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Evidence of strong metal–oxide interactions in promoted Rh/SiO_2 on CO hydrogenation: Analysis at the site level using SSITKA

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ABSTRACT

It has been suggested that the behavior of Group VIII metal catalysts supported on transition metal oxides can be significantly affected by pretreatment conditions due to strong metal–oxide interactions (SMOI). However, the origins for the SMOI effect are still in debate. In this research, SMOI of Rh and vanadium oxide (as a promoter) supported on SiO_2 were studied at the site level for the first time, which provides an insight into the modification of surface properties after high temperature reduction. H_2 chemisorption, Fischer–Tropsch synthesis (FTS), and SSITKA (steady-state isotopic transient kinetic analysis) were used to probe the SMOI effects. The catalytic properties of the catalysts for CO hydrogenation were investigated using a differential fixed bed reactor at 230 °C and 1.8 atm, while for SSITKA, a reaction temperature of 280 °C and an excess of H_2 was used to maximize methane production. The addition of V to Rh/SiO_2 suppresses H_2 chemisorption, and high reduction temperature further decreases H_2 chemisorption on $Rh/V/SiO_2$ but has little effect on Rh/SiO_2. As reduction temperature increases, the activity for CO hydrogenation on Rh/SiO_2 remains essentially unchanged, but the activity of $Rh/V/SiO_2$ decreases significantly. SSITKA shows that the concentration of surface reaction intermediates decreases on $Rh/V/SiO_2$ as the reduction temperature increases, but the activities of the reaction sites increase. The results suggest that Rh being covered by VO_x species is probably the main reason for the decreased overall activity induced by high reduction temperature, but more active sites appear to be formed probably at the Rh–VO_x interface.

1. Introduction

It was found 30 years ago that the activity and selectivity of catalysts consisting of Group VIII metals supported on transition metal oxides are strongly dependent on the pretreatment conditions [1–3]. In 1978, Tauster and co-workers first proposed that strong metal–support interactions (SMSI) were the reason for this behavior on particular reducible oxide [1,2]. Since then, there have been numerous studies regarding the effect of so-called SMSI [3–25]. It was suggested that metal catalysts (Rh, Pt, Pd, etc.) supported on certain oxide supports (TiO_2, Nb_2O_5, V_2O_3, MnO, MoO_x) have a high activity in CO hydrogenation due to SMSI [26–28]. Kunimori and co-workers have used the concept of strong metal–oxide interactions (SMOI) to include the effects when transition metal oxides are used not only as supports, but also as promoters [28–32]. Thus, in our study, the term "SMOI" is used because of the emphasis on the promoting effects of V oxide on Rh. Obviously, "strong" is a relative term that can apply for a variety of interactions and effects. In addition, while higher temperatures of reduction are classically important for SMSI, no such requirement is suggested by our use of SMOI. We use SMOI to describe in a succinct fashion, a major modification of metal catalyst properties caused by the presence of a metal oxide.

In recent years, there has been a marked increase in interest for the application of the Fischer–Tropsch synthesis (FTS) to the conversion of syngas into easily transportable liquid hydrocarbon products. Production of ethanol from coal or natural gas has been attracting much attention due to the easy transport of ethanol, its use as a gasoline additive and alternative fuel, and its ability to serve as a means to transport and store hydrogen for use in fuel cells. The activities of catalysts for FTS or CO hydrogenation are more or less decreased where SMOI are suggested to be present [16]. Among transition metals, Rh catalysts have been extensively studied for the CO hydrogenation reaction because of their high selectivity for ethanol [33–39]. SMOI effects have been found for Rh/SiO_2 promoted by Group VIII transition metal oxides but they have been less widely studied than for other transition metals [26,29,40–44]. Moreover, there has been no study reported probing Rh at the site level during reaction in the presence of SMOI.

