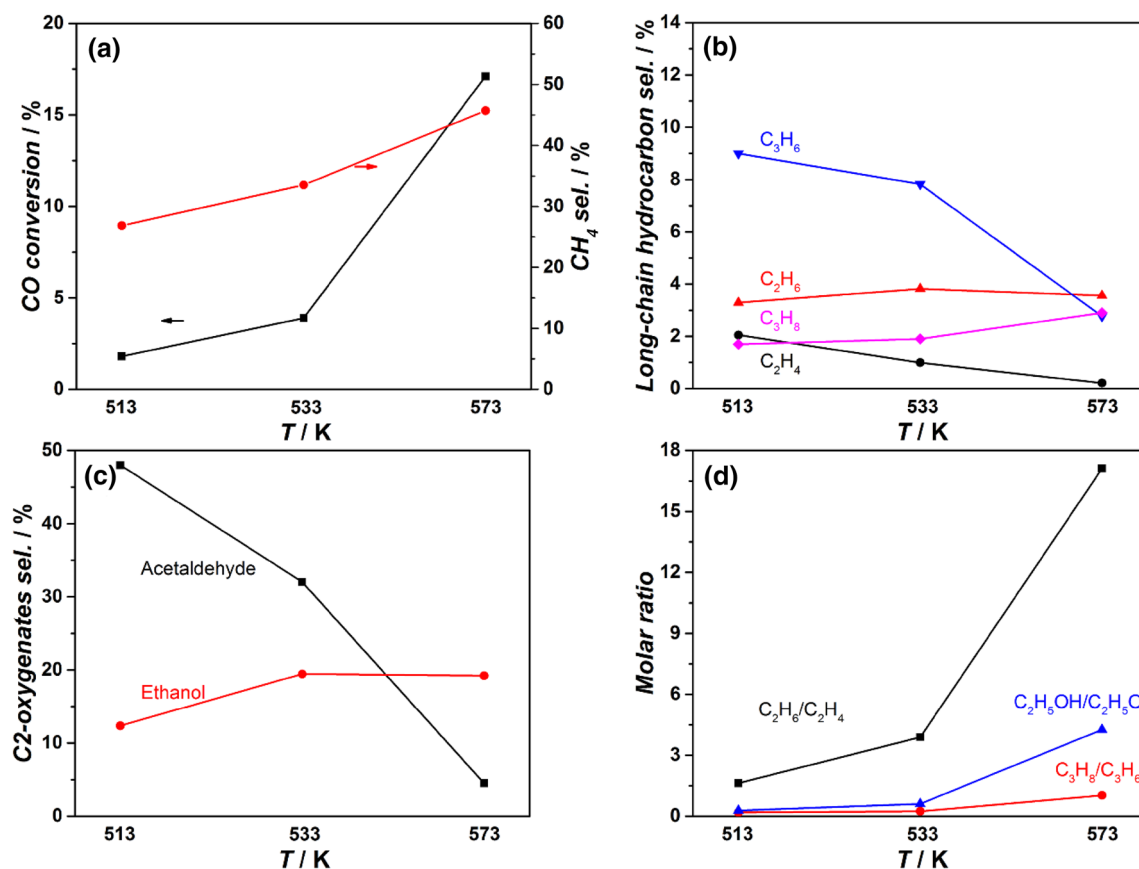
The products distributions for all these Rh based catalysts after 8 h are included in Fig. 4a–d. Negligible CO<sub>2</sub> and methanol was detected in all these as-synthesized Rh based catalysts under this experimental condition. Previous studies demonstrated that both metallic and partially positive Rh sites are necessary in the production of C2-oxygenates [15, 50]. Metallic Rh (Rh<sup>0</sup>) was considered for C–O bonds dissociation to produce ‘-CH<sub>x</sub>’ species, and positive Rh (Rh<sup>δ+</sup>) was responsible for CO insertion [15]. In this sense, parameters that can adjust the molar ratio of Rh<sup>0</sup>/Rh<sup>δ+</sup> in Rh nanoparticles are supposed to influence products distribution [27, 29]. Haider et al. proved that Rh/SiO<sub>2</sub> with a weak Rh-support interaction mainly produces hydrocarbons, while more C2-oxygenates were detected on Rh/TiO<sub>2</sub> with a strong-metal-support-interaction (SMSI) at the expense of hydrocarbons [27]. The improvement in C2-oxygenates production on TiO<sub>2</sub> was attributed to its stronger interaction with Rh nanoparticles, which creates more Rh<sup>δ+</sup> sites. Similarly in the current work, the thin TiO<sub>2</sub> layer on SiO<sub>2</sub> support interacts strongly with Rh nanoparticles, and generates numerous partially positive Rh sites necessary for CO insertion in C2-oxygenates production. Besides, the particle size of supported Rh nanoparticles can also influence the molar ratio of Rh<sup>0</sup>/Rh<sup>δ+</sup> at the surface of Rh nanoparticles.



