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On the Selectivity of Rh Catalysts in the Formation of Oxygenates

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In order to gain information on the factors which determine the selectivity of catalysts in the syngas reactions, a number of Rh catalysts with various carriers have been studied. It has been found that Rh on V_2O_3 is, under certain conditions of preparation, a rather selective catalyst for C_2-oxygenates. The selectivity in methanol formation has been found to be related to the presence of Rh ions, similarly as with Pd (or Pt). However, Rh ions are not the centers for the formation of C_2-oxygenates. Experimental data made plausible that catalysts selective for the ethanol synthesis must contain rhodium metal which is partly covered by the support material.

INTRODUCTION

It is an interesting problem to understand why Ni, Pd, and Rh catalysts are so much different in their product distributions when synthesis gas (CO/H_2) is passed over these catalysts under the same conditions. Some sources of the different selectivities have already been identified (vide infra), but it is still desirable to gain new information on this problem. Let us summarize first the present state of affairs.

Nickel is known to be a catalyst for methanation and hydrocarbon synthesis. Several studies have shown that the main route of these reactions runs via CO dissociation (easy on nickel) and formation of CH_x intermediates. The concentration of oxygen-containing intermediates is very low on this metal (*1–4*).

With respect to the concentration of oxygen-containing intermediates, palladium is the other extreme (*5*). In combination with a suitable support palladium can be a very good catalyst for the synthesis of methanol (*6*). There have been several ideas expressed in the literature explaining the role of the support in methanol synthesis by Pd: (i) the support itself is active in the methanol synthesis (*7,8*); (ii) the support induces a certain type of facetting of Pd particles, which increases the number of special Pd^0 sites active in methanol synthesis (9–11); (iii) the support participates (together with the Pd metal) in CO activation (*6,12*); (iv) the support stabilizes Pd^{n+} centers which are required for methanol synthesis (*13–15*).

The conclusion regarding the necessity of the presence of Pd ions in the working catalyst is supported by results of several other research groups. Hindermann *et al.* (*16*) showed by using the chemical trapping method that the activity in methanol synthesis with Pd is directly proportional to the surface concentration of formyl species. Anikin *et al.* (*17*) performed quantum mechanical calculations on the formation of formyl from CO and H on palladium and they found that a positive charge on Pd substantially decreases the activation energy of this process and increases considerably the thermodynamic stability of the formyl species.

Since formyl intermediates are on Pd the most essential species (*16*) and since these intermediates are stabilized by a positive charge on Pd (*17*) it is certainly not a coincidence that the activity in methanol synthesis is so well correlated (linearly) with the

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concentration of Pd^{n+} ions in the catalyst (*13*).

Rhodium is clearly the intermediate (between Ni and Pd) and the most complicated case. As a pure metal (*18*) or on an "inert" carrier (*19*) it can catalyze hydrocarbon synthesis (with a medium activity), on a suitable carrier it becomes a catalyst for methanol synthesis (*20,21*), and, what is most important, also a catalyst for C_2-oxygenate formation (*22,23*). These most desirable (*24*) products are formed only when certain oxides are used as promoters (*25*) and when a certain method of catalyst preparation is followed. It is important to understand why this should be so.

It is remarkable that the optimal supports (MgO, La_2O_3) for methanol synthesis catalysts (Pt, Pd, Rh) are sometimes very poor in inducing C_2-oxygenate production and vice versa; supports bad for methanol synthesis appear to be optimal when C_2-oxygenates have to be produced [V_2O_5,Ta_2O_3, TiO_2, etc. (*25*)]. Does this mean that the synthesis of various oxygenates, methanol, as well as ethanol (acetaldehyde), need the presence of ionic centers (Pd^{n+}, Rh^{n+}), but require different oxides to stabilize these centers? Or does it mean that the function of the support is different with Pd–methanol catalysts and Rh–C_2-oxygenate catalysts? The answer can be given if the relation between the catalytic activity in C_2-oxygenate formation and the concentration of Rh^{n+} ions is known. We addressed ourselves to this problem and the results of this study are presented below.

