Carbon monoxide hydrogenation over alkali-promoted Rh/Al₂O₃, Rh/V₂O₃/SiO₂ and Rh/ThO₂/SiO₂

Citation for published version (APA):

Kip, B. J., Hermans, E. G. F., & Prins, R. (1987). Carbon monoxide hydrogenation over alkali-promoted Rh/Al₂O₃, Rh/V₂O₃/SiO₂ and Rh/ThO₂/SiO₂. *Applied Catalysis*, 35(1), 141-152. [https://doi.org/10.1016/S0166-9834\(00\)82427-6](https://doi.org/10.1016/S0166-9834(00)82427-6)

DOI:

[10.1016/S0166-9834\(00\)82427-6](https://doi.org/10.1016/S0166-9834(00)82427-6)

Document status and date:

Published: 01/01/1987

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Carbon Monoxide Hydrogenation over Alkali-Promoted Rh/Al₂O₃, Rh/V₂O₃/SiO₂ and Rh/ThO₂/SiO₂

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(Received 31 March 1987; accepted 14 June 1987)

ABSTRACT

Addition of Li, Na, K and Cs to a 1.5 wt% Rh/Al₂O₃ catalyst resulted in a decrease of the hydrocarbon formation rate, while the methanol formation rate was almost unaffected. The overall result is an increased oxygenate selectivity at a decreased total activity. The oxo-selectivity increased in the order unpromoted < Li < Na < K < Cs. The results suggest that the main role of the alkali promoter is to decrease the carbon monoxide dissociation reaction.

Rh/SiO₂ catalysts promoted with ThO₂ or V₂O₃ had higher C₂-oxygenate selectivities and a higher activity than a Rh/SiO₂ catalyst. Addition of Li, Na, K and Cs did not increase the oxo-selectivity of the ThO₂- and V₂O₃-promoted Rh/SiO₂ catalysts. Independent of the kind of alkali added, it mainly decreased the activity and lowered the hydrogenation rate, suggesting that the added alkali blocked the special perimeter sites which are held responsible for the ThO₂ and V₂O₃ promotion effect or that the added alkali formed a mixed oxide with the promoter oxide. Alkali ions, therefore, did not improve the catalytic behaviour of the ThO₂- and V₂O₃-promoted Rh/SiO₂ catalysts.

INTRODUCTION

The hydrogenation of carbon monoxide over supported rhodium catalysts produces both hydrocarbons and oxygenated compounds such as alcohols and aldehydes [1-11]. From an economic point of view, C₂-oxygenates are the favoured products [12]. Modification of the catalytic behaviour of rhodium catalysts by the support [1-4] or by a promoter [5-11] has been a topic of considerable interest and debate. Drastic changes in selectivity and activity have been observed with different supports and promoters, and high ethanol selectivities can be reached with rhodium catalysts containing transition metal oxides. Promoters can influence the carbon monoxide hydrogenation at different steps, i.e. the adsorption of carbon monoxide, the formation of C₁-intermediates by carbon monoxide dissociation and subsequent hydrogenation, the C-C bond formation for chain-growth, and the carbon monoxide insertion into a growing chain, forming oxygenates [5-7].

In previous studies, we investigated the influence of V_2O_3 - [13,14] and ThO_2 - and MoO -promotion [15] on the carbon monoxide hydrogenation over Rh/SiO_2 at 4.0 MPa. The major influence of these promoters is to enhance the carbon monoxide dissociation, thereby strongly increasing the total activity of the catalysts. Addition of ethylene to a working catalyst showed that the carbon monoxide insertion reaction, which is thought to be responsible for C_2 -oxygenated products [5-7,16], is only slightly influenced by the promoter oxides. The selectivity to C_2 -oxygenates was relatively high for the ThO_2 - and V_2O_3 -promoted catalysts (40-50%). However, further improvement of the selectivity to oxygenated products is necessary for industrial application.

