The catalytic behaviour of rhodium supported on Al2O3 and TiO2 in synthesis gas reactions

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THE CATALYTIC BEHAVIOUR OF RHODIUM SUPPORTED ON $\text{Al}_2\text{O}_3$ AND $\text{TiO}_2$

IN SYNTHESIS GAS REACTIONS

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ABSTRACT

The catalytic activity of Rh/TiO$_2$ and Rh/Al$_2$O$_3$ catalysts for the hydrogenation of CO at atmospheric pressure and 523 K was investigated. Normal, non-SMSI state Rh/TiO$_2$ as well as Rh/TiO$_2$ catalysts in the SMSI state with varying dispersion were studied. In all cases only hydrocarbons and no oxygenated products were formed. When measured at equal dispersions the activities of Rh/Al$_2$O$_3$ and non-SMSI Rh/TiO$_2$ catalysts hardly differed. The specific activity of Rh/TiO$_2$ catalysts increased an order of magnitude when changing the dispersion from 1.10 to 0.12. This increase in specific activity was accompanied by an increase in the olefin-to-paraffin ratio, but neither the selectivity to methane nor the probability for chain growth was affected much. Reduction of the Rh/TiO$_2$ catalysts at 773 K decreased their initial activities substantially compared to reduction at 523 K, whereas the steady-state activities were hardly affected. Apparently the SMSI state is removed to a great extent during CO hydrogenation. The lowering effect of SMSI on activity was a function of dispersion. The effect was much more pronounced for small metal particles, indicating that SMSI might be due to covering.

INTRODUCTION

Over the past years rhodium has been gaining importance in catalytic chemistry. Not only is rhodium widely recognized as the best catalyst to promote the reduction of NO in three way catalysts [1-3], it also takes a special place in the conversion of
synthesis gas, since its product range can include oxygenated products (alcohols, aldehydes, acids) besides hydrocarbons [4-11]. From literature it is obvious that the character of the support is of main importance for the selectivity and activity of the supported rhodium catalysts in syngas conversion. Nowadays the exotic support titania has enjoyed increased interest. Although titania is a metal oxide support which has been found to strongly inhibit chemisorption of \( \text{H}_2 \) and CO on group VIII metals after reduction at elevated temperatures, which effect is known as Strong Metal Support Interaction (SMSI) [12], some metals have been found to have their highest activities for CO hydrogenation when dispersed on TiO\(_2\). An outstanding example is the titania-supported nickel catalyst [13-16] which shows turnover frequencies one to two orders of magnitude higher than other Ni catalysts. The increase in activity is accompanied by an increase in selectivity to higher-molecular-weight paraffins. Not all group VIII metals show favourable trends in catalytic behaviour when supported on TiO\(_2\) [17]. Iron for instance has a very low activity probably because it becomes easily immersed in the support [18]. With respect to rhodium Solymosi et al. [19] have found that the specific rate of \( \text{CH}_4 \) formation on Rh/TiO\(_2\) was more than one order of magnitude higher than that of Rh/MgO and Rh/SiO\(_2\) catalysts. This effect was attributed to an electronic interaction between the TiO\(_2\) and Rh. The authors speculated that TiO\(_2\) may influence the bonding and reactivity of species chemisorbed on metal particles.

The anomalous catalytic behaviour of titania-supported catalysts has often been ascribed exclusively to SMSI. However, in many of the studies reported one may doubt if the SMSI effect really was present, because in some cases the reduction temperature used was too low to create SMSI and in other cases a sintering of the metallic particles could not be excluded. In this paper we will present the results of a study of the catalytic behaviour of Rh supported on titania in the normal, non-SMSI-state, as well as in the SMSI-state, and on the more conventional alumina support in the conversion of syngas. A number of rhodium catalysts with different dispersions were used for this study in order to investigate also the influence of metal particle size on the catalytic behaviour. An extensive characterization study of these catalysts, using temperature programmed reduction and oxidation and transmission electron microscopy, has previously been published [20].
TiO$_2$ (anatase, Tioxide Ltd., CLDD 1367, surface area 20 m$^2$ g$^{-1}$, pore volume 0.5 cm$^3$ g$^{-1}$) and γ-Al$_2$O$_3$ (Ketjen, 000 1.5 E, surface area 200 m$^2$ g$^{-1}$, pore volume 0.6 cm$^3$ g$^{-1}$) were impregnated with aqueous solutions of RhCl$_3$.xH$_2$O via the incipient wetness method. In the following the catalysts will be denoted as RT (Rh/TiO$_2$) and RA (Rh/Al$_2$O$_3$) followed by the metal loading in weight percent. After impregnation the catalysts were dried in air at 355, 375 and 395 K for 2 h successively, followed by direct reduction in flowing H$_2$ at 773 K for 1 h and subsequently passivated and stored for further use.