V is an important promoter for ethanol synthesis on Rh/SiO_2 [26,30–32,40,45,46]. In our previous studies [47–49], it was found that the addition of V increases activity by a factor of three com-

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pared to that of non-promoted Rh/SiO_2 at 230 °C and 1.8 atm, and also suppresses methane formation significantly [49]. It also has a synergistic effect on La and LaFe promotion of Rh/SiO_2 [47,49]. However, there is little agreement about how V modifies the catalyst behavior of Rh/SiO_2. It has been reported that V can produce tilted CO on the catalyst surface and enhance CO dissociation and insertion [50]. Kip et al. suggested that V enhances reactivity and selectivity towards ethanol by enhancing CO dissociation [46], but they had no direct evidence except for the increased overall activity using V as a promoter for Rh/SiO_2. Other researchers have proposed that the function of V is to boost hydrogenation [26,40,51,52]; however, Kip et al. [46] disagreed with this suggestion since they did not observe an increased rate for ethylene to form ethane with the addition of V to Rh/SiO_2. Nevertheless, there is an agreement that the changes in catalytic behavior are related to the interaction of Rh with vanadium oxide (SMOI).

Instead of simple interaction between metal and support/promoter, it has been proposed by various researchers that the origin of SMOI may be due to an electronic interaction with the promoter or support oxide [3,7,19,21,53], the formation of an alloy [23,25,27,34,40], or a partial covering of the metal particles by the promoter or support oxide after reduction at high temperature [9,12,22–25,40,46,54]. With respect to V-promoted Rh/SiO_2, Ito et al. [30] proposed that VO_x species block part of the Rh active metal surface; Rupprechter et al. [55] believed that high temperature reduction led to a change in the structure of the Rh particles; Jenewein et al. [5] suggested the formation of stable bulk alloy phases. However, there has been to date no direct evidence regarding the number and activity of active sites measured using an *in situ* technique to support any of these proposed hypotheses.

The focus of this study was to probe the SMOI of Rh and vanadium oxide on $Rh/V/SiO_2$ reduced at different temperatures using SSITKA (steady-state isotopic transient kinetic analysis) during CO hydrogenation. SSITKA is a powerful tool to analyze surface reaction and may be the most accurate kinetic technique for characterizing surface reaction parameters under reaction conditions [56,57]. In this study, SSITKA provided some insight into the modification by V of the active sites on Rh/SiO_2 for CO hydrogenation, leading to a better understanding of the promoting effect of V and the status of Rh under SMOI effects.

2. Experimental

2.1. Catalyst preparation

Since the catalysts used in this study were the same as those used in our studies reported earlier, catalyst preparation is summarized here but a detailed description can be found elsewhere [47]. Silica gel (99.95%, Alfa Aesar) was used as a support. It was reported by Beutel et al. [40] that the SMOI effects could be induced when the temperature of calcination is higher than 700 °C. Thus, a 500 °C calcination was used to eliminate the possibility of calcination temperature causing SMOI. $Rh(NO_3)_3$ hydrate (Rh ~ 36 wt%, Fluka) and NH_4VO_3 (99.5%, Alfa Aesar) were used as purchased. Rh content was always ca. 1.5 wt% and V was 1.5 wt% if added. The nomenclature used is as follows: Rh/SiO_2 for the silica-supported Rh catalyst and $Rh/V/SiO_2$ for the silica-supported Rh catalyst prepared by sequential impregnation: first V and then Rh with a drying and calcination step in between.

2.2. H_2 chemisorption

The number of exposed rhodium surface atoms was determined by H_2 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 a particular temperature in a hydrogen flow for 30 min, followed by evacuation at 10^{-6} mm Hg and the reduction temperature for 120 min. After cooling under vacuum to 35 °C, the adsorption isotherm was recorded. Based on total H_2 chemisorption, the metal dispersion was calculated subsequently assuming $H/Rh_s = 1$, where Rh_s denotes a Rh surface atom.

