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

Citation for published version (APA):

DOI:
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:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain.
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Carbon Monoxide Hydrogenation over Alkali-Promoted Rh/Al₂O₃, Rh/V₂O₅/SiO₂ and Rh/ThO₂/SiO₂

B.J. KIP*, E.G.F. HERMANS and R. PRINS

Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

(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 V₂O₅ had higher C₅-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 V₂O₅-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 V₂O₅ 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 V₂O₅-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, C₅-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 \( \text{V}_2\text{O}_5^- \) \[13,14\] and \( \text{ThO}_2\) 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 \( \text{V}_2\text{O}_3 \)-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 McCloory 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\(_2\)O\(_3\) 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 \( \text{M}_2\text{PdCl}_4 \) complexes (\( \text{M} = \) 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: \( \text{Li} > \text{Na} \gg \) 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\(_2\)O\(_3\) 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 > Li > K > 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 C₂-oxygenates was intermediate (by a factor of 22). Van der Lee [27] studied the influence of alkali addition to a Rh/V₂O₅ catalysts. Alkali salts enhanced the activity of the Rh/V₂O₅ catalyst, but the C₂-oxygenate selectivity decreased.

In this paper the addition of alkali metals to V₂O₅- and ThO₂-promoted Rh/SiO₂ catalysts is studied in order to investigate the possibility of further improvement of activity and selectivity to C₂-oxygenates. For comparison, we examined the alkali addition to a Rh/Al₂O₃ 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/SiO₂ 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% Rh/Al₂O₃ catalyst was made by impregnating γ-Al₂O₃ (Ketjen, type 000-1.5E, surface area 200 m² g⁻¹, pore volume 0.6 ml g⁻¹) with an aqueous solution of Rh(NO₃)₃ (pH = 2.5, Drijfhout, Amsterdam, The Netherlands). V₂O₅- and ThO₂-promoted 1.5 wt% Rh/SiO₂ catalysts were made by sequential impregnation of the SiO₂ support (Grace, type 113, surface area 360 m² g⁻¹, pore volume 1.1 ml g⁻¹) by a solution of NH₄VO₃ (Merck, p.a.) and Th(NO₃)₄·xH₂O (Merck, p.a.), respectively, and by a solution of Rh(NO₃)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 LiNO₃, NaNO₃, KNO₃ (Merck) and CsNO₃ (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 Rh/Al₂O₃ catalyst and an alkali/rhodium ratio of 0.5 was used for the ThO₂- and V₂O₅-promoted 1.5 wt% Rh/SiO₂ 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 V₂O₅ [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 (GHSV = 4000 l l⁻¹ h⁻¹, H₂/CO = 3.0, P = 4.0 MPa and T_react = 528 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.

<table>
<thead>
<tr>
<th></th>
<th>Rh/-</th>
<th>Rh/Li</th>
<th>Rh/Na</th>
<th>Rh/K</th>
<th>Rh/Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO/Rh</td>
<td>1.85</td>
<td>1.60</td>
<td>1.52</td>
<td>1.47</td>
<td>1.41</td>
</tr>
<tr>
<td>Act.</td>
<td>4.1</td>
<td>3.3</td>
<td>2.7</td>
<td>2.1</td>
<td>1.9</td>
</tr>
<tr>
<td>Sel. (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>59.5</td>
<td>54.8</td>
<td>51.0</td>
<td>49.9</td>
<td>42.8</td>
</tr>
<tr>
<td>C₂</td>
<td>8.3</td>
<td>5.3</td>
<td>6.2</td>
<td>4.2</td>
<td>4.6</td>
</tr>
<tr>
<td>C₃OH</td>
<td>6.3</td>
<td>12.5</td>
<td>17.0</td>
<td>20.9</td>
<td>26.8</td>
</tr>
<tr>
<td>C₅oxy</td>
<td>22.4</td>
<td>25.6</td>
<td>23.6</td>
<td>22.8</td>
<td>21.1</td>
</tr>
<tr>
<td>Oxo sel.</td>
<td>32.2</td>
<td>39.9</td>
<td>42.8</td>
<td>45.9</td>
<td>48.1</td>
</tr>
<tr>
<td>C₃ = /C₄</td>
<td>0.53</td>
<td>0.28</td>
<td>0.24</td>
<td>0.17</td>
<td>1.09</td>
</tr>
<tr>
<td>Formation rates</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂OH</td>
<td>0.26</td>
<td>0.41</td>
<td>0.46</td>
<td>0.44</td>
<td>0.51</td>
</tr>
<tr>
<td>C₅oxy</td>
<td>0.93</td>
<td>0.83</td>
<td>0.64</td>
<td>0.48</td>
<td>0.40</td>
</tr>
<tr>
<td>C₆H₄</td>
<td>2.8</td>
<td>2.0</td>
<td>1.6</td>
<td>1.2</td>
<td>0.9</td>
</tr>
<tr>
<td>CO disso.</td>
<td>3.4</td>
<td>2.4</td>
<td>2.0</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>CO non disso.</td>
<td>0.76</td>
<td>0.87</td>
<td>0.69</td>
<td>0.72</td>
<td>0.71</td>
</tr>
<tr>
<td>Ethers</td>
<td>1.4</td>
<td>1.3</td>
<td>0.5</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Dehydration</td>
<td>2.4</td>
<td>2.1</td>
<td>1.2</td>
<td>0.9</td>
<td>1.1</td>
</tr>
</tbody>
</table>