In general, as Rh nanoparticles become smaller, the electron-interaction between the support and Rh nanoparticles becomes stronger, and more electrons from Rh can be withdrawn by the support; hence more  $\text{Rh}^{\delta+}$  sites at the surface can be created. Indeed, the ‘-673’ samples exhibit a much higher fraction of  $\text{Rh}^{\delta+}$  sites than CAT-I-773, as confirmed in Fig. 2c. Previous study by Hironori et al. reported a volcano-like relationship between Rh nanoparticle size and C2-oxygenates selectivity with the maximum C2-oxygenates selectivity at Rh particle size of  $\sim 3.0$  nm on a Rh/SiO<sub>2</sub> catalyst [51]. The CAT-I-773 catalyst with a similar Rh particle size ( $\sim 2.8$  nm) also exhibits a higher C2-oxygenates (sum of acetaldehyde and ethanol) selectivity ( $\sim 55\%$ ) than the ‘-673’ samples with a smaller Rh particle size of  $\sim 1.5$  nm ( $\sim 50\%$ ). At the same time, CAT-I-773 produces more C2-C4 hydrocarbons and less CH<sub>4</sub> (33% vs. 38%) compared to CAT-I-673, as shown in Fig. 4a, b. Indeed, large nanoparticles are known to contain more terrace sites for carbon chain growth towards long chain hydrocarbons instead of methane [52].

Beside the effects of the support and Rh particle size on products selectivity, the presence of Li and Mn in supported Rh catalysts is also of great importance for the production of

C2-oxygenates in this study. Egbebi et al. and Schwartz et al. indicated that a small amount of Li ( $\sim 0.1$  wt%) significantly improved the products selectivity towards C2-oxygenates of 1 wt% Rh/TiO<sub>2</sub> at the expense of CH<sub>4</sub> production [25, 26]. The presence of Li was stated to improve the stability of the ‘-CH<sub>x</sub>’ intermediate species on the surface of Rh, making the insertion of adsorbed CO species into ‘-CH<sub>x</sub>’ to produce C2-oxygenates more competitive than the direct hydrogenation of ‘-CH<sub>x</sub>’ into methane [25, 40]. Moreover, Liu et al. reported that the addition of Mn into 3 wt% Rh/CNTs significantly promoted the production of C2-oxygenates, and C2-oxygenates selectivity seemed to increase with the loadings of Mn in the catalyst [32]. A similar phenomenon was as well observed by Schwartz et al. after introducing 0.5 wt% Mn into a 1 wt% Rh/TiO<sub>2</sub> catalyst [26]. Manganese species in oxidation states are well-known to act as electron acceptors and withdraw electrons from Rh to create partially positive Rh sites, necessary for CO insertion in C2-oxygenates production [32, 34]. At the same time, the tilt-adsorbed CO species at the Rh–MnO interfacial sites was reported by Wang et al. to be the precursor for the formation of oxygenates [53]. Interestingly, although CAT-I-673 and



