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Citation for published version (APA):

DOI:
10.1016/S0166-9834(00)81221-X

Document status and date:
Published: 01/01/1986

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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THE INFLUENCE OF THE SUPPORT ON THE CATALYTIC PROPERTIES OF Ru CATALYSTS IN THE CO HYDROGENATION

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ABSTRACT
The hydrogenation of CO is studied over SiO₂, Al₂O₃, TiO₂ and V₂O₃ supported Ru catalysts. The catalytic activity, measured in a micro flow reactor at 550 K showed that Ru/SiO₂ is the most active and stable catalyst, while the other systems are less active and are sensitive for deactivation. This deactivation may be related to the formation of aromatic compounds observed at the first exposure of a fresh catalyst to small amounts of CO/H₂.

INTRODUCTION
Several studies dealing with the Fischer-Tropsch synthesis over supported Ru (1-6) have shown that the support can influence the catalytical properties. Whereas unsupported and silica supported Ru mainly produce methane, substantial amounts of olefins are formed using Ru/TiO₂ and Ru/V₂O₃. These effects can be ascribed to modification of the H₂ and CO adsorption properties which are due to metal/support interactions or to differences in metal dispersion (1, 7-10). The reported studies have been primarily dealing with the initial activity or steady state activity of the catalysts and the formation of higher hydrocarbons. No information is available on deactivation phenomena in correlation with the support.

In the present work we studied the role of the support in this respect and correlated activity/selectivity properties with deactivation phenomena. As deactivation may be caused by the initial formation of coke precursors, we carried out low pressure experiments. As low pressure retards all reactions and facilitates detection of small amounts of reaction products by mass spectroscopy, some insight can be gained in the initial events occurring on a fresh catalyst. The support studied comprise SiO₂, Al₂O₃, TiO₂ and V₂O₃.

EXPERIMENTAL
Materials and catalyst preparation
Different supported Ru catalysts are prepared by incipient wetness impregnation of the support with an acidified solution of RuCl₃.xH₂O (Johnson Matthey).
The supports are obtained from Akzo (SiO₂, Al₂O₃), Degussa (TiO₂) and Merck (V₂O₅).

Except for the V₂O₅ support, all the supports are mechanically treated to obtain a particle size distribution of 0.2-0.6 mm. The silica and alumina tablets are crushed to smaller particles, while the TiO₂ powder is first isostatically pressed (400 MPa) to a tablet, which is then crushed. The V₂O₅ support is reduced to V₂O₃ before impregnation is carried out.

The pore volume and the BET area of the support are respectively: SiO₂ (1.9 ml/g, 600 m²/g), Al₂O₃ (1.2 ml/g, 195 m²/g), TiO₂ (0.43 ml/g, 50 m²/g), V₂O₅ (0.39 ml/g, 6 m²/g). After impregnation, the catalyst is dried in vacuum at room temperature followed by a thermal treatment at 400 K in air at atmospheric pressure. Next, hydrogen treatment is carried out at 525 K for 2 hours to remove the excess of chloride. The catalyst is cooled down in a hydrogen stream to room temperature after which it is passivated in air.

H₂ chemisorption

The H₂ uptake experiments are performed in a conventional glass adsorption equipment. The passivated catalysts are reduced in situ in H₂ for 2 hours at 525 K, followed by evacuation at 475 K for another hour. The H/Ru values are determined according to the method of Benson and Boudart (11).

CO hydrogenation at 101 kPa

Measurements of the CO hydrogenation activity and selectivity are carried out in a differential fixed bed reactor as described previously (12).

A fresh, passivated catalyst (0.5 g) is reduced in flowing hydrogen (3 l/h) for 2 hours at 675 K. According to our TPR experiments this treatment is sufficient to reduce the catalyst completely. After this period the reactor is cooled to 550 K at which the CO+H₂ reaction is studied. High space velocities (15,000-20,000 h⁻¹) are used to achieve low conversion levels. The H₂ and CO partial pressures are 40 and 20 kPa respectively. Helium is added as a diluent. The hydrocarbon product distribution is determined up to C₅ by GLC analysis.

CO hydrogenation at 0.5-1.5 kPa

The high vacuum apparatus is made of stainless-steel Leybold-Heraeus equipment parts, except for the reactor which is made of quartz glass. The system is kept at a temperature of 400 K. The reaction mixture (CO, H₂, He and Ne) is prepared by mixing accurately controlled flows and storing that mixture in a feed vessel at 101 kPa. The pressure in the reactor is controlled by two variable leak valves which connect the reactor to the feed section and the analysis section respectively. A membrane differential pressure gauge (Datametrics BEM 1174) mounted between the reactor and the vacuum pump is used for pressure measurements. The flow rate into the reactor is calculated from the rate of pressure drop in the feed vessel, measured with a PD differential pressure cell. The gas composition in the reactor
is monitored with a quadrupole mass spectrometer (Leybold-Heraeus, Quadruvac Q200) equipped with a Puzzle PSDS 20 microcomputer to control the scan over the selected mass range and to collect the data. Regression procedures are applied to interpret the data and to calculate the concentrations and reaction rates. Neon is used as an internal standard.