(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 ±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 ±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 ±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 ±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
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/Al$_2$O$_3$ 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/TiO$_2$. Mori et al. [19] came to the same conclusion for alkali carbonate addition to Ru/Al$_2$O$_3$ 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/Al$_2$O$_3$ with studies of alkali
promotion of Rh/TiO\textsubscript{2} [25,26] and Rh/SiO\textsubscript{2} [24], it becomes clear that for the same alkali/Rh ratios, the effect of alkali is much smaller for the Rh/Al\textsubscript{2}O\textsubscript{3} than for the Rh/SiO\textsubscript{2} and Rh/TiO\textsubscript{2} 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/Al\textsubscript{2}O\textsubscript{3}.

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.

\textit{Rh/V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2}}

In Table 2, the effect of alkali addition to 1.5 wt\% Rh/V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} (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 $E_{\text{act}} = 100$ kJ mol$^{-1}$. This activation energy was measured for the Rh/V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} (V/Rh = 1) catalyst [14]. As is shown in Table 2, the Rh/V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} catalyst exhibited a relatively high total oxo-selectivity (56\%) and C\textsubscript{2}-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/V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} catalysts decreased by almost a factor of 2 by addition of alkali, but not much difference was observed between the different alkali metals. The C\textsubscript{2}-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/V\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} catalysts. The fraction of unsaturated products in the C\textsubscript{2}-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/Al\textsubscript{2}O\textsubscript{3}. 
### TABLE 2

Hydrogenation of carbon monoxide over alkali-promoted 1.5 wt% Rh/V₂O₅/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 11⁻¹ h⁻¹, H₂/CO = 3.0. See Table 1 for the notation.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₁</td>
<td>C₂/C₁, C₂Oxy/C₂, CO/X, C₄_H₄, CO disso, CO non disso.</td>
</tr>
<tr>
<td>Rh/V</td>
<td>0.29</td>
<td>530</td>
<td>8.6</td>
<td>8.0</td>
<td>28.6</td>
<td>0.71</td>
</tr>
<tr>
<td>Rh/V + Li</td>
<td>0.20</td>
<td>533</td>
<td>5.7</td>
<td>4.6</td>
<td>26.3</td>
<td>0.45</td>
</tr>
<tr>
<td>Rh/V + Na</td>
<td>0.18</td>
<td>533</td>
<td>5.1</td>
<td>4.1</td>
<td>25.3</td>
<td>0.41</td>
</tr>
<tr>
<td>Rh/V + K</td>
<td>0.17</td>
<td>534</td>
<td>5.9</td>
<td>4.6</td>
<td>26.9</td>
<td>0.38</td>
</tr>
<tr>
<td>Rh/V + Cs</td>
<td>0.18</td>
<td>533</td>
<td>5.1</td>
<td>4.1</td>
<td>24.3</td>
<td>0.31</td>
</tr>
</tbody>
</table>