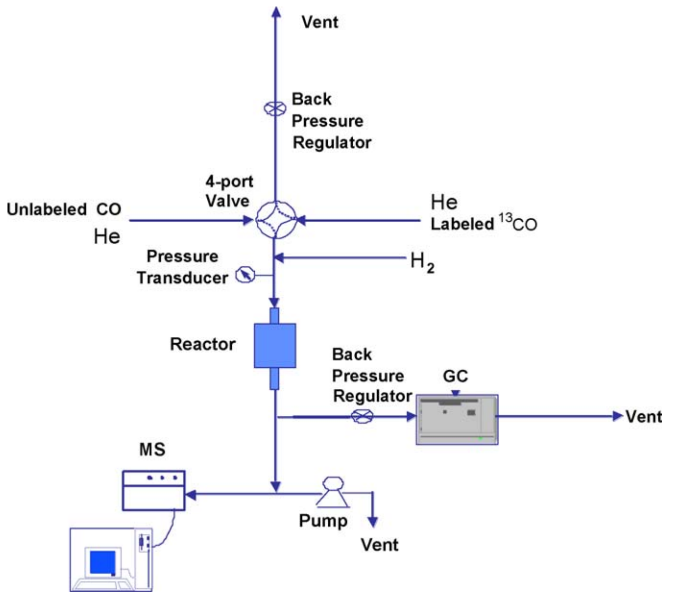

Fig. 1. SSITKA reaction system for methanation.

2.3. Reaction

For reaction, 0.3 g of catalyst and 3 g of inert were mixed and loaded in the middle of the reactor with a thermocouple close to the catalyst bed. Prior to reaction, the catalyst was reduced *in situ* with hydrogen (flow rate = 30 mL/min) at a specific reduction temperature for 1 h. In our study, the activity of Rh/SiO_2 reduced at 700 °C was significantly lower than that reduced at 600 °C, which probably indicated pronounced sintering at the higher temperature. Thus, the effect of reduction temperature was studied only in the range 300–600 °C in this investigation. After reduction, the catalyst was then cooled down to reaction temperature and reaction started as gas flow was switched to H_2/CO (H_2 flow rate = 30 mL/min, CO flow rate = 15 mL/min) for the initial reaction (FTS) study.

The reaction products were separated chromatographically (Varian 3800) using a Restek RT-QPLOT column (30 m, 0.53 mm ID) with detection with an FID (flame ionization detector) and a Restek HayeSep® Q column with a TCD (thermal conductivity detector). The analysis details can be found in our previous paper [47]. The reaction conversion was always kept at less than 5% to avoid mass or heat transfer effects.

2.4. SSITKA

A surface reaction study was carried out in a steady-state isotopic transient kinetic analysis (SSITKA) system as described elsewhere [58]. Fig. 1 shows the reaction system setup for SSITKA. Isotopic transient measurements were carried out by switching between two feed streams with the same flow rate but containing different isotopic labeling of reactant species (95% ^{12}CO + 5% Ar vs. ^{13}CO) after reaction reached steady state. The effluent gas was analyzed on-line by GC (as described for the standard reaction) and a Pfeiffer mass spectrometer (MS) with a high speed acquisition system. Back-pressure regulators on both the reactor and

Table 1
H_2 chemisorption results and accessible surface Rh dispersion as a function of reduction temperature.

Catalyst	Reduction temperature (°C)	H_2 chemisorbed (μmol/gcat)[a]		Metal dispersion (%)[b]
		Total	Irrev.	
Rh/SiO_2[c]	300	31.1	13.9	46.6
	600	31.1	15.0	48.1
$Rh/V/SiO_2$[d]	300	1.2	0.2	(1.8)[e]
	400	0.6	0.2	(0.9)[e]
	500	0.4	–	(0.5)[e]
	600	0.3	–	(0.4)[e]