Addition of alkali compounds is widely used in carbon monoxide hydrogenation reactions to influence the activity and selectivity of the catalysts. For iron catalysts, it has been shown that alkali compounds shift the selectivity to longer chain hydrocarbons [17]. McLaughlin McClory and Gonzalez [18] reported that alkali addition to Ru/SiO_2 catalysts suppressed the activity, mainly due to a suppressed hydrogenation activity because of site blocking by the alkali atoms. Mori et al. [19] studied the effect of addition of alkali carbonate to a Ru/Al_2O_3 catalyst. They used a pulse micro reactor in conjunction with an emissionless diffuse-reflectance infrared spectrometer, and in this way they could study the dynamics of adsorbed carbon monoxide as well as produced methane, be it under non-steady-state conditions. The alkali carbonate decreased the rate constant for C-O bond dissociation, but hardly affected the hydrogenation of the surface carbon species produced. Kikuzono et al. [20] reported that palladium catalysts prepared from M_2PdCl_4 complexes (M =alkali metal) selectively produced methanol even below atmospheric pressure, be it at a low conversion. The catalytic activity for methanol formation depended sharply on the alkali metal cation in the order: $Li > Na \gg \text{unpromoted} > K$. The Cs- and Rb-promoted Pd catalysts did not produce methanol and had a low total activity.

Also for Rh catalysts, several authors reported that the catalytic behaviour is improved by the addition of alkali metals. Wilson et al. [21] reported that addition of alkali to a Mn-promoted Rh/SiO_2 catalyst resulted in an increased C_2 -oxygenate selectivity. Tamaru et al. [22,23] studied the syngas reaction over alkali metal-doped rhodium catalysts at pressures below 0.1 MPa. Addition of Na and K resulted in an increased selectivity and formation rate of C_2 -oxygenates for Rh/Al_2O_3 catalysts [22], Li- and Na-doped Rh/TiO_2 also exhibited an increased activity and selectivity to C_2 -oxygenates, while the addition of K and Cs resulted in a decreased formation rate [23]. Iwasawa et al. [24] reported that addition of alkali chlorides to Rh/SiO_2 resulted in an increased C_2 -oxygenate selectivity for Li, Na and K, whereas Rb and Cs caused a decreased C_2 -oxygenate selectivity compared with the unpromoted Rh/SiO_2 . Chuang et al. [25,26] studied promotion of Rh/TiO_2 by Li, K and Cs. The carbon monoxide conversion during syngas reaction at 573 K and 1.0 MPa

decreased in the order unpromoted $> \text{Li} > \text{K} > \text{Cs}$. Although the formation rate of all products decreased by alkali promotion, the decrease was largest for the hydrocarbons (by a factor of 55) and small for methanol (by a factor of 4). The decrease for the C_2 -oxygenates was intermediate (by a factor of 22). Van der Lee [27] studied the influence of alkali addition to a $\text{Rh}/\text{V}_2\text{O}_3$ catalysts. Alkali salts enhanced the activity of the $\text{Rh}/\text{V}_2\text{O}_3$ catalyst, but the C_2 -oxygenate selectivity decreased.

In this paper the addition of alkali metals to V_2O_3 - and ThO_2 -promoted Rh/SiO_2 catalysts is studied in order to investigate the possibility of further improvement of activity and selectivity to C_2 -oxygenates. For comparison, we examined the alkali addition to a $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst under the same experimental condition because, as can be derived from the literature, the effect of alkali addition strongly depends on the metal, support and experimental conditions. We did not study the addition of alkali to a Rh/SiO_2 catalyst for comparison, because this catalyst has a low activity and should therefore be studied at high reaction temperatures (above 573 K), resulting in low oxygenate selectivities [14,15]. To make sure that metal particle size did not influence the results, the alkali metal salts were added to the catalysts after calcination of the (promoted) rhodium-on-support catalysts. Since a preliminary study indicated that chlorine had a (positive) influence on catalyst activity, we used alkali metal nitrates throughout this investigation.