EXPERIMENTAL

Catalytic measurements were performed in an open fixed-bed, plug-flow reactor, at 1 pressure; for every experiment 1 g of catalyst was used. The catalyst bed had a diameter of 18 mm and a height of about 2–3 mm depending on the catalyst. The H_2/CO ratio was 2 except with the rhodium/magnesium (hydr)oxide catalysts where the H_2/CO ratio was 7; this high ratio was necessary to prevent catalyst poisoning. The flow of hydrogen was always 8 ml/min; the GHSV was between 900 and 1400 h^{-1}, depending on the catalyst. All catalysts were tested at 200°C. Analysis of the products was performed by gas chromatography with a column filled with Porapak R (3 m long, $\frac{1}{4}$ in. diameter). Hydrogen was used as a carrier gas (flow 1.5 liters/h), detection was by FID and the column temperature was 160°C. The product signals were integrated and converted into values proportional to the molar concentrations by using theoretical (hydrocarbons) and experimental (oxygenates) calibration factors. Corrected signals were used to calculate the conversion (α) defined as

$$\alpha = \frac{\Sigma N[C_N]}{[CO]} \times 100\%$$

where N = number of carbon atoms in product C_N, $[C_N]$ = molar concentration of a product with N carbon atoms, and [CO] = moles CO in feed.

The selectivity for C_2-oxygenates is defined as

$$S_{C_2-ox} = \frac{2([C_2H_5OH] + [C_2H_4O] + [C_2H_4O_2])}{\Sigma N[C_N]} \times 100\%$$

where $[C_2H_5OH]$, $[C_2H_4O]$, and $[C_2H_4O_2]$, are the molar concentrations of ethanol, acetaldehyde, and acetic acid, respectively.

In general the selectivity for a product is defined as

$$S = \frac{I[C_I]}{\Sigma N[C_N]} \times 100\%$$

where $[C_I$ = molar concentration of a product with I carbon atoms, I = number of carbon atoms in product C_I, $[C_N]$ = molar concentration of a product with N carbon atoms, N = number of carbon atoms in product C_N.

Most catalysts (Rh on V_2O_5, V_2O_3, and La_2O_3) were prepared by wet impregnation of the support with an aqueous solution of $RhCL_3 \cdot 3H_2O$. One catalyst [Rh on $Mg(OH)_2$] was prepared by the ion exchange method. All catalysts were dried during 16 h at 383 K in air and reduced overnight at different temperatures. Determination of the number of Rh^{n+} ions in the rhodium catalysts was always performed after reaction. X-Ray diffraction was carried out with a Philips goniometer PW 1050/25 with an X-ray tube Cu 2103/00.

RESULTS

Determination of Soluble (Ionic) Rh

Driessen *et al.* (*13*) succeeded in determining the number of Pd^{n+} ions in various reduced or used Pd catalysts by extracting these catalysts with oxygen-free acetylacetone, under vigorous shaking during 16 h at ambient temperatures (every step was performed with the exclusion of air). At the beginning of the present study on Rh, it appeared that Rh^+ compounds could be extracted easily but samples containing Rh(III) species could not be extracted quantitatively solely by acetylacetone as done by Driessen *et al.*, so a new extracting agent had to be found. After several unsuccessful attempts with various agents (pyridine, acetonitrile, ethylene diamine, acetic acid), the combination of the N-donating acetonitrile CH_3CN with acetylacetone led to a quantitative extraction of Rh(III) model compounds from the surface of various oxides and the following procedures was finally adopted. An oxygen-free mixture (1:1 volumetric ratio) of CH_3CN and acetylacetone was added to the catalysts. These samples were heated under reflux to 340 K and kept for 15 h at this temperature. During the extraction oxygen-free nitrogen was bubbled through the sample. The cell used for extraction was the same as used by Driessen *et al.* (*13*). After extraction the Rh^{n+} content of the solution was determined by atomic absorption spectroscopy. The detection limit with the procedure applied and the equipment available was 2.65×10^{-6} mg Rh^{n+}/ml. Zero extraction from some well-reduced catalysts (some of them also with small Rh particles) shows that the extraction solution does not dissolve the Rh metal of the catalyst. On the other hand, extraction of Rh(III) model compounds $RhCl_3 \cdot 3H_2O$ and $Rh(NO_3)_3 \cdot xH_2O$ was quantitative, within about 1%.

