

## Promotion by vanadium compound of the elementary reaction steps in the synthesis gas reaction catalyzed by rhodium

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PROMOTION BY VANADIUM COMPOUND OF THE ELEMENTARY REACTION STEPS IN THE  
SYNTHESIS GAS REACTION CATALYSED BY RHODIUM

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Abstract

In order to understand the promoting effect of vanadium compound on rhodium catalysts in synthesis gas conversion, changes in reaction rates of elementary steps and the surface concentration of intermediates have been monitored. Vanadium promotion enhances the rate of CO dissociation which is the most important effect. Reactive surface carbon is stabilized by vanadium what results in a slightly decreased reactivity in methane formation. Transient experiments using isotopes and GCMS detection show that CO insertion is not promoted by vanadium. The hydrogenation of ethanal to ethanol is enhanced by vanadium while the desorption rate of ethanal is decreased.

Introduction

It is well known that the catalytic performance of rhodium catalysts during synthesis gas reactions is greatly improved by addition of highly oxophilic promoters [1-3] as thorium, manganese, titanium, cerium and vanadium compounds. Reported overall effects of such oxygenate promotion are [4-6] an improved total activity, an enhanced selectivity for oxygenated products and C<sub>2</sub>+ hydrocarbons, a higher ratio of ethanol/ethanal formation and a faster deactivation of the catalyst.

In the work to be presented a vanadium compound is chosen as a model promoter for rhodium [7,8]. The influence of vanadium on the surface concentration and intrinsic reactivity of reaction intermediates is studied. The reaction steps from the generally accepted reaction scheme which is shown in figure 1, are therefore assumed to be valid.

The first elementary reaction step in the formation of C<sub>2</sub>+ products is CO dissociation. With model techniques like Temperature Programmed Surface Reaction (TPSR) and Pulse Surface Reaction rate Analysis (PSRA), the rate of this step is analysed. Carbon monoxide adsorption at temperatures above 250 °C results in adsorbed surface carbon. Changes in the reactivity as well as surface concentration of this carbon caused by vanadium promotion is measured. Whether the formation of ethanol and ethanal needs a common reaction intermediate is still a point of discussion

in literature [9-12b]. With transient kinetic isotopic labelling experiments the rate of CO insertion is investigated during the steady state synthesis gas reaction.

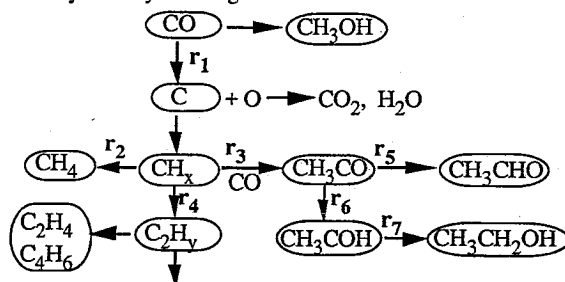


Figure 1. General reaction mechanism

### Catalyst

Rhodium and rhodium/vanadium catalysts were prepared with the same rhodium metal particle size, so that the observed differences in kinetics are not due to differences in particle size. The rhodium catalyst was prepared by incipient wetness impregnation of silica (Grace 332) by an aqueous solution of  $\text{RhCl}_3$ . Grace type silica was used because of good reproducibility of catalyst preparation and the high rhodium dispersion achieved. After drying at  $110\text{ }^\circ\text{C}$  and a reduction at  $350\text{ }^\circ\text{C}$  for 24 hours, the vanadium promoter was 'post impregnated' from a solution of  $\text{NH}_4\text{VO}_3$ . The amount of added vanadium was 0.5% what resulted in the Rh/V ratio of 3 on molar basis. In this way a rhodium/vanadium catalyst system was created in which the vanadium promoter reduced the CO adsorption capacity by 55%. This suppression was independent of the reduction temperature between  $200$  and  $450\text{ }^\circ\text{C}$ . Thus no strong SMSI effects were present. The average rhodium particle size was  $22\text{ \AA}$  as established by TEM and CO chemisorption measurements. As already known this catalyst produces ethanol in synthesis gas conversion [13]. This can be improved by the addition of vanadium.