Catalyst dispersion (percentage exposed) was determined by hydrogen chemicsorption and is expressed as the total amount of hydrogen atoms adsorbed at room temperature after re-reduction of the RA and RT catalysts at respectively, 773 and 523 K per total amount of rhodium atoms (H/Rh). Note that the titania-supported catalysts were reduced at 773 K during preparation (and thus will have been in the SMSI-state) and passivated and stored afterwards (which removed the SMSI-state [20]). Since the RT catalysts were re-reduced at 523 K the H/M values correspond to real dispersions, without interference of sintering effects. For more details we refer to [20].

The hydrogenation of CO was investigated in a flow microreactor at 523 K and atmospheric pressure. Two types of mixtures could be passed through the fixed-bed reactor, either a mixture of hydrogen, nitrogen and oxygen, with which the passivated catalysts were pre-treated, or a mixture of hydrogen, carbon monoxide and nitrogen (synthesis gas). Except for oxygen the gases were purified over a BTS column and molecular sieves. The products formed during reaction were analysed on-line by gaschromatography. The GC-equipment consisted of a Packard Becker 427 gaschromatograph equipped with a 904 TCD detector, and a Pye Unicam gaschromatograph with a flame-ionisation detector. A column packed with Porapack QS, using He as carrier gas, allowed complete separation of CO$_2$, ethene, ethane, H$_2$O, propene and propane. Using a squalane column with nitrogen as carrier gas the amount of C$_1$ to C$_8$ hydrocarbons could be determined. The amount of catalyst used for an experiment was circa 0.2 g. Prior to the passage of synthesis gas through the reactor, the passivated catalyst was re-reduced in flowing hydrogen for 0.5 h after which the catalyst was cooled under flowing hydrogen to reaction temperature. The alumina-supported catalysts were re-reduced at 773 K and the titania supported catalysts at 523 K or 773 K. The ratio of
H₂:CO:N₂ in the reaction gas mixture was 2:1:1. The gas hourly space velocity used was 3000 ± 100 h⁻¹. In order to measure under differential conditions the conversion of CO was kept below 10%. If necessary, this was achieved by diluting the catalyst with bare support. The absence of diffusional limitation was confirmed by the method suggested by Körs and Nowak [21]. Under these reaction conditions only hydrocarbons were formed and no oxygenates.

As the difference in CO concentration between the ingoing and outgoing gas stream could not be accurately determined the amount of CO converted to hydrocarbons was determined in another way. Under reaction conditions the products showed a logarithmic (Flory-Schultz or Anderson [22]) distribution indicating that a constant ratio of propagation and termination rates existed, especially in the molecular range above C₂ [23]: ln (mole % Cₙ) = K + n.ln α. The probability of chain growth is α and (1-α) is the probability of chain termination, i.e., product formation [22,23]. From the experimentally determined C₃ to C₈ hydrocarbons the probability of chain growth α was obtained. Assuming α to be independent of molecular size the concentrations of C₉ to Cₘ were calculated. The sum of the products (Σₙ∞ nCₙ) yielded the amount of CO converted to hydrocarbons. The activity is expressed as a turnover frequency: 

\[ \text{TOF}_{\text{CO}} = \frac{\text{CO molecules reacted to hydrocarbons}}{\text{surface metal atoms x sec}} \]