Catalytic Activity and Selectivity

Ichikawa *et al.* (*25*) found that the combination of rhodium metal and vanadium pentoxide had the highest activity and a very high selectivity (S_{C_2-ox}) in the formation of C_2-oxygenates. Consequently we focused our attention on this rhodium/vandium pentoxide catalyst system. However, it soon appeared that after the standard reduction of the catalyst and after the reaction with CO/H_2, V_2O_5 was quantitatively converted into V_2O_3 (as seen by X-ray diffraction). Therefore, catalysts were subsequently prepared directly by using V_2O_3 as support, produced by prereduction of V_2O_5 at different temperatures during 2 days. Prereduction of the support led to an increase in the selectivity of C_2-oxygenates. Variations in the temperature of prereduction of V_2O_5 influenced the surface area of the V_2O_3 and the catalyst activity in the CO/H_2 reaction, but the selectivity for C_2-oxygenates remained constant (Table 1).

The activity and selectivity of the Rh/V_2O_3 catalysts depend strongly on the compound used as the Rh precursor and on the method of preparation.

Magnesium oxide used as a support is converted by the procedure of catalyst preparation into magnesium hydroxide. Reduction at 473 K does not destroy the hydroxide structure, but reduction at 588 K converts the support back into the oxide structure. These changes are reflected by characteristic changes in the product distribution. The most relevant results obtained with various catalysts are collected in Table 2.

The following points deserve attention. (i) Catalysts 1 and 2 with no Rh ions detected are not active in CH_3OH synthesis.

TABLE 1

Influence of Prereduction of the Support on the Rate and Selectivity of Rhodium Supported on Vanadium Oxide for Syngas Reactions

Oxide	T_{red} (K)	SSA ($m^2 g^{-1}$)	S_{C_2-ox} (%)	α_{CO} (%)
V_2O_5				
V_2O_5	—	6	30	1.5
V_2O_3	653	28	45	5.0
V_2O_3	773	13	49	3.4
V_2O_3	873	5	46	2.0

Note. SSA = total surface area measured by physical adsorption of N_2. α = total conversion (into all products, except CO_2). S_{C_2-ox} and α were determined under steady conditions.

It can be seen from the table that the activity in methanol formation increases with increasing concentration of Rh ions (compare Nos. 3 and 4, and Nos. 4 and 6). (ii) In all cases (V_2O_3, La_2O_3, and MgO) the selectivity, but not always the activity, in ethanol synthesis increases with increasing temperature of reduction and decreasing concentration of extractable (ionic) rhodium. (iii) Catalysts based on V_2O_3, most active and selective in C_2-oxygenate formation, contain no detectable amounts of Rh ions. (iv) None of the catalysts studied produced acetic acid.

It has been shown by EXAFS (*26*) and IR (*27*) that Rh particles can be converted into carbonyls. It has been speculated that rhodium in carbonyls formed in this way is positively charged. Consequently, we determined the rhodium content of the Rh/$Mg(OH)_2$ catalyst after reduction at 175°C and after a contact with solely CO at 175°C (24 h with a CO flow of 4 ml/min). The number of Rh^{n+} species decreased from 27% found just after reduction to 14% determined after the CO exposure, although this catalyst showed an extended carbonyl formation (*21*).

Figure 1 shows a more detailed picture of the product distribution obtained with Rh/V_2O_3 catalysts. The data reveal that reduction of the catalyst at 400°C results in a higher selectivity in oxygenates than reduction at 200°C.

The experiments with various V_2O_3-supported catalysts were repeated many times and it appeared that a high selectivity for C_2-oxygenates (*S* as high as 70%) can be obtained when a certain well-defined Rh chlorine complex is used as the rhodium

TABLE 2

Activity and Selectivity of Rh Catalysts in Syngas Reactions

Catalyst	H_2/CO ratio	Metal loading (wt%)	T_{red} (K)	Selectivity, *S* (%)						α_{CO} (%)	Rh ionic (%)	S_{C_2-ox} (%)
				C_1	C_2^+	MeOH	CH_3CHO	EtOH	ProOH			
Rh/V_2O_3	2	4.5	473	50	22	—	4	24	—	1.3	0	28
Rh/V_2O_3	2	4.5	673	26	25	—	3	46	—	3.4	0	49
Rh/La_2O_3	2	4.5	473	17	8	45	—	30	—	0.3	11	30
Rh/La_2O_3	2	4.5	673	21	17	13	—	49	—	0.1	4	49
Rh/$Mg(OH)_2$	7	3.0	473	47	24	16	2	9	—	0.1	36	11
Rh/MgO	7	3.0	588	38	39	—	18	5	2	0.2	0	23