[a] Catalyst: 0.2 g.
[b] Metal dispersion is based on total H_2 chemisorbed and an assumption of $H/Rh_s = 1$.
[c] Experimental error ≤ ±8%.
[d] Experimental error ≤ 15%.
[e] Impacted by significant suppression of H_2 chemisorption and therefore not meaningful.

vent streams were used to ensure a constant reaction pressure and to avoid a pressure surge during CO switching. Thus, switching of the feed streams resulted in minimum disturbance of reaction conditions. The gas lines used in the system were designed to be as short as possible to minimize gas holdup in the system. The 5% Ar in the ^{12}CO flow was used as an inert tracer to determine the gas phase holdup time. The reaction conditions were the same as for standard reaction except for the temperature and flow rates. For SSITKA, in order to maximize methane production, a reaction temperature of 280 °C was used, and the H_2 flow rate was 20 times higher than the CO flow rate (total flow rate = 60 mL/min, H_2:He:CO = 20:19:1).

3. Results

3.1. H_2 chemisorption

Table 1 shows the influence of reduction temperature on H_2 chemisorption at 35 °C. The amounts of total and irreversible H_2 chemisorbed are both provided. The metal dispersion was calculated by assuming an adsorbed H atom (total chemisorption) to surface Rh atom stoichiometry of 1:1. For Rh/SiO_2, the strong irreversible H_2 chemisorption took up nearly half of the total amount of H_2 chemisorption and the reduction temperature did not influence the H_2 chemisorption results. However, it is obvious that H_2 chemisorption was suppressed significantly by the addition of V, similar to what was previously found for CO chemisorption [47]. The extremely low dispersions of Rh in $Rh/V/SiO_2$, calculated based on the total H_2 chemisorption, are not the real metal dispersions because our XRD and TEM results did not suggest the existence of Rh particles larger than 5 nm [47].

3.2. Standard FTS reaction

Table 2 shows the catalytic activities and selectivities of Rh/SiO_2 and $Rh/V/SiO_2$ reduced at different temperatures. Consistent with the results reported before [47], the addition of V increased the activity and decreased methane selectivity, resulting in an increase in C_{2+} hydrocarbon selectivity. Moreover, it can be seen in Table 2 that the activity difference between Rh/SiO_2 and $Rh/V/SiO_2$ was greatest at lower reduction temperature. For Rh/SiO_2, when reduction temperature was increased from 300 to 600 °C, the activities were similar within experimental error. The molar ratios of olefin-to-paraffin for (C_2 or C_3 hydrocarbons) were also almost the same. Similarly, the oxygenate selectivities were essentially independent of the reduction temperature. However, there was less C_{2+} hydrocarbon production but more methane produced for Rh/SiO_2 reduced at higher reduction temperatures.

The effect of reduction temperature on the V-promoted catalyst for CO hydrogenation was significantly different from that for Rh/SiO_2. The activity decreased dramatically with increasing reduction temperature. Moreover, there was a decrease in methane selectivity but an increase in methanol selectivity as reduction temperature increased.

3.3. SSITKA

The SSITKA experiments were carried out under methanation conditions (i.e., at a slightly higher reaction temperature than that for standard reaction and in a large excess of H_2 in order to develop a better understanding of the change in activity). The purpose of the increase in temperature and H_2 partial pressure was to obtain CH_4 as the primary product in order to simplify the mass spectrometric

Table 2
Catalytic FTS activities and selectivities of Rh/SiO_2 and of $Rh/V/SiO_2$ reduced at different temperatures.