### Methods and results

By monitoring the Boudouard reaction [14,15] no correct information can be obtained on CO dissociation on the catalysts because reactive oxygen species are still present in the catalyst system after reduction at  $400\text{ }^\circ\text{C}$ . Therefore, CO dissociation was studied by TPSR and PSRA. During TPSR the reactivity of CO adsorbed at room temperature was tested. Reduction was followed in a diluted hydrogen flow as a function of temperature. With PSRA, a small pulse of CO is injected at a point in front of the reactor, which is kept isotherm. The methane formation rate is analysed on line with a Quadrupole Mass Spectrometer. The rate of methane formation is assumed to be the same as the rate of CO dissociation, because under the experimental conditions CO dissociation is the rate limiting step according to the literature [16,17]. The results of both TPSR and PSRA show that the dissociation of CO is enhanced by vanadium promotion. The activation energy for CO dissociation is decreased from  $96\text{ kJ/mol}$  for the rhodium catalyst to  $67\text{ kJ/mol}$  for the vanadium promoted catalyst as shown in figure 2 (also reported in [18]). An enhanced CO dissociation has been also found by Rieck and Bell [19] with Pd/La and Mori et.al.[20] with Ru/V catalysts.

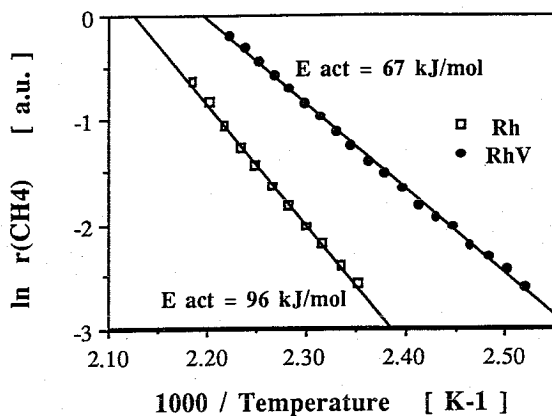


Figure 2. Arrhenius plot from TPSR data characteristic for CO dissociation.

In a TPSR experiment performed after CO adsorption at temperatures above 250 °C two methane peaks appear: one under 100 °C from hydrogenation of adsorbed carbon atoms and another one around 240 °C from adsorbed CO. We can define the "fraction of reactive carbon" in a TPSR plot (see figure 4), as the ratio of the amount of methane formed under 100 °C divided by the total amount of methane formed. It is possible to create the same surface fraction of reactive carbon species on a rhodium and rhodium-vanadium catalyst by adsorbing CO at different temperatures. The reactivity of a constant fraction of about 15% of adsorbed carbon was tested as a function of temperature in its hydrogenation to methane. The results are presented in figure 3.

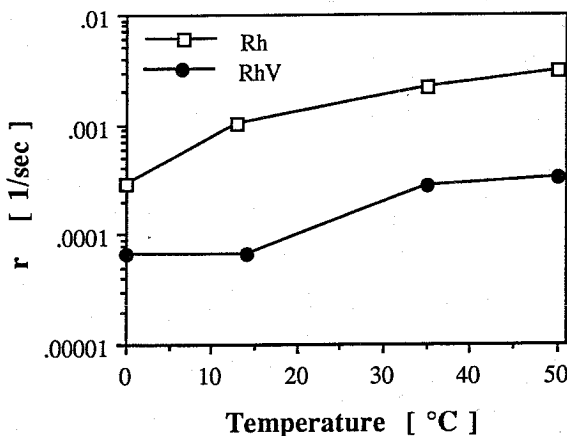


Figure 3. Hydrogenation reactivity of the reactive surface carbon adsorbed on a rhodium and a rhodium-vanadium catalyst. The reaction rate  $r$  is calculated from the mean residence time ( $\tau$ ) of the adsorbed carbon species ( $r = \tau^{-1}$ ).