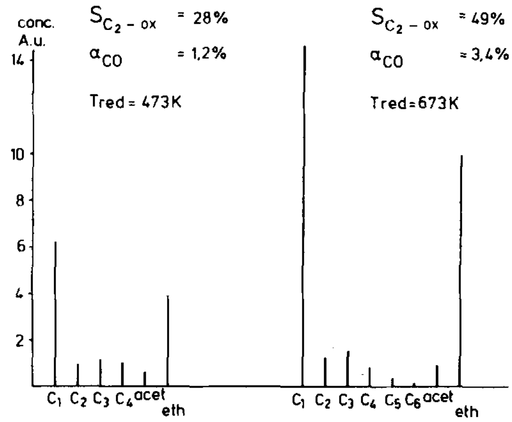


FIG. 1. Product distributions of Rh/V_2O_3 catalysts at different reduction temperatures. C_x = total concentration of hydrocarbon with x carbon atoms. Acet = acetaldehyde concentration. Eth = ethanol concentration.

precursor (we will deal with this subject in another article). The C_2-oxygenate selectivity has always been found to be higher after reduction at a higher temperature (200 and 400°C have been compared). A higher temperature of reduction led in some cases not only to a relative suppression of hydrocarbon formation but also to an absolute lower formation of them.

DISCUSSION

Data presented in Table 2 allow two conclusions to be made in a straightforward way.

(i) A sympathetic correlation exists between the concentration of ionic Rh and the selectivity in methanol synthesis. It should be mentioned that an additional argument in favor of this correlation between methanol synthesis and Rh ions comes from the work of Poels *et al.* (*21*). By using ESR spectroscopy it was found that catalysts active in methanol synthesis contained Rh(II) ions. Recently, Botman and one of us (*28*) found, by using extraction techniques, that such a sympathetic correlation also exists for Pt catalysts. Together with data in an earlier publication on Pd catalysts (*13*) there is now evidence for three metals (Pt, Pd, and Rh) that the activity in methanol synthesis is related to the presence of Rh^{n+}, Pt^{n+}, and Pd^{n+} ions.

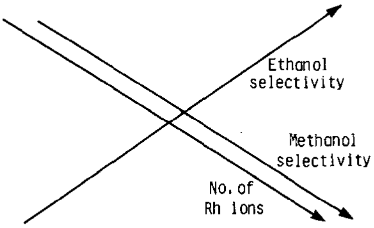
(ii) The presence of Rh ions in the catalyst is evidently not necessary for the formation of C_2-oxygenates. The relation between various factors mentioned up to now can be summarized by Scheme 1.

The industrial catalyst for methanol synthesis is based on the Cu–ZnO combination. The question is whether the conclusions concerning Pt, Pd, and Rh (see above) can also be extended to the Cu–ZnO catalysts. We have not made any detailed study on this question but let us state here the following remarks:

(a) Herman *et al.* (29) found that active Cu catalysts always contain some unreduced Cu(I); these authors suggest Cu(I) as the catalytic center for methanol synthesis.

(b) It is known that addition of CO_2 to the syngas mixture increases the rate of methanol synthesis (*30*) and the stability of the Cu catalysts. One of the functions of CO_2 is most probably to oxidize Cu (or to keep it oxidized).

(c) Driessen *et al.* (*13*) observed that Pd catalysts reached steady-state activity after an induction period. They made comparative experiments with the Cu–ZnO catalysts and revealed that these catalysts behave in the same way, having also an induction period. The induction period of the Cu–ZnO catalyst can be considerably shortened when the catalysts are preoxidized before they are brought into contact with the syngas.



SCHEME 1. Schematic representation of the correlation between methanol and ethanol selectivity and the number of rhodium ions.

All three points (a–c) are compatible with a model in which, similar to Pt, Pd, and Rh, the Cu ions are centers of the catalytic activity in methanol formation.

Data presented in this paper, as well as various points from the papers by Ichikawa *et al.* (*6,25*), lead to the conclusion that the catalytic centers for CH_3OH formation are not identical to those for C_2-oxygenate formation. The latter sites can be located on the support and function as Orita *et al.* (*31*) suggested: a formate intermediate on the supports reacts with alkyl groups supplied from the metallic surface. Alternatively the metallic M^0 surface can be modified to form C_2-oxygenates, while the M^{n+} sites are active in CH_3OH synthesis.