RESULTS AND DISCUSSION

The activities of all catalysts in the H₂ + CO reaction decreased with time on stream. Two deactivation regions could be distinguished, in the beginning of the reaction a fast decline of the reaction rate took place, while after circa 4 h the activity decreased in a more moderate way. Therefore, we define the "initial activity" as the activity obtained by extrapolating the function from the first region (t < 4 h) to reaction time zero, and the "steady-state activity" as the activity obtained by extrapolating the second region (t > 4 h) to time zero. The activity and selectivity data obtained are summarized in Table 1. Besides the initial and steady-state turnover frequencies (expressed in molecules of CO converted per rhodium surface atom per sec), also the dispersions (H/Rh) and the methane selectivity (SCH₄), the probability of chain growth (α) and the propene/propane ratio (C₃/C₃) in steady-state are given.
### TABLE 1

Selectivities and activities obtained at $P = 100$ kPa, $H_2:CO:N_2 = 2:1:1$, and $T = 523$ K.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H/Rh</th>
<th>$T^{O}FCO$</th>
<th>$T^{O}FCO$</th>
<th>$S_{CH4}^g$</th>
<th>$a^h$</th>
<th>$C_3/C_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$x 10^2$</td>
<td>$x 10^2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RA 2.3</td>
<td>1.53</td>
<td>0.31</td>
<td>0.17</td>
<td>0.59</td>
<td>0.44</td>
<td>0.80</td>
</tr>
<tr>
<td>RA 4.6</td>
<td>0.96</td>
<td>0.63</td>
<td>0.28</td>
<td>0.61</td>
<td>0.45</td>
<td>1.18</td>
</tr>
<tr>
<td>RA 8.5</td>
<td>0.81</td>
<td>0.82</td>
<td>0.35</td>
<td>0.65</td>
<td>0.45</td>
<td>1.56</td>
</tr>
<tr>
<td>RA 11.6</td>
<td>0.67</td>
<td>0.73</td>
<td>0.31</td>
<td>0.63</td>
<td>0.45</td>
<td>2.52</td>
</tr>
<tr>
<td>RT 0.3</td>
<td>1.10</td>
<td>0.45</td>
<td>0.10</td>
<td>0.50</td>
<td>0.45</td>
<td>1.50</td>
</tr>
<tr>
<td>RT 0.7</td>
<td>0.61</td>
<td>0.74</td>
<td>0.34</td>
<td>0.55</td>
<td>0.51</td>
<td>2.07</td>
</tr>
<tr>
<td>RT 1.0</td>
<td>0.40</td>
<td>2.10</td>
<td>0.47</td>
<td>0.49</td>
<td>0.48</td>
<td>2.52</td>
</tr>
<tr>
<td>RT 2.0</td>
<td>0.35</td>
<td>2.67</td>
<td>0.58</td>
<td>0.48</td>
<td>0.43</td>
<td>3.41</td>
</tr>
<tr>
<td>RT 3.2</td>
<td>0.22</td>
<td>4.11</td>
<td>1.48</td>
<td>0.48</td>
<td>0.42</td>
<td>2.11</td>
</tr>
<tr>
<td>RT 8.1</td>
<td>0.12</td>
<td>4.06</td>
<td>1.43</td>
<td>0.50</td>
<td>0.42</td>
<td>6.50</td>
</tr>
<tr>
<td>RT 0.4</td>
<td>1.10</td>
<td>0.01</td>
<td>0.01</td>
<td>0.48</td>
<td>0.40</td>
<td>1.20</td>
</tr>
<tr>
<td>RT 0.7</td>
<td>0.61</td>
<td>0.08</td>
<td>0.07</td>
<td>0.47</td>
<td>0.43</td>
<td>1.95</td>
</tr>
<tr>
<td>RT 1.0</td>
<td>0.40</td>
<td>0.40</td>
<td>0.20</td>
<td>0.43</td>
<td>0.42</td>
<td>2.31</td>
</tr>
<tr>
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<td>0.35</td>
<td>0.78</td>
<td>0.33</td>
<td>0.48</td>
<td>0.41</td>
<td>3.06</td>
</tr>
<tr>
<td>RT 3.2</td>
<td>0.22</td>
<td>1.38</td>
<td>0.91</td>
<td>0.53</td>
<td>0.40</td>
<td>2.05</td>
</tr>
<tr>
<td>RT 8.1</td>
<td>0.12</td>
<td>1.11</td>
<td>0.83</td>
<td>0.44</td>
<td>0.42</td>
<td>5.60</td>
</tr>
</tbody>
</table>