Catalyst	Reduction temperature (°C)	SS rate[a] (μmol/gcat/s)	Selectivity (%)[b]						$C_{2=}/C_2$[e]	$C_{3=}/C_3$[e]
			CH_4	C_{2+}HC[c]	MeOH	Acetaldehyde	EtOH	Other C_{2+} oxy[d]		
Rh/SiO_2	300	0.03	34.3	46.4	–	4.1	15.2		2.0	2.6
	400	0.03	35.2	43.7	–	3.3	17.9	–	1.8	2.7
	500	0.03	48.1	28.7	1.2	6.5	15.6	–	1.9	2.6
	600	0.04	55.4	19.6	–	4.9	20.1	–	1.8	2.5
$Rh/V/SiO_2$	300	0.63	20.0	58.0	2.6	3.9	14.2	1.3	2.6	11.7
	400	0.45	18.2	56.9	2.9	4.0	16.5	1.4	3.1	12.1
	500	0.10	12.4	60.5	6.5	3.1	15.8	1.7	3.2	10.1
	600	0.05	11.4	59.5	11.7	2.1	15.4	–	3.3	8.4

[a] Steady-state rate where rate is in μmol CO converted/gcat/s. Catalyst: 0.3 g, inert: α-alumina 3 g; reaction at 230 °C; $P = 1.8$ atm, flow rate = 45 mL/min ($H_2/CO = 2$), data taken at 15 h after steady state reached. Reaction conversion was less than 5% in all cases. Experimental error: ±10%.
[b] Carbon selectivity = $n_i C_i / \sum n_i C_i$.
[c] Hydrocarbons with 2 or more carbons.
[d] Oxygenates with 2 or more carbons, excluding ethanol and acetaldehyde.
[e] Molar ratio of C_n olefin/C_n paraffin.

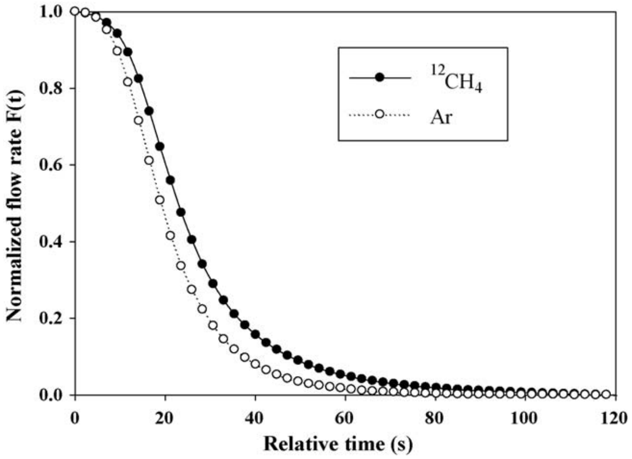

Fig. 2. Typical normalized transient responses of $^{12}CH_4$ and Ar for Rh/V/SiO_2 following switch to ^{13}CO during steady-state CO hydrogenation at 280 °C.

(MS) analysis. In our SSITKA study of Rh/V/SiO_2, the selectivities for methane formation for Rh/SiO_2 and for Rh/V/SiO_2 were 80–99% for the different reduction temperatures. An example of a normalized transient of $^{12}CH_4$ compared to the Ar tracer obtained by switching from ^{12}CO to ^{13}CO during steady-state reaction is given in Fig. 2. The area between the normalized transient curves of a particular species and the inert tracer (Ar) gives the average surface residence time (τ_i) for that species. A type of turnover frequency (TOF) is related to average surface residence time by $TOF_{ITK} = 1/\tau_i$. The concentration of active surface intermediates (N_i) can be calculated by $N_i = rate_i \times \tau_i$ [56], where i indicates a particular product. Thus, TOF_{ITK} gives the rate of reaction per site occupied by a reaction intermediate [57].

The results of the SSITKA study are summarized in Table 3. The SSITKA experiments show that the activity and the concentration of intermediates on the surface remained the same for Rh/SiO_2 even when reduced at different temperatures. The overall Rh catalytic activity for methanation was not modified as obviously with the addition of V as in the standard FTS study. While the Rh/SiO_2 catalyst had a similar activity under both FTS and methanation conditions, the V-promoted catalyst had a significantly lower activity at methanation conditions even though the reaction temperature was much higher. Thus, high partial pressure of H_2 and low partial pressure of CO greatly reduced the activity of Rh/V/SiO_2 for CO hydrogenation to the point where the activity of Rh/V/SiO_2 was less than that for Rh/SiO_2 (Table 3). However, although the methanation activity of Rh/V/SiO_2 did not change as much with reduction temperature as that for FTS, it still decreased significantly.