It appears that vanadium decreases the rate of methane formation from adsorbed surface carbon at low hydrogenation temperatures. However, the formation of  $C_2+$  hydrocarbons from the same surface concentration of carbon species is during hydrogenation at 200 °C about 5 times higher on the vanadium promoted catalyst. The enhanced reactivity of this carbon in the formation of  $C_2+$  hydrocarbons could also be established during a reaction with synthesis gas at 200 °C [21].

The influence of the vanadium promoter on the surface concentrations of reactive carbon during a steady state synthesis gas reaction was analysed with TPSR, after 1 hour of exposure of the catalysts to synthesis gas at 200 °C at 1 atmosphere (figure 4).

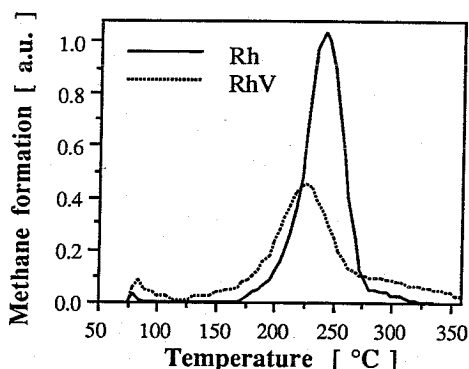


Figure 4. TPSR after 1 hour of synthesis gas reaction. Methane formation rate as a function of hydrogenation temperature.

From this figure it can be calculated that the fraction of reactive carbon during the steady state reaction is increased from 0.34% for the rhodium to 1.4% for the rhodium vanadium catalyst. This agrees with the higher CO dissociation activity of the vanadium promoted catalyst whereas the intrinsic reactivity of adsorbed carbon is much less affected. The total amount of methane produced corresponds with exactly one monolayer of carbonaceous intermediates. Whereas on ruthenium catalysts more than one monolayers have been observed [22], it appears that no carbide overlayers are formed on rhodium catalysts under the conditions used.

In our previous work we monitored the synthesis gas reaction at a steady state condition at 200 °C. From the product distribution, the total rate of production of the  $CH_x$  units can be calculated. It has been established in this way that total production increases about 4 times when the rhodium catalyst is promoted by vanadium. Since the surface concentration of reactive carbon species, the intermediate of the synthesis gas reaction [23-27], is increased by a factor 4.1 (figure 4) one can conclude that the promotion of CO dissociation is the most important effect of vanadium.

The influence of vanadium promotion on the CO insertion into a  $CH_x$  species was studied in situ by a transient response isotope experiment. After one hour of steady state reaction the reaction gas was switched from  $^{12}CO$  to  $^{13}CO$ . The insertion reaction of  $^{13}CO$  or  $^{12}CO$  into surface  $CH_x$  species leading to ethanol and ethanal, was measured as a function of time. A time based GCMS system [28] was used by which incorporation of  $^{13}C$  into the aldo group of acetaldehyde and into the enol group of ethanol, could be detected from the fragment mass spectra. In this way the rate of

the insertion step could be measured independent of the CO dissociation rate. In figures 5 a and b the disappearance of  $^{12}\text{C}$  in the inserted CO group of ethanal and ethanol after switch is plotted as a function of time in a logarithmic scale.