EXPERIMENTAL

Catalyst preparation

A 1.5 wt% $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst was made by impregnating $\gamma\text{-Al}_2\text{O}_3$ (Ketjen, type 000-1.5E, surface area $200 \text{ m}^2 \text{ g}^{-1}$, pore volume 0.6 ml g^{-1}) with an aqueous solution of $\text{Rh}(\text{NO}_3)_3$ ($\text{pH}=2.5$, Drijfhout, Amsterdam, The Netherlands). V_2O_3 - and ThO_2 -promoted 1.5 wt% Rh/SiO_2 catalysts were made by sequential impregnation of the SiO_2 support (Grace, type 113, surface area $360 \text{ m}^2 \text{ g}^{-1}$, pore volume 1.1 ml g^{-1}) by a solution of NH_4VO_3 (Merck, p.a.) and $\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ (Merck, p.a.), respectively, and by a solution of $\text{Rh}(\text{NO}_3)_3$. After each impregnation step the catalysts were dried in air at 395 K for 16 h (heating rate 2 K min^{-1}) and subsequently calcined in air at 723 K for 3 h in order to remove nitrogeneous residues from the precursor.

Li, Na, K and Cs were added to these catalysts by impregnation using solutions of LiNO_3 , NaNO_3 , KNO_3 (Merck) and CsNO_3 (Janssen). After drying at 395 K these catalysts were also calcined in air at 723 K for 3 h. An alkali/rhodium ratio of 1.0 was used for the $\text{Rh}/\text{Al}_2\text{O}_3$ catalyst and an alkali/rhodium ratio of 0.5 was used for the ThO_2 - and V_2O_3 -promoted 1.5 wt% Rh/SiO_2 catalysts.

Carbon monoxide chemisorption measurements

Volumetric carbon monoxide chemisorption measurements were performed as described elsewhere [13–15,28]. Catalysts were reduced at 723 K (heating rate 8 K min^{-1}) for 1 h and evacuated for 0.5 h at 723 K before the chemisorption experiment. Carbon monoxide chemisorption was preferred over hydrogen chemisorption, because hydrogen chemisorption also takes place on V_2O_3 [13], preventing its use for the determination of the rhodium dispersion.

Carbon monoxide hydrogenation

The high pressure reactor and analysis system were described in detail elsewhere [13]. The catalysts were reduced in situ in pure hydrogen at 0.1 MPa, using a temperature ramp of 5 K min^{-1} between 298 and 723 K and holding the final temperature for 1 h. All catalysts were measured under the same reaction conditions ($\text{GHSV}=4000\text{ l l}^{-1}\text{ h}^{-1}$, $\text{H}_2/\text{CO}=3.0$, $P=4.0\text{ MPa}$ and $T_{\text{react}}=528\text{ K}$). The behaviour of the various catalysts was compared after 15 h time on stream.

RESULTS AND DISCUSSION

Rh/Al₂O₃

The effect of alkali addition to the 1.5 wt% Rh/Al₂O₃ catalyst, using an alkali/Rh ratio of 1.0 is presented in Table 1. The high CO/Rh value for the unpromoted Rh/Al₂O₃ catalyst points to almost completely dispersed rhodium [13,14]. Clearly, the CO/Rh chemisorption values of the alkali-promoted catalysts are lower than that of the unpromoted Rh/Al₂O₃ catalyst. This may be due to site-blocking of the rhodium surface by the alkali promoter. The alkali-promoted and unpromoted 1.5 wt% Rh/Al₂O₃ catalysts were tested in the carbon monoxide hydrogenation reaction at 723 K and 4.0 MPa. The total activity and hydrocarbon selectivity decreased in the order unpromoted > Li-promoted > Na-promoted > K-promoted > Cs-promoted, while the methanol selectivity increased in that order. The C₂-oxygenate selectivity was not much influenced by the addition of alkali metal, with the exception of lithium, which gave a slightly higher C₂-oxygenate selectivity.

From the formation rates calculated for the various products (Table 1), one can conclude that the formation rates of methanol and hydrocarbons are higher, respectively lower, for the alkali-promoted catalysts than for the unpromoted catalyst. The suppression of the formation rate of C₂-oxygenates by alkali was less than that of the hydrocarbons, as is reported before by Chuang et al. [25] for alkali-promoted Rh/TiO₂.

In order to distinguish between different mechanisms of carbon monoxide

TABLE 1

Hydrogenation of carbon monoxide over 1.5 wt% Rh/Al₂O₃ catalysts promoted with alkali, using an alkali/Rh ratio of 1.0

In situ reduction at 723 K. Reaction conditions: 528 K, 4.0 MPa, GHSV=4000 l l⁻¹ h⁻¹, H₂/CO=3.0.