The significantly different catalytic performances of Rh/SiO_2 and Rh/V/SiO_2 activities under methanation and FTS conditions can be explained by the effects of the partial pressures of reactants (H_2 and CO), reaction temperature and the addition of V. Obviously, increasing the reaction temperature from 230 °C (FTS) to 280 °C (methanation) would cause all rate constants to increase exponentially. However, the rate of CO hydrogenation is also a strong function of the partial pressures of H_2 and CO, and the addition of different promoters can result in different functionalities in terms of the partial pressure exponents in the power law rate expression [59–61]. In our work, it was found that at constant total pressure (1.8 atm), when CO partial pressure was lower than 0.1 atm and the ratio of H_2/CO was larger than 10, the methane formation rate increased significantly with increasing CO partial pressure but held almost constant with increasing H_2 partial pressure for all the Rh-based catalysts (data not shown). Thus, the low CO and high H_2 partial pressures used for SSITKA in this study ($P_{CO} = 0.05$ atm, $P_{H_2} = 1.08$ atm) led to much decreased activities compared to regular CO hydrogenation at the same reaction temperature. Moreover, the negative effect of low CO partial pressure on the activity was more significant for Rh/SiO_2 promoted with V since V partially suppressed CO chemisorption [47]. These effects shrank the differences seen under FTS conditions between the activity of Rh/SiO_2 and that of Rh/V/SiO_2, resulting in comparable activities under methanation conditions. However, use of methanation conditions still permitted the determination of the effect of V promotion on the surface reaction kinetic parameters for CO hydrogenation on Rh/SiO_2.

As shown in Table 3, the addition of V significantly decreased the amounts of CO adsorbed reversibly (N_{CO}) and of intermediates forming CH_4 (N_{CH_4}) while the activity of the sites (TOF_{ITK}) increased. It can also be seen that there were significant differences in overall activity, TOF_{ITK} and number of active surface intermediates (N) with different reduction temperatures for Rh/V/SiO_2. Similar to the results found for FTS conditions, under methanation reaction conditions the overall activity of Rh/V/SiO_2 decreased when reduction temperature increased. The surface concentration of reversibly adsorbed CO (N_{CO}) (i.e., CO that adsorbed and desorbed without further reaction) also decreased with increasing reduction temperature. The higher reduction temperature also led to a shorter residence time for reaction, a higher TOF_{ITK}, and a lower amount of active intermediates on the surface for methane formation. Thus, while a higher reduction temperature brought about a higher TOF_{ITK} for the reaction sites on Rh/V/SiO_2, this was more than compensated for by the loss in active site (intermediates) concentration, resulting in a lower overall rate of reaction.

4. Discussion

There were obviously significant differences in catalytic activity and selectivities between Rh/SiO_2 and Rh/V/SiO_2, which indicate that the addition of V played an important role related to catalytic behavior. Moreover, the SSITKA study found that the addition of V led to a much increased average activity (TOF_{ITK}) of the surface active sites but decreased the amount of surface reaction interme-

Table 3
The effect of reduction temperature on surface reaction kinetic parameters at steady-state methanation conditions.