The first possibility cannot be completely excluded on basis of the presented data, but there are some arguments against application of this idea to our catalysts. First, reduction of catalysts at higher temperatures, such as reduction of Rh on magnesium (hydr)oxide, results in a decrease in the number of OH groups on the surface because of the dehydration of this surface and, as a consequence, in a decrease in the probability of formate formation. However, the results show that reduction at higher temperatures of this catalyst results in an increase in ethanol selectivity. Second, V_2O_3, the best support when C_2-oxygenates are to be formed, is not known as an oxide particularly suitable for formate formation (*31*). Third, Poels *et al.* (*21*) did not observe by IR the presence of formate species on the catalyst surfaces with either $Mg(OH)_2$ or MgO as the carrier, although these catalysts were active in methanol or ethanol synthesis, respectively. Because of all these points we prefer to speculate that the Rh^0 metal surface is the place where the activity in $C_{2\text{-ox}}$ formation is localized. However, it is then necessary to explain the crucial role of the supports, if they are not alone the active surface for the formation of C_2-oxygenates and also if their function is not limited just to the stabilization of Rh ions.

Tauster *et al.* (*32,33*) discovered that metals on supports, when reduced by H_2 at sufficiently high temperature, lose their ability to interact with H_2 or CO and show a very low catalytic activity in some reactions. They studied this effect in more detail with Ir and various supports (*32*) and they have seen that the suppression of chemisorption capacity for CO and H_2 is particularly high with oxides like V_2O_3 or TiO_2, the "best" supports for Rh when C_2-oxygenates have to be formed. The suppression of CO and H_2 chemisorption is not due to sintering (only) and Tauster *et al.* suggested that the reduced form of the support, formed by high-temperature reduction, interacts so strongly with the metal that the metal loses its chemisorption capacity. They called the phenomenon "Strong Metal Support Interaction (SMSI)." In the meantime a vast volume of information on SMSI has accumulated and the explanation almost generally accepted now is as follows (*34–37*). The high-temperature reduction produces a lower oxide which, due to its extra *d* electrons, interacts more strongly with the metal. The lower oxide is transported by diffusion onto the metal (*36*) and spreads over the surface during reduction. Also the oxidic material which comes onto the metal in previous steps of catalyst preparation can spread over the metal during reduction. Oxidation causes recrystallization of this spread oxide and reinstalls almost fully the original capacity. The data of Tauster and Fung (*32*) (see Fig. 1, Table 1), as well as our own preliminary data indicate that a metal on V_2O_3 is, after reduction at 673 K, in the SMSI state. According to the most plausible explanation of SMSI it means that it is covered by the oxidic material originating from the support.

The last-mentioned explanation of SMSI would also help us to understand why the Rh/V_2O_3 (or Rh/TiO_2, Rh/Ta_2O_3, etc.) catalysts in the SMSI state show a higher selectivity for C_2-oxygenates than when reduced at the lower temperature. Blocking of the rhodium surface can diminish hydrocarbon synthesis, since this reaction requires a large ensemble of active atoms (*1,2*). On the other hand, an oxide promoter can influence CO dissociation and insertion in the way that Sachtler has postulated (*38*). It is interesting to note that other oxides also known as promoters of C_2-oxygenate formation can appear on the rhodium surface (*39*).

Data presented in this paper are at variance with the mechanism suggested by van den Berg *et al.* (*40*). According to this work Rh^{n+} ions are the sites on which the alkyl fragments produced on Rh metal recombine with CO to form oxygen-containing products. We have seen that the most active catalysts in C_2-oxygenate formation do not contain unreduced Rh^{n+} centers and the activity of the other catalysts is actually antipathically correlated with the concentration of Rh^{n+} species.

Watson and Somorjai (*18,41*) observed that partially oxidized Rh surfaces and rhodium on lanthanum oxide showed an activity in C_2-oxygenate formation. This observation also can be explained by a model in which lanthanum oxide or rhodium oxide act as a promoter on the rhodium surface.

CONCLUSIONS

(1) Presence of Rh ions is essential for the activity in the methanol synthesis. The same holds for Pt and Pd catalysts.

(2) Rh ions are not the active centers of the C_2-oxygenate formation; activity in this reaction is related to the metal surface modified by the presence of the support on it.

(3) A high selectivity in the C_2-oxygenate formation can be achieved with Rh/V_2O_3 catalysts.

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