	Rh/-	Rh/Li	Rh/Na	Rh/K	Rh/Cs
CO/Rh ^a	1.85	1.60	1.52	1.47	1.41
Act. ^b	4.1	3.3	2.7	2.1	1.9
Sel. (%) ^c					
C ₁ ^d	59.5	54.8	51.0	49.9	42.8
C ₂ ^e	8.3	5.3	6.2	4.2	4.6
C ₁ OH ^f	6.3	12.5	17.0	20.9	26.8
C ₂ oxy ^g	22.4	25.6	23.6	22.8	21.1
Oxo sel. ^h	32.2	39.9	42.8	45.9	48.1
C ₄ =/C ₄ ⁱ	0.53	0.28	0.24	0.17	1.09
Formation rates ^j					
C ₁ OH	0.26	0.41	0.46	0.44	0.51
C ₂ oxy	0.93	0.83	0.64	0.48	0.40
C _x H _y	2.8	2.0	1.6	1.2	0.9
CO disso. ^k	3.4	2.4	2.0	1.4	1.2
CO non disso. ^l	0.76	0.87	0.69	0.72	0.71
Ethers ^m	1.4	1.3	0.5	0.5	0.4
Dehydration ⁿ	2.4	2.1	1.2	0.9	1.1

(a) Carbon monoxide chemisorption results, (b) activity in mmol converted carbon monoxide (mol Rh)⁻¹ s⁻¹ at 528 K, estimated uncertainty in the activity $\pm 5\%$, (c) selectivities expressed as %C efficiency, (d) methane, (e) hydrocarbons containing two or more C atoms, (f) total amount of methanol, ethers and esters included, (g) total amount of C₂-oxygenates, ethanol, acetaldehyde and acetic acid, ethers and esters included, (h) total oxo-selectivity, (i) amount of unsaturated hydrocarbons in C₄ fractions, (j) in mmol carbon monoxide converted (mol Rh)⁻¹ s⁻¹, estimated uncertainty $\pm 10\%$, (k) formation rate of products or part of products formed via a dissociative mechanism [mmol converted carbon monoxide (mol Rh)⁻¹ s⁻¹], uncertainty $\pm 10\%$, (l) formation rate of products or part of products formed via a non-dissociative mechanism [mmol converted carbon monoxide (mol Rh)⁻¹ s⁻¹], uncertainty $\pm 10\%$, (m) dehydration of alcohols into corresponding ethers in mol water (g Al₂O₃)⁻¹ s⁻¹, (n) dehydration of alcohols into ethers or esters in mol water (g Al₂O₃)⁻¹ s⁻¹.

conversion, we calculated the conversion of carbon monoxide via a non-dissociative mechanism and via a dissociative mechanism. For the non-dissociative mechanism, we added together the formation rate of methanol, half of the formation rate of C₂-oxygenates, one third of the C₃-oxygenates etc., because methanol is thought to be formed via the hydrogenation of non-dissociated carbon monoxide [29] and higher oxygenates are thought to be formed by carbon monoxide insertion into a growing carbonaceous intermediate [5,7,16,30]. The conversion of carbon monoxide via a dissociative mechanism

Fig. 1. Influence of alkali promoters on the carbon monoxide conversion rate via the dissociative mechanism (a) and via the non-dissociative mechanism (b) for Rh/Al₂O₃ (○), Rh/V₂O₅/SiO₂ (×) and Rh/ThO₂/SiO₂ (●).

is clearly suppressed by the presence of alkali and different suppression levels are observed for the several alkali metals. The following order is observed: unpromoted > Li > Na > K > Cs (see Fig. 1). The conversion of carbon monoxide via a non-dissociative mechanism is unaffected by the presence of alkali.