Catalyst	Reduction temperature (°C)	SS rate (μmol/gcat/s)[a]	CH_4 selectivity (%)	τ_{CO} (s)	N_{CO} (μmol/gcat)[b]	τ_{CH_4} (s)	TOF_{ITK} (s^{-1})[b]	N_{CH_4} (μmol/gcat)[c]
Rh/SiO_2	300	0.038	98.4	8.38	15.42	9.81	0.10	0.39
	600	0.040	99.8	8.75	16.10	9.52	0.11	0.38
Rh/V/SiO_2	300	0.048	90.2	4.98	9.04	5.77	0.17	0.25
	400	0.039	93.6	3.90	7.11	4.50	0.22	0.17
	500	0.029	84.8	2.42	4.42	2.69	0.37	0.07
	600	0.022	79.1	0.62	1.13	0.63	1.59	0.01

[a] Steady-state rate where rate is in μmol CO converted/gcat/s. Catalyst: 0.3 g, inert: α-alumina 3 g; reaction at 280 °C; P = 1.8 atm, flow rate = 60 mL/min (H_2:He:CO = 20:19:1). Reaction conversion was less than 5% in all cases. Experimental error: ±10%.
[b] TOF based on SSITKA, calculated as $TOF_{ITK} = 1/\tau_{CH_4}$.
[c] $N_i = rate_i \times \tau_i$.

diates (and by inference the number of active reaction sites). Due to the change in active site properties, a possibility of simple Rh particle growth with the addition of V to explain chemisorption results can be ruled out, which is also consistent with the TEM results [47]. A reasonable explanation for the promoting effect of V is that VO_x covers part of the Rh particles and the SMOI of Rh and VO_x results in increased activity of sites at the interfacial region of Rh and VO_x with much enhanced overall activity for CO hydrogenation. This SMOI appears to have two effects: one is to reduce the total number of active Rh sites due to the partial covering of the Rh surface, and the other is to increase the activity of available sites for the reaction.

Our results are consistent with our previous studies and the literature. In our previous IR study [48], it was found that different from other promoters, the addition of V suppresses CO adsorption, but significantly enhances the mobility and/or reactivity of these adsorbed CO species on the V singly promoted catalyst, judging from the depletion rate of linearly adsorbed CO in a He or H_2/He flow. Kip et al. [46,62] also found by TPR that Rh helped V reduction while V hampered Rh reduction in V-promoted Rh/SiO_2, which is consistent with our previous TPR results [49], indicating an intimate contact between Rh and V. Beutel et al. [26,40] found with FTIR spectroscopy an SMOI effect for V-promoted Rh/SiO_2 with high temperature reduction or high temperature calcination and suggested there was a decrease in activity for CO hydrogenation because of SMOI. By studying CO_2 reforming of methane over V-promoted Rh/SiO_2, Sigl et al. [63] suggested the formation of a partial VO_x overlayer on the Rh surface when the calcination temperature was higher than 500 °C and hypothesized new sites being created at the Rh–VO_x interface that are relatively active for CO_2 reforming. Ioannides and Verykios [19] have hypothesized for Rh/TiO_2 that new adsorption sites may be created at the metal–metal oxide interface and these new sites are probably very active due to SMOI of Rh and TiO_2. It is highly possible that, similar to Rh and TiO_2, SMOI between Rh and VO_x may also form some new sites at high reduction temperatures, and these sites are certainly (based on SSITKA) relatively more active for CO hydrogenation.