The catalyst is pre-treated in a similar way as in the 101 kPa experiments. The reaction is investigated at 550 K and 0.5-1.5 kPa with a mixture of H₂, CO, He and Ne with a volumic ratio of 40:20:40:5 at a feed rate of 9 nmol/s.

RESULTS

The results of the hydrocarbon synthesis at 550 K and 101 kPa are summarized in table 1, together with the hydrogen chemisorption data.

An estimate of the metal dispersion and particle size can be made from the chemisorption data. Assuming no SMSI effect in case of the TiO₂ and V₂O₃ catalysts and according to Dalla Betta (13), the H/Ru values of 0.34-0.53 found here, indicate an average particle size of 3.2-1.7 nm.

The reaction rates, expressed both as CH₄ turnover number and as CO conversion rate per gram of Ru metal show that the SiO₂ supported catalyst is the most active, but also the least selective with respect to olefin formation. The other Ru catalysts produce substantial amounts of C₂₄ hydrocarbons, besides methane.

Remarkably high olefin to paraffin ratios are found for the TiO₂ and V₂O₃ catalysts compared to the alumina catalyst. Similar results have been reported by King (1), Vannice et al (2) and Kikuchi et al (6). Small amounts of oxygenated organic compounds (mainly ethanol) are also detected for these two catalysts.

| TABLE 1 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| CATALYST        | H/Ru | NCH₄ | REACTION RATE | HYDROCARBON SELECTIVITY (C-ATOM %) |
| SUPPORTED ON    |       |      | (10³ S⁻¹)     | C1  | C2  | C2= | C3  | C3= | C4  | C4= | C5  | C5= |
| SiO₂            | 0.34 | 53   | 180           | 98  | 1.0 | TR  | TR  |     |     |     |     |     |
| Al₂O₃           | 0.53 | 4.4  | 46            | 49  | 11  | 5.6 | 2.3 | 16  | 1.1 | 7.4 | 1.8 | 5.6 |
| TiO₂            | 0.43 | 0.73 | 8.2           | 38  | 7.8 | 13  | 2.0 | 20  | 0.8 | 12  | 1.1 | 5.0 |
| V₂O₃            | 0.48 | 0.51 | 4.4           | 54  | 6.8 | 11  | 1.8 | 14  | TR  | 6.4 | TR  | 5.3 |

TEMP. 550 K, H₂/CO = 2

*: AT 180 MINUTES
FIGURE 1 Catalytic activity of supported Ru, expressed as $N_{\text{CH}_4}$, as a function of time. ($T = 550$ K, $H_2/CO = 2$)

FIGURE 2 Catalytic activity of Ru/SiO$_2$ (a) and Ru/TiO$_2$ (b) at 0.6 kPa, $T = 550$ K and $H_2/CO = 2$.

CO (●), $H_2$ (○), CO$_2$ (●), H$_2$O (▲), CH$_4$ (□), C$_2$H$_4$ (■), EtOH (■), C$_6$H$_6$ (●●), C$_7$H$_8$ (▼), C$_{10}$H$_8$ (▲).
Activity levels as a function of time on stream are depicted in fig. 1. The activity is expressed as the CH4 turnover number ($N_{CH4}$). The curves clearly show that the rate of reaction- and deactivation of the catalysts strongly depends on the nature of the support. The Ru/SiO2 catalyst is very active and stable, while the other catalysts are much less active and rapidly decline in activity. Two regions can be distinguished: A rapid decline of activity in the first three hours, followed by a more gradual decay.

In the low pressure experiments the untreated supports and an unsupported Ru catalyst were examined first. The supports do not show any catalytic activity. Pure ruthenium appears to convert CO to a large extent (95%), CH4, CO2 and water being the only products observed.

The results of the Ru/SiO2 and the Ru/TiO2 catalysts are shown in fig. 2. The results of the Ru/V2O3 and the Ru/Al2O3 are very similar to those of the Ru/TiO2 and are not presented in detail here. The product distribution of the Ru/SiO2 (fig. 2a) is almost identical to that of pure Ru. Besides methane, water and CO2, traces of ethanol are observed. The results of Ru/TiO2 (fig. 2b) are much different showing a variety of products besides methane.