These results suggest that the main role of the alkali promoter in the Rh/Al₂O₃ catalysts is to suppress the carbon monoxide dissociation reaction. From the results of Chuang et al. [25], this can also be concluded for alkali promotion of Rh/TiO₂. Mori et al. [19] came to the same conclusion for alkali carbonate addition to Ru/Al₂O₃ catalysts. Alkali carbonate added to the Ru catalyst decreased the rate constant for C–O bond dissociation, but hardly affected the hydrogenation of the surface carbon species produced. Also in our study the hydrogenation activity was not suppressed by the alkali metal. The amount of unsaturated hydrocarbons even slightly decreased by the addition of alkali. Furthermore, the results of Mori et al. show that the rate constant for the C–O bond dissociation was much smaller than that for the hydrogenation of the resulting formed CH_x species, suggesting that the C–O bond dissociation is rate limiting for the methanation reaction. Mori et al. postulated a hydroxy carbene [(CHOH)_{ad}] species as an intermediate in the carbon monoxide dissociation and ascribed the suppressing effect of the alkali metal on the C–O bond dissociation to an increased electron density on the Ru metal, resulting in a stabilization of (CO)_{ad} and therefore a decrease in the equilibrium concentration of (CHOH)_{ad}. We think that the suppression of the carbon monoxide dissociation reaction also can be a result of the blocking of the active centers for carbon monoxide dissociation, as the CO/Rh value decreased by the addition of alkali.

Comparing the results of alkali promotion of Rh/Al₂O₃ with studies of alkali

promotion of Rh/TiO₂ [25,26] and Rh/SiO₂ [24], it becomes clear that for the same alkali/Rh ratios, the effect of alkali is much smaller for the Rh/Al₂O₃ than for the Rh/SiO₂ and Rh/TiO₂ catalysts. This suggests that the major part of the added alkali does not directly interact with the rhodium metal particle, but that a significant part is scavenged by the alumina support. Using IR studies of adsorbed carbon monoxide and hydrogen desorption studies, Blackmond et al. [31] came to the same conclusion for Cs promotion of Rh/Al₂O₃.

In Table 1, two additional data sets are given for reactions which are thought to proceed over the alumina support. The amount of ether, formed by dehydration of the corresponding alcohols over acidic sites on the alumina support [32], decreased by addition of alkali. The formation of esters from alcohols and acetic acid is also thought to take place at sites on the alumina support. The total dehydration of alcohols to ethers and esters was clearly suppressed by alkali addition (cf. Table 1), proving that the alkali not only changed the properties of the metal, but also of the support, demonstrating that part of the alkali is positioned on the support.

Rh/V₂O₃/SiO₂

In Table 2, the effect of alkali addition to 1.5 wt% Rh/V₂O₃/SiO₂ (V/Rh = 1) is presented. An alkali/Rh ratio of 0.5 was used and the catalysts were tested at 4.0 MPa and around 532 K. In order to compare activities at the same temperature, we calculated the activity at 528 K, using $E_{\text{act}} = 100 \text{ kJ mol}^{-1}$. This activation energy was measured for the Rh/V₂O₃/SiO₂ (V/Rh = 1) catalyst [14]. As is shown in Table 2, the Rh/V₂O₃/SiO₂ catalyst exhibited a relatively high total oxo-selectivity (56%) and C₂-oxygenate selectivity (41%).

Addition of alkali to this catalyst resulted in a decreased CO/Rh chemisorption ratio, pointing to the covering of adsorption sites. The catalytic activity of the Rh/V₂O₃/SiO₂ catalysts decreased by almost a factor of 2 by addition of alkali, but not much difference was observed between the different alkali metals. The C₂-oxygenate and total oxygenate selectivities were slightly influenced by alkali addition. Hydrogenation activity was suppressed by the presence of alkali, as judged from the fact that the amount of unsaturated hydrocarbons was higher for the alkali-promoted Rh/V₂O₃/SiO₂ catalysts. The fraction of unsaturated products in the C₂-oxygenates (acetic acid and acetaldehyde) increased due to alkali promotion, also suggesting a decreased hydrogenation reaction for these catalysts.

The conversion rate of carbon monoxide via the non-dissociative and the dissociative route were both suppressed by the presence of alkali, and the extent of the suppression was independent on the kind of alkali (Fig. 1). These results are in contrast with the effect of alkali on Rh/Al₂O₃.

TABLE 2

Hydrogenation of carbon monoxide over alkali-promoted 1.5 wt% Rh/V₂O₃/SiO₂, V/Rh = 1.0 catalysts, using an alkali/Rh ratio of 0.5

In situ reduction at 723 K. Reaction temperature around 533 K, P = 4.0 MPa, GHSV = 4000 l l⁻¹ h⁻¹, H₂/CO = 3.0. See Table 1 for the notation.