a: The catalysts were re-reduced at 773 K.
b: The catalysts were re-reduced at 523 K.
c: $E^{CO} = 103$ kJ mol$^{-1}$ for RT 1.0.
d: $E^{CO} = 81$ kJ mol$^{-1}$ for RT 8.1.
e: The catalysts were re-reduced at 773 K.
f: Based on $H_2$ adsorption at room temperature after re reduction of the $M/Al_2O_3$ and $M/TiO_2$ catalysts at respectively, 773 and 473 K.
g: $S_{CH4}^g$ = selectivity to methane.
h: $a$ = probability of chain growth.
RA and RT in non-SMSI-state

First we will focus our attention to the RA series and RT series in the non-SMSI-state. Table 1 clearly demonstrates that there exists a correlation between specific activity and dispersion. The rate of CO hydrogenation increased by about a factor of 2.5 as the dispersion of Rh on alumina decreased from 1.53 to 0.67. For the RT series the activity increased one order of magnitude going from a dispersion of 1.10 to 0.12. The increase in activity was accompanied by an increase in the olefin-to-paraffin ratio. Neither the selectivity to methane nor the probability of chain growth was greatly affected. The TOF\textsubscript{CO}'s in steady-state for the RA series and the RT series are presented in Figure 1 as a function of dispersion. The resemblance between the TOF\textsubscript{CO}'s of the alumina- and titania-supported rhodium catalysts is clear. Both systems have the same variation of activity with dispersion and the catalysts with the same H/Rh value have, within the accuracy of the measurements, the same turnover frequency. This leads to the conclusion that one must pay attention to dispersion effects when comparing activities in H\textsubscript{2} + CO reactions of rhodium supported on alumina and titania.

Figure 2 shows that the titania-supported catalysts exhibited a very rapid decrease in the turnover frequencies for the synthesis of

![Figure 1](image-url)  
Figure 1 Steady-state turnover frequency in the H\textsubscript{2} + CO reaction versus H/Rh (dispersion) for alumina- and titania-supported Rh-catalysts. P = 100 kPa, H\textsubscript{2}:CO:N\textsubscript{2} = 2:1:1, T = 523 K.
Figure 2 Initial and steady-state turnover frequencies in the H₂ + CO reaction versus H/Rh (dispersion) for titania-supported Rh-catalysts re-reduced at 523 and 773 K. P = 100 kPa, H₂:CO:N₂ = 2:1:1, T = 523 K.

all products when the dispersion increased above 0.3. An influence of dispersion on the performance of supported group VIII metals for the synthesis of hydrocarbons via CO hydrogenation has been reported previously [24-27]. In a detailed study Kellner and Bell [27] reported a dramatic decrease in the specific activity for Ru/Al₂O₃ catalysts with dispersions above 0.7. The decrease in activity was accompanied by a slight decrease in the probability of chain growth and a rapid decrease in the olefin-to-paraffin ratio. Vannice [25] and Bartholomew et al. [26] observed that the methanation activity of Ni catalysts decreased with increasing dispersion. By contrast the specific activity for methanation of Pt catalysts was found to increase slightly with increasing dispersion, while no clear cut dependence on Pd particle size was observed [24].

Several explanations for the decrease in specific activity with increasing dispersion can be given. One explanation, originally proposed by King [28], is that the electronic properties of the
particles may be changed. Theoretical studies [29] of the electronic properties of small metal particles show that deviations from the properties of bulk metal occur, primarily, for crystallites smaller than about 20 Å. This critical size corresponds to a dispersion of about 0.5. The observed H/Rh value of 0.3, at which a decline of the specific activity takes place, is of the right order of magnitude. A small difference in the electronic properties between large and small rhodium particles follows from XPS measurements [30]. The observed Rh 3d_{5/2} electron binding energies for RT 8.1 (the least dispersed catalyst) and for RT 0.3 (the most dispersed catalyst) after in situ reduction at 483 K are 307.05 and 307.25 eV, respectively. (This small variation in binding energy is most likely caused by differences in the extra-atomic relaxation of metal particles of different sizes. In small particles there is less effective screening of the core holes created during photoemission). This indicates a small change in the electronic properties going from a rhodium loading of 8.1 to 0.3 per cent by weight.