- Sel. (%C)
  - C₁: 28.6, 26.3, 25.3, 26.9, 24.3
  - C₂: 15.6, 12.4, 14.4, 16.4, 16.7
  - C₂/OH: 8.9, 9.7, 10.1, 8.2, 7.6
  - C₂/Oxy: 41.3, 45.0, 42.6, 40.6, 44.0
  - Oxo sel.: 55.9, 61.3, 60.3, 56.7, 59.0
  - C₂= /C₂: 0.2, 0.3, 0.4, 0.5, 1.0
  - C₄= /C₄: 1.2, 1.5, 2.0, 2.0, 2.1

- Formation rates
  - C₁OH: 3.3, 2.1, 1.9, 1.9, 1.8
  - C₂Oxy: 3.5, 1.8, 1.6, 2.0, 1.7
  - C₄H₄: 5.5, 3.0, 2.7, 3.2, 2.9
  - CO disso.: 2.5, 1.5, 1.4, 1.4, 1.2
  - 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 $E_{act} = 100$ 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/ThO\textsubscript{2}/SiO\textsubscript{2}, 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 1 l\textsuperscript{-1} h\textsuperscript{-1}, H\textsubscript{2}/CO = 3.0. See Table 1 for the notation.

<table>
<thead>
<tr>
<th>Catalyst system</th>
<th>Rh/Th</th>
<th>Rh/Th + Li</th>
<th>Rh/Th + Na</th>
<th>Rh/Th + K</th>
<th>Rh/Th + Cs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO/Rh</td>
<td>0.63</td>
<td>0.42</td>
<td>0.45</td>
<td>0.39</td>
<td>0.38</td>
</tr>
<tr>
<td>Act.</td>
<td>5.7</td>
<td>2.6</td>
<td>2.3</td>
<td>1.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Sel. (%C)

<table>
<thead>
<tr>
<th></th>
<th>C\textsubscript{1}</th>
<th>C\textsubscript{2}</th>
<th>C\textsubscript{2}OH</th>
<th>C\textsubscript{2}oxy</th>
<th>Oxo sel.</th>
<th>C\textsubscript{1}=/C\textsubscript{2}</th>
<th>C\textsubscript{1}=/C\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>32.3</td>
<td>5.8</td>
<td>7.7</td>
<td>51.8</td>
<td>61.9</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>28.9</td>
<td>3.4</td>
<td>13.0</td>
<td>52.1</td>
<td>67.7</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>30.6</td>
<td>4.9</td>
<td>17.9</td>
<td>43.6</td>
<td>64.7</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>30.9</td>
<td>4.9</td>
<td>19.6</td>
<td>41.6</td>
<td>64.2</td>
<td>0.3</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>32.4</td>
<td>5.2</td>
<td>18.5</td>
<td>40.4</td>
<td>62.5</td>
<td>0.4</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Formation rates

<table>
<thead>
<tr>
<th></th>
<th>C\textsubscript{1}OH</th>
<th>C\textsubscript{2}oxy</th>
<th>C\textsubscript{2}H\textsubscript{2}</th>
<th>CO disso.</th>
<th>CO non disso.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.44</td>
<td>3.0</td>
<td>2.2</td>
<td>3.6</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>1.4</td>
<td>0.84</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>0.41</td>
<td>1.0</td>
<td>0.81</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>0.75</td>
<td>0.64</td>
<td>1.1</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>0.73</td>
<td>0.68</td>
<td>1.1</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Rh/Al\textsubscript{2}O\textsubscript{3} 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 ThO\textsubscript{2}- and V\textsubscript{2}O\textsubscript{3}-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 ThO\textsubscript{2}- and V\textsubscript{2}O\textsubscript{3}-promoted Rh/SiO\textsubscript{2} 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 V\textsubscript{2}O\textsubscript{3}- and ThO\textsubscript{2}-promoted Rh/SiO\textsubscript{2} 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 cannot 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/V$_2$O$_3$/SiO$_2$ and Rh/ThO$_2$/SiO$_2$ did not result in a higher C$_2$-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).

REFERENCES