Catalyst system	Rh/V	Rh/V + Li	Rh/V + Na	Rh/V + K	Rh/V + Cs
CO/Rh ^a	0.29	0.20	0.18	0.17	0.18
React. temp. (K)	530	533	533	534	533
Act.	8.6	5.7	5.1	5.9	5.1
Corr. act. ^b	8.0	4.6	4.1	4.6	4.1
Sel. (%C)					
C ₁	28.6	26.3	25.3	26.9	24.3
C ₂	15.6	12.4	14.4	16.4	16.7
C ₁ OH	8.9	9.7	10.1	8.2	7.6
C ₂ oxy	41.3	45.0	42.6	40.6	44.0
Oxo sel.	55.9	61.3	60.3	56.7	59.0
C ₂ = /C ₂	0.2	0.3	0.4	0.5	1.0
C ₄ = /C ₄	1.2	1.5	2.0	2.0	2.1
Formation rates ^b					
C ₁ OH	0.71	0.45	0.41	0.38	0.31
C ₂ oxy	3.3	2.1	1.9	1.9	1.8
C _x H _y	3.5	1.8	1.6	2.0	1.7
CO disso.	5.5	3.0	2.7	3.2	2.9
CO non disso.	2.5	1.5	1.4	1.4	1.2

(a) Reduction at 523 K and evacuation at 723 K. The reason for this special pretreatment is discussed in ref. 13. (b) calculated activity and formation rates at 528 K [in mmol converted carbon monoxide (mol Rh)⁻¹ s⁻¹] using $E_{\text{act}} = 100 \text{ kJ mol}^{-1}$, estimated uncertainty 10%.

Rh/ThO₂/SiO₂

The results of alkali addition to ThO₂-promoted Rh/SiO₂ catalysts are presented in Table 3. The CO/Rh chemisorption ratio decreased by the addition of alkali. The activity decreased due to alkali promotion in the following order: unpromoted $\gg$ Li > Na > K, Cs. The hydrocarbon selectivity was almost unaffected by alkali addition, but the methanol selectivity increased and the C₂-oxygenate selectivity decreased in the order unpromoted, Li, Na, Cs, K. The hydrogenation rate decreased by addition of the alkali promoter, as can be concluded from the increase of the C₄ = /C₄ ratio. The conversion rate of carbon monoxide via the dissociative and via the non-dissociative route were both suppressed by the presence of alkali.

Our results indicate that the role of the alkali promoter in the ThO₂- and V₂O₃-promoted catalysts is different from that in the Rh/Al₂O₃ catalysts. For

TABLE 3

Hydrogenation of carbon monoxide over alkali-promoted 1.5 wt% Rh/ThO₂/SiO₂, Th/Rh = 1.0 catalysts, using an alkali/Rh ratio of 0.5

In situ reduction at 723 K. Reaction temperature 528 K, P = 4.0 MPa, GHSV = 4000 l l⁻¹ h⁻¹, H₂/CO = 3.0. See Table 1 for the notation.

Catalyst system	Rh/Th	Rh/Th + Li	Rh/Th + Na	Rh/Th + K	Rh/Th + Cs
CO/Rh	0.63	0.42	0.45	0.39	0.38
Act.	5.7	2.6	2.3	1.8	1.8
Sel. (%C)					
C ₁	32.3	28.9	30.6	30.9	32.4
C ₂ -	5.8	3.4	4.9	4.9	5.2
C ₁ OH	7.7	13.0	17.9	19.6	18.5
C ₂ oxy	51.8	52.1	43.6	41.6	40.4
Oxo sel.	61.9	67.7	64.7	64.2	62.5
C ₂ =/C ₂	0.2	0.2	0.2	0.3	0.4
C ₄ =/C ₄	0.7	1.0	0.9	0.9	1.0
Formation rates					
C ₁ OH	0.44	0.34	0.41	0.35	0.33
C ₂ oxy	3.0	1.4	1.0	0.75	0.73
C _x H _y	2.2	0.84	0.81	0.64	0.68
CO disso.	3.6	1.6	1.4	1.1	1.1
CO non disso.	2.1	1.0	0.9	0.8	0.7

Rh/Al₂O₃ the rate of carbon monoxide bond dissociation is decreased and the hydrogenation rate is unaffected. This of course only influenced the carbon monoxide conversion via a dissociative mechanism. For the ThO₂- and V₂O₃-promoted catalysts we also observed a suppression of the hydrogenation reaction by the addition of alkali. This might explain why for these catalysts the carbon monoxide conversion via a non-dissociative mechanism is also suppressed.