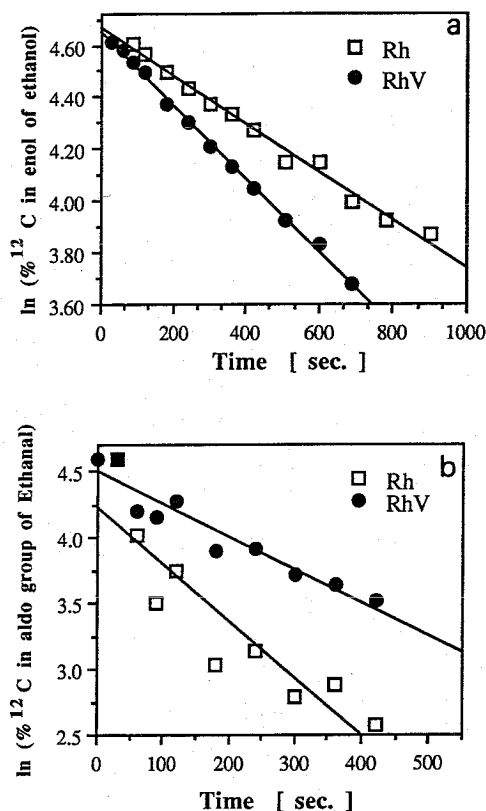


Figure 5 a and b. The disappearance of  $^{12}\text{CO}$  in the enol group of ethanol and in the aldo group of ethanal on the Rh and RhV catalyst as a function of time. a: ethanol b: ethanal.

These results show that after CO dissociation the intermediates reacting towards ethanol have a longer residence time  $\tau$  (steeper curve) on the catalyst surface than the ethanal intermediates. Apparently, the hydrogenation of the acetate intermediate [9] from which ethanol is formed is slow. Vanadium promotion decreases the residence time of ethanol intermediates (see the steeper line in figure 5a). On the other hand, ethanal intermediates have a longer residence time on the promoted surface. This implies that the desorption rate of Ethanal is decreased by vanadium promotion. This result is in good agreement with the conclusion based on Infra Red spectra [29] that acetate species is stabilized by the vanadium promoter. The transient response experiment accounts only for those acetate species that are true reaction intermediates. Combining the data of the activity measurements, the measured surface concentration of  $\text{CH}_x$  intermediates and the results of the transient response technique, it is possible to calculate the changes in the normalized reaction rates  $r_3$ ,  $r_5$ ,  $r_6$  and  $r_7$  as

well as in the concentration of the reaction intermediate  $\text{CH}_3\text{CO(a)}$  from the mechanism in figure 1. Preliminary results for the Rh and RhV catalyst are shown in Table 1 (for a more detailed discussion see [28]).

Table 1. Ratios of elementary reaction rates and the  $\Theta_{\text{CH}_3\text{CO}}$  values obtained with promoted and non promoted catalyst (see figure 1)

| Reaction step      | $r_3^1$ | $r_5^1$ | $r_6^1$ | $r_7^1$ | $\Theta(\text{CH}_3\text{CO})$ |
|--------------------|---------|---------|---------|---------|--------------------------------|
| Ratio <sup>2</sup> | 0.9     | 0.2     | 0.7     | 1.5     | 6                              |

<sup>1</sup>  $r$  in (mol converted  $\text{C}_2\text{O}$  species) · (mol surface Rh)<sup>-1</sup> · second<sup>-1</sup>

<sup>2</sup> Value of RhV/Rh is given.

The decreased residence time of the ethanol producing intermediate suggests that vanadium enhances the hydrogenation of the acetate intermediates [9] to ethanol. This was confirmed from a separate hydrogenation experiment in which a flow of 58 ml/min of 2% ethanal and 8.5% hydrogen in helium was passed over 300 mg of catalyst at 110 °C. The results are presented in Table 2.

Table 2. Hydrogenation of ethanal at 110 °C on Rh and Rh/V

|                      | Activity in TON <sup>1</sup> | Ethanol Selectivity % |
|----------------------|------------------------------|-----------------------|
| Rh/SiO <sub>2</sub>  | 0.11                         | 65                    |
| RhV/SiO <sub>2</sub> | 0.97                         | 93                    |

<sup>1</sup> TON in mmol ethanal converted per second per mol surface rhodium.

### Conclusion

By using different techniques, it is possible to explain the role of vanadium promotion in synthesis gas reaction in terms of changes in reaction rates of elementary steps and surface concentrations of intermediates. The vanadium compound decreases the activation energy of CO dissociation leading to an enhanced activity. Reactive carbon intermediates are stabilized what results in a higher coverage of surface carbon and a changed selectivity. Also oxygen containing species are stabilized. The desorption rate of ethanal is decreased while the hydrogenation rate to ethanol is enhanced. The CO insertion rate is not enhanced by vanadium.

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