The most striking result is the formation of relatively large amounts of aromatic compounds (benzene, toluene, naphthalene) which are not observed at atmospheric conditions. Remarkably, the curves of these compounds exhibit a maximum, after which the formation rate decreases rapidly. Some experiments carried out at higher pressures (3-9 kPa) have demonstrated that increasing pressure causes sharpening of the curve, i.e. the occurrence of the maximum at shorter reaction time, a higher top value and a faster decline. This explains why aromatic compounds are not observed at 101 kPa.

Finally it is worth mentioning that all catalysts, except for the unsupported ruthenium, show HCl in the mass spectrum when running the Fischer Tropsch reaction. The amount of HCl varies from traces for the silica supported catalyst to significant amounts for the other catalysts.

DISCUSSION

The results reported in this study and summarized in table 2 have shown that large differences exist in catalytic properties between unsupported and silica supported Ru on one hand and Ru/Al2O3, Ru/TiO2 and Ru/V2O3 on the other hand. It appears that the Ru catalysts which produce olefins and aromatic compounds are less active and more sensitive to deactivation. Obviously the carriers concerned (Al2O3, TiO2 and V2O3) somehow modify the Ru particles or take part in the reaction.

One might suggest that Strong Metal Support Interaction causes the reported effects, particularly in case of TiO2 and V2O3. The high reduction temperature used (675 K) will bring the Ru/TiO2 and Ru/V2O3 in a SMSI state, characterised by suppressed chemisorption of H2 and CO (14). Changes in activity/selectivity properties can then be expected. We think, however, that our catalysts have not much suffered
from SMSI at the reaction conditions used because:
(a) Some catalysts are reduced at lower temperature (475-550 K) and showed only slight differences in activity and selectivity. (b) The Al₂O₃ supported catalyst behaves similar while no SMSI is known for this system.

TABLE 2
General properties of supported Ru catalysts

<table>
<thead>
<tr>
<th></th>
<th>Ru/Ru/SiO₂</th>
<th>Ru/Al₂O₃, TiO₂, V₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACTIVITY LEVEL</td>
<td>HIGH</td>
<td>MODERATE/LOW</td>
</tr>
<tr>
<td>STABILITY</td>
<td>GOOD</td>
<td>POOR</td>
</tr>
<tr>
<td>OLEFIN SELECTIVITY</td>
<td>0</td>
<td>30 - 50 %</td>
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<tr>
<td>AROMATICS</td>
<td>NONE</td>
<td>SUBSTANTIAL</td>
</tr>
<tr>
<td>HCL RELEASE</td>
<td>NONE/TRAces</td>
<td>SIGNIFICANT</td>
</tr>
</tbody>
</table>

Another factor of importance may be found in the acidity of the support (Al₂O₃, TiO₂ and V₂O₃ are all acidic) in the presence of residual chlorine. We doubt about the special role of acidity as K₂O added to Ru/SiO₂ as promoter appears to have a similar effect: activity decrease and improved olefin selectivity (15-17). The effect of chlorine may be more important. Chlorine is known for it poisoning effect on iron catalysts with a similar selectivity change towards more olefins (18), but little information is available for Ru: Shiflett and Dumesic (19) showed that chlorine poisons a Ru/Al₂O₃ catalyst in the ammonia synthesis while Ru/SiO₂ is not affected, Ohkura (9) reports that a Ru/Al₂O₃ catalyst prepared from Ru carbonyl is more active than those prepared from RuCl₃. Finally the effect of chlorine on alumina supported metals in catalytic reforming is well known (20).

The formation of aromatics deserves special comments. In fact the appearance of aromatics is completely unexpected in view of the normal growth of linear chains. Moreover, the amount of C₆⁺ produced in the form of aromatics largely exceeds the expected quantities of so heavy molecules according to the Schulz Flory distribution. We therefore think that an entirely different mechanism is operative, suggestedly involving carbidic species, getting arranged in ring structures at the surface. This might imply that the detection of aromatics in the gas phase signifies the start of the formation of a graphitic carbon layer on the metal surface.

As a conclusion one can state that Ru, supported on carriers like Al₂O₃, TiO₂ and V₂O₃ by impregnation of the chloride, appears "modified" in several respect. SMSI is not the essential factor. Chlorine, in combination with these carriers is strongly suspected. Further experiments will be needed to achieve more insight and conformation of suggested ideas.
ACKNOWLEDGEMENTS

The financial support of the Netherlands Organization for the Advancement of Pure Research (ZWO) is gratefully acknowledged. We also thank Johnson Matthey Chemicals Ltd. for supplying the ruthenium trichloride.

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