**Fig. 5** a CO conversion and CH<sub>4</sub> selectivity; b long-chain hydrocarbon selectivity; c C2-oxygenates selectivity and d products molar ratio for CAT-I-773 catalyst at different temperatures, 20 bar total pressure, and feed composition H<sub>2</sub>/CO = 2

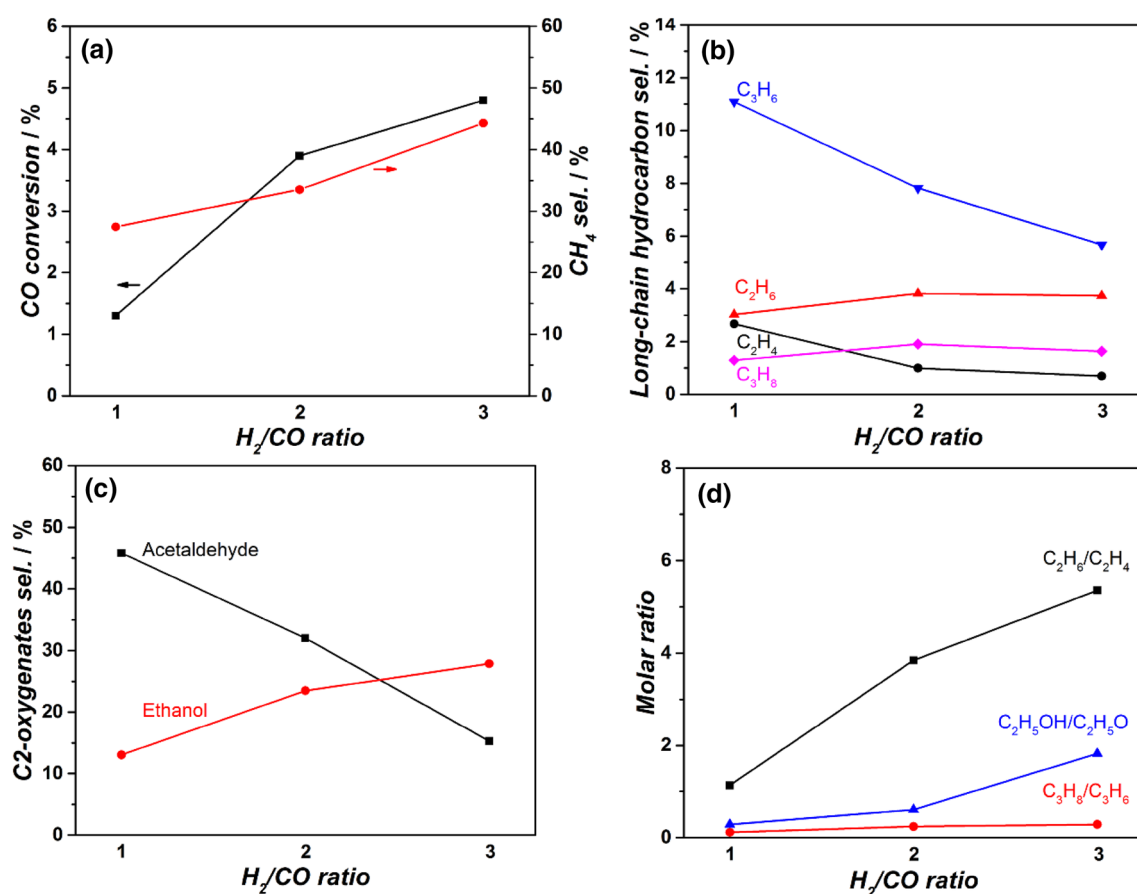
CAT-II-673 show similar C2-oxygenates (sum of acetaldehyde and ethanol) selectivity, CAT-II-673 exhibits a higher ethanol selectivity (33%) than CAT-I-673 (26%), indicative of a higher hydrogenation capability of CAT-II-673 with MnO underneath Rh nanoparticles, as shown in Fig. 4c, d. Indeed, H<sub>2</sub>-TPR profile of CAT-II-673 indicates that a lower reduction temperature is needed compared to that of CAT-I-673, suggestive of a relatively weaker interaction between Rh and manganese oxide and/or TiO<sub>2</sub> in CAT-II-673. The higher hydrogenation ability of CAT-II-673 can be also demonstrated by higher ethane/ethylene and propane/propylene ratios, as shown in Fig. 4d.