As the reduction temperature changed, significant differences were also observed in catalytic behavior for the V-promoted Rh/SiO_2 catalyst compared to the non-promoted catalyst. Even though the amount of H_2 chemisorption was already significantly lower for $Rh/V/SiO_2$ than for Rh/SiO_2, there was still a decrease in H_2 chemisorption ability for $Rh/V/SiO_2$ with increasing reduction temperature (even taking into account experimental error) while there was no such trend for Rh/SiO_2. As shown by SSITKA results, the site activity (TOF_{ITK}) of $Rh/V/SiO_2$ increased as reduction temperature increased, while there was no such trend for Rh/SiO_2. There are two possibilities to explain the site activity change with reduction temperature. One is sintering of Rh particles on catalyst surface, which can be excluded when the catalyst is reduced in the temperature range of 300–600 °C since the dispersion of Rh and the overall activity of the catalyst were essentially the same regardless of the reduction temperature for the catalyst. The other is that SMOI was more significant as the reduction temperature increased. The reduction temperature could affect SMOI in two ways: one is that a higher reduction temperature may result in a greater migration of VO_x onto the Rh surface, and the other one is that, with a higher reduction temperature, a greater reducibility of VO_x could result. As reported in the literature [4–6], VO_x can be partially reduced in the temperature range of 300–600 °C. Hence, different oxidation states of V obtained using different reduction temperatures may also affect the activity of the active Rh surface sites. Electronic transfer between VO_x and Rh could form $RhVO_4$ on a SiO_2 surface, which might enhance the activity for CO hydrogenation [26,31]. Thus, the presence of V increases the overall rate of reaction at the lower reduction temperature even though there appears to be less reaction sites (per g catalyst) compared to on Rh/SiO_2. However, even with the increase in average TOF_{ITK}, the greater loss of active reaction sites with high reduction temperatures cannot be compensated, resulting in a lower overall rate of reaction. On the other hand, it is also possible that the formation of a Rh–VO_x overlayer could be accompanied with the formation of a bulk alloy phase or the change in the morphology of the Rh particles at high reduction temperature. Rupprechter et al. [55] suggested that in the most active state the structure of the Rh particles should be highly disordered and with higher reduction temperature the particles are more likely to exhibit rounded profiles.

With respect to the effect of SMOI on the selectivity for $Rh/V/SiO_2$, there is a trend of decreasing methane selectivity but increasing methanol selectivity under FTS conditions with higher reduction temperature. It is possible that methane and methanol are formed by the same kind of intermediates on the surface. However, even though there is a shift in methane and methanol selectivities, both of their formation rates (product formation rate = total reaction rate × product selectivity) decreased with increasing reduction temperature. Clearly, the results in this study are not enough to support this conclusion. It is, on the other hand, also possible that the active sites for the formation of methane and methanol responded differently to SMOI of Rh and VO_x, leading to a shift in selectivities. Further investigation is needed to probe the effect of SMOI on selectivity.

For Rh/SiO_2, the activity for both FTS (at 230 °C) and methanation (at 280 °C) held constant when the reduction temperature varied from 300 to 600 °C. The only changes in the selectivities for hydrocarbons with reduction temperature may be due to the interaction between Rh and SiO_2 as reported in the recent literature [64,65]. Hayashi et al. [65] proposed that this interaction causes the formation of $Rh^{\delta+}$ and, thus, modifies the selectivities.

5. Conclusion

Even though the SMOI effects have received a great deal of attention in the past, this study has explored for the first time at the site level the effect of SMOI induced by high temperature reduction of $Rh/V/SiO_2$. SMOI effects caused by V promotion significantly modified CO hydrogenation on Rh/SiO_2. Using SSITKA, surface kinetic parameters were able to be determined, which permits a better understanding of the surface modification of the catalyst by SMOI.

It has been concluded based on the data for Rh/SiO_2 and TEM results for $Rh/V/SiO_2$ that sintering of Rh does not occur for reduction temperatures from 300 to 600 °C. H_2 chemisorption indicated that H_2 adsorption at room temperature is suppressed with V addition. The product distribution for FTS on Rh/SiO_2 was constant with rising reduction temperature except for hydrocarbon chain growth which was somewhat improved. However, for $Rh/V/SiO_2$, the overall catalyst activity decreased significantly with increasing reduction temperature because of detrimental SMOI effects. Also, there was a shift between methane and methanol selectivities with increasing reduction temperature. As indicated by SSITKA, the site activity of V-promoted Rh/SiO_2 was enhanced with higher reduction temperature. However, as shown also by SSITKA, SMOI effects decreased the concentration of active intermediates, which caused a decrease in overall activity by more than compensating for the increase in site activity. The reaction and SSITKA results are consistent with the formation of a partial VO_x overlayer on the Rh surface and of new sites with higher activity being created probably at the Rh–VO_x interface due to the SMOI effects.

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