Another explanation for the decrease in specific activity with increasing dispersion might be that the fraction of sites which are most active for the hydrogenation of CO decreases with increasing dispersion. Such a trend would be expected if Rh atoms at the faces of crystallites were more active than those at the edges or corners [31,32]. The apparent activation energy E_{CO} for RT 8.1 is 81 kJ mol^{-1} which is significantly lower than the activation energy for RT 1.0 which is 103 kJ mol^{-1}. This result is in accordance with the model because it indicates a change in nature of the active sites with dispersion. This indicates that the nature of the active sites changes with dispersion, but can still be explained by both models.

A completely different explanation is that small particles are much more reactive and therefore prone to deactivation. Larger metal particles have surfaces which deactivate less quickly and on which hydrogen can still adsorb. The resulting hydrogen atoms may diffuse to more reactive surfaces or sites and raise their steady state activities. The different hydrogenation capabilities of different metals might then explain the difference in activity-dispersion behaviour between Rh, Ru and Ni on one hand, and Pt on the other hand.

**Comparison of RT series in non-SMSI-state and SMSI-state**

The activity and selectivity data obtained by measurements on the Rh/TiO₂ catalysts after re-reduction at 773 K are also given
Figure 3 Ratio of initial turnover frequencies in the \( H_2 + CO \) reaction of Rh/TiO\(_2\) catalysts re-reduced at 773 and 523 K as a function of H/Rh (dispersion). \( P = 100 \) kPa, \( H_2:CO:N_2 = 2:1:1, T = 523 \) K.

in Table 1. Note that the influences of dispersion on the catalytic properties of the RT-series in the SMSI-state and in the non-SMSI-state are comparable. Significant differences between the catalysts after a low and high temperature re-reduction appear to be present in the specific activities only. Neither the selectivity for methane nor the hydrogenation capacity is affected, whereas the probability for chain growth tends to decrease somewhat.

Plots of initial and steady-state TOF\(_{CO}\)'s as a function of dispersion for the RT series after low and high temperature re-reduction are presented in Figure 2. It is obvious that the initial specific activity is affected most by the SMSI. The effect on the steady-state activity is, however, moderate. As suggested in the previous section, this result indicates that SMSI is indeed destroyed during reaction, if not completely then at least to a great extent. We consider water, formed during reaction, to be responsible for this. The difference in the initial activity between a catalyst re-reduced at low temperature (LT) and the same catalyst re-reduced at high temperature (HT) and TOF\(_{CO}\) initial (LT) is a measure for SMSI with a ratio of zero indicating a complete suppression of activity by SMSI, and a ratio of one indicating a
complete lack of SMSI. In order to investigate the influence of dispersion on SMSI we plotted $\text{TOF}_{\text{CO}}$ initial (HT)/$\text{TOF}_{\text{CO}}$ initial (LT) versus $H/Rh$ in Figure 3. This figure clearly indicates that SMSI is more pronounced for the dispersed systems. An effect of crystallite size on the onset of SMSI has previously been reported by Ko et al. [33]. They found that with titania-supported nickel catalysts more severe reduction conditions were necessary to induce strong metal-support interactions when the nickel crystallites were larger.

Two explanations for SMSI have acquired most support over the years. Originally charge transfer from the support to the metal, with a concurrent change in the electron properties of the metal was favoured [12, 34]. Lately covering of the metal by suboxides of TiO$_2$ is thought to explain the reduced catalytic activity [35–37]. We observed that in situ reduction of Rh/TiO$_2$ at 523 K or 823 K led to essentially the same Rh $3d_{5/2}$ binding energy [30]. This indicates that SMSI is probably not caused by a charge transfer from the support to the metal or vice versa. A plausible explanation for the decrease of the ratio $\text{TOF}_{\text{CO}}$ initial (HT)/$\text{TOF}_{\text{CO}}$ initial (LT) with dispersion might be that SMSI is caused by covering. It is obvious that small particles can more easily be encapsulated than larger ones and that this leads to a more pronounced suppression of the initial activity for highly dispersed systems.

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