Several explanations might be given for the effect of alkali additives on the carbon monoxide hydrogenation over ThO₂- and V₂O₃-promoted Rh/SiO₂ catalysts.

(i) An electronic effect has been suggested for the alkali promotion of group VIII metal catalysts by many authors [33–40]. We do not think that this effect can completely explain the results of alkali addition to the V₂O₃- and ThO₂-promoted Rh/SiO₂ catalysts. As can be seen in Tables 2 and 3 and in Fig. 1, the effect of alkali addition was almost independent on the kind of alkali metal used. The electronic effect is expected to be different for Li, Na, K and Cs and therefore, an electronic influence of the alkali metal on the rhodium metal can not be the major reason for the lower activity. The electronic effect might

explain the influence of alkali promotion of the Rh/Al₂O₃ catalysts because for these catalysts differences are observed between the several alkali promoters.

(ii) It is known that alkali metals can react with both V₂O₃ and ThO₂ [41] and form mixed oxides. The mixed oxides of Na₂O and ThO₂ and of K₂O and ThO₂ can be made at temperatures of 823–1023 K. For Li₂O and ThO₂ no mixed oxides have been reported. Alkali oxides can form bronzes with vanadium oxide. For Li and Na, mixed oxides with V(III), V(IV) and V(V) oxides have been reported and for K, bronzes are known with V(IV) and V(V). The formation of mixed oxides could explain the decrease in activity, because by removing the promoter oxides one may decrease the promoter effect of V₂O₃ and ThO₂. It is also possible that the alkali promoter only adsorbs on ThO₂ or V₂O₃, not forming a new chemical compound, but still influencing the promoter role of ThO₂ or V₂O₃.

(iii) The CO/Rh ratio decreased by alkali addition. This suggests that (at least part of) the added alkali promoter is positioned on top of the rhodium metal. If the added alkali metal is situated at the perimeter of the ThO₂ or V₂O₃ patches covering the rhodium metal, it blocks the special perimeter sites which have been hold responsible for the promoter effect [14,15,42]. In this way the effect of ThO₂ and V₂O₃ is counteracted, resulting in a decreased carbon monoxide conversion via the dissociative and non-dissociative route and a decreased hydrogenation activity. This also explains that the results for all alkali promoters are the same, the alkali only physically blocks the active centers.

From our measurements, it is not possible to distinguish between the second and third explanation, the formation of mixed oxides and the physically blocking of active centers, respectively. A combination of these explanations cannot be ruled out either.

CONCLUSIONS

Addition of Li, Na, K and Cs to Rh/Al₂O₃ decreased the activity, but increased the total oxo-selectivity due to an increased methanol selectivity. The results suggest that alkali addition decreased the C–O bond dissociation, without affecting the hydrogenation activity. Most of the alkali is positioned on the support, only a small part of the added alkali is positioned on top of the rhodium metal particles.

Addition of Li, Na, K and Cs to Rh/V₂O₃/SiO₂ and Rh/ThO₂/SiO₂ also decreased the activity, but the oxo-selectivity was hardly affected. The results suggest that in this case the alkali addition reversed the promoter function of V₂O₃ and ThO₂ by the physical blocking of the active sites at the perimeter of the promoter oxide patches covering the rhodium metal particle, or by the formation of a mixed oxide of alkali and promoter oxide. The alkali addition decreased the carbon monoxide dissociation as well as the hydrogenation. Thus,

the alkali addition to the Rh/V₂O₃/SiO₂ and Rh/ThO₂/SiO₂ did not result in a higher C₂-oxygenate selectivity.

ACKNOWLEDGEMENTS

This study was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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