

# Controlled stepwise preparation of alumina supported $\text{Re}_2(\text{CO})_{10}$ catalysts by gas-phase adsorption technique: TPR, TPO and pulse chemisorption study

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## Abstract

Carbonyl-precursor-based alumina supported rhenium catalysts were prepared by controlled gas-phase sublimation technique. Oxygen pulse chemisorption results showed the rhenium particles to be well dispersed. With successive deposition–decarbonylation cycles metal loading was increased by controlled manner, and the dispersion was better than for catalysts with similar metal content prepared in a single deposition step. Temperature-programmed reduction profiles showed that the interaction between oxidised rhenium particles and the support becomes weaker with increasing rhenium content. Reduction behaviour of the catalysts prepared with total decarbonylation steps differed from that of catalysts prepared by single-step method. Accurate oxidation temperatures were determined by temperature-programmed oxidation. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Supported rhenium oxide particles are reported to form an active and selective catalyst for metathesis reaction [1–5]. The interaction between support and rhenium as well as the nature of the oxidised phase have been studied by a number of different techniques, such as IR [6], XANES [7], Raman [8–10], NMR [2] and XPS [5]. There is disagreement about the nature of the oxidised phase however [11].

Information about the structure of the supported rhenium oxide phase has been obtained from Raman studies. Rhenium oxide is present as two kinds of monomeric  $\text{ReO}_4^-$  species on the alumina sur-

face, each containing three terminal  $\text{Re}=\text{O}$  bonds and one bridging  $\text{Re}-\text{O}-\text{Al}$  bond. The ratio between the two species depends on the rhenium loading [8]. Differences have been characterised by temperature-programmed reduction (TPR) [10]. Other authors have reported the presence of  $\text{ReO}_4^-$ -species on alumina surface [11–15].

Only a few authors have characterised the oxidation behaviour of supported rhenium particles [11,16–19]. The molar ratio between oxygen and rhenium during the oxidation depends on the temperature of the adsorption [18]. Maximum level of oxygen uptake was obtained in the between 300 and 500°C. Catalysts with low metal loading are more difficult to oxidise and reduce than catalysts with higher rhenium loadings, probably due to the strong interaction between metal particles and support. Furthermore, the oxidation is a slow process

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that occurs both on the surface and in the body of rhenium [17]. Okal et al. [11] reported four temperature regions for oxygen chemisorption on sintered Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Paryjczak et al. [18] in turn, distinguished three temperature regions for oxygen adsorption. In spite of above studies, alumina supported rhenium particles have not been well characterised by temperature-programmed oxidation (TPO).

Reducibility of supported rhenium has been discussed in several papers and various TPR profiles have been published [16,20–29]. Comparison of the results is limited due to the different methods of preparation and pre-treatment of the catalysts. Arnoldy et al. [25] showed that reducibility depends on both the rhenium content and support properties. Temperature of the peak maximum varies between 275 and 600°C.

Most of the samples and catalysts discussed above were prepared by impregnation. Our method is controlled gas-phase adsorption in a fluidised-bed reactor with an highly accurate control of the preparation procedure. In earlier work we have prepared supported rhenium catalysts with different metal loadings by controlled gas-phase deposition method and discovered good activity and selectivity of the catalysts in thiophene HDS reaction [30]. The same reactor arrangement has been successfully applied for the preparation of molybdenum, tungsten and cobalt catalysts [31–33].

The aims of the present work were to characterise, by oxygen pulse chemisorption, the dispersion of rhenium in the surface with increasing metal loading and with different methods of preparation. TPR profiles were recorded to study the reduction behaviour of the catalysts since hydrogen has a significant role in the hydrotreating processes.

## 2. Experimental

### 2.1. Reactants and catalyst preparation

Precursor (Re<sub>2</sub>(CO)<sub>10</sub>, 99%) was supplied by Strem chemicals and used without further purification. Aldrich provided the support material (aluminium oxide, Brockmann I, standard grade, neutral and activated, 150 mesh, 58 Å, surface area 155 m<sup>2</sup>/g). The support was preheated at 500°C under vacuum for 10 h so that all physisorbed water was removed

from the pores and a sufficient amount of OH-groups was obtained on the surface. Handling of the support and catalyst the preparation were carried out in air-sensitive manner.