### 3.3 Influence of Reaction Variables: Temperature and H<sub>2</sub>:CO Ratio on Catalytic Performance

The effect of reaction temperature on the hydrogenation activity and products selectivity of the representative CAT-I-773 sample is summarized in Fig. 5a–d. CO conversion increases from 1.8 to 17.1% as the reaction temperature increase from 513 to 573 K, while the selectivity to paraffins,

especially methane increases from ~27 to ~46% at the expense of total olefins and C2-oxygenates selectivity, which decreases from 60 to 24%. These results indicate a dominant hydrogenation of ‘–CH<sub>x</sub>’ species at high temperature and the activation energy for methane formation is higher than that for C2-oxygenates synthesis [54]. The preferable hydrogenation reaction at high temperature is further proved by an increase of paraffin/olefin and/or ethanol/acetaldehyde ratio.

Figure 6 summarizes the influence of H<sub>2</sub>:CO ratio ranging from 1 to 3 on the hydrogenation activity and products selectivity over CAT-I-773. As shown in Fig. 6a, c, despite that the CO conversion increases from 1.3 to 4.8% with H<sub>2</sub> concentration in the feed, the selectivity to methane also increased from 27 to 44% at the expense of acetaldehyde, which decreases from 46 to 12%. Indeed, a high concentration of hydrogen on the surface on one hand promotes the termination step of ‘–CH<sub>x</sub>’ species, leading to high CH<sub>4</sub> production; on the other hand enhances the hydrogenation steps of unsaturated C=C and C=O bonds, resulting in high product selectivity to paraffin and ethanol at the expense of olefins and acetaldehyde, as confirmed in Fig. 6b–d. These



**Fig. 6** a CO conversion and CH<sub>4</sub> selectivity; b long-chain hydrocarbon selectivity; c C2-oxygenates selectivity and d products molar ratio for CAT-I-773 catalyst at 533 K, 20 bar total pressure, and different feed compositions

results suggest that to target C2-oxygenates synthesis, reaction is preferred to be operated at a low temperature with a low H<sub>2</sub>/CO molar ratio in the feed.

## 4 Conclusions

In this work, Mn and Li promoted Rh catalysts supported on SiO<sub>2</sub> with a thin TiO<sub>2</sub> layer were prepared by stepwise incipient wetness impregnation method. The thin TiO<sub>2</sub> layer on the surface of SiO<sub>2</sub> was crucial to stabilize those small Rh nanoparticles and hamper their agglomeration. The reducibility of Rh on these catalysts is dependent on both Rh particle size and the location of manganese oxide. Large Rh nanoparticles beneath MnO can be reduced at a higher temperature than small Rh nanoparticles on MnO. Large Rh particles show a higher CO conversion and higher products selectivity towards long chain hydrocarbons and C2-oxygenates, but a lower methane selectivity compared to a similar catalyst with smaller Rh particles. The high catalytic performance to C2-oxygenates with large Rh nanoparticles is ascribed to both the promotion effect of Mn and Li, and a proper molar ratio between metallic Rh (Rh<sup>0</sup>) sites and partially positive Rh (Rh<sup>δ+</sup>) sites on the surface of Rh nanoparticles. Moreover, the catalyst with MnO underneath the Rh nanoparticles is more efficient in promoting hydrogenation of acetaldehyde to ethanol than a similar catalyst with MnO on Rh nanoparticles. In order to reach high C2-oxygenates selectivity, reaction is recommended to be performed at a low temperature together with a low H<sub>2</sub>/CO ratio in the feed.

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