The catalysts were prepared by gas-phase adsorption technique; the fluidized bed reactor used for the preparation is described elsewhere [31]. Two temperatures (115 and 120°C) were applied during the deposition of the precursor. Nitrogen (99.999%, AGA) was used as carrier gas. The deposition time varied between 4 and 17 h when a single deposition pulse was employed. Catalysts with higher rhenium loading were prepared by multiple pulse technique in which the samples were partially decarbonylated (PDC) under N<sub>2</sub> flow at 200°C or totally decarbonylated (TDC) under H<sub>2</sub> (99.999%, AGA) flow between two deposition pulses. In this case, we used standard reaction temperature (115°C) and time (6 h). Further details of the preparation procedure as well as the HDS activity results are given elsewhere [30].

### 2.2. Determination of rhenium content

Combined AAS (atomic absorption spectrometry)-EDXRF (energy dispersive X-ray fluorescence) technique was used to the determination of metal content. The EDXRF was calibrated on the basis of the AAS results. A sample of the rhenium catalyst was dissolved in acidic solvent and the rhenium content was measured by AAS. The calibration standard for the AAS measurements was KReO<sub>4</sub> (99.99%, supplied by Aldrich) and the procedure followed the instructions given in the instrument manufacturer (Varian, Spectr AA-400) manual.

Metal contents of the catalysts were measured by EDXRF. The instrument was equipped with a Si-Li detector and Cd (109) radioisotope was the source of radiation. The resolution of the apparatus was 0.15 KeV and the measurement time 100 s. All samples were measured three times and between each measurement the sample holder was turned 90° to obtain the most accurate results.

### 2.3. Temperature-programmed methods

Oxygen pulse chemisorption, temperature-programmed reduction and oxidation were performed by a Micromeritics AutoChem 2910 instrument equipped

with a thermal conductivity detector (TCD). The measurements were based on difference in conductivity between flows running through the sample tube and reference changed when oxygen pulse chemisorption ( $\text{PCO}_2$ ) was carried out after the carbonyl groups had been removed from the surface. As soon as a stable baseline had been achieved by using helium (99.9999%, AGA) as carrier gas, a standard volume (1 ml) pulse of oxygen (99.9999%, AGA) was introduced through the sample tube. Different amounts of oxygen were adsorbed on the surface depending on the sample. The instrument continued pulsing until no more oxygen was adsorbed. The flow rate of the carrier gas was 10 ml/min and the temperature of the oven was 250°C.

Temperature-programmed reduction was performed after  $\text{PCO}_2$ . The sample was cooled at room temperature and 10%  $\text{H}_2/\text{Ar}$  mixture gas flow was switched on (flow rate 10 ml/min). As soon as a stable baseline was achieved, 10°C/min ramp rate was applied and the final temperature was 500°C.

After the reduction tests, (TPO) profiles were measured. The flow gas containing 5%  $\text{O}_2/\text{He}$ . Flow and the ramp rate were similar to those in the TPR experiments.

#### 2.4. Powder X-ray diffraction

X-ray diffraction spectra were collected with a Bruker-AXS D8 diffractometer utilising a Cu  $K\alpha$  ( $\lambda = 1.540$  nm) X-ray source and  $2\theta$  range between 5.0 and 75.0°. Measurements were made after oxidation and the pure alumina background was subtracted from the spectra.

### 3. Results and discussion

#### 3.1. Oxygen pulse chemisorption

$\text{PCO}_2$  results for the alumina supported rhenium catalysts are presented in Table 1. Dispersions and other properties were calculated assuming that  $\text{ReO}_4$  particles would form on the surface.

In our previous TPD study, we observed a two-stage desorption process for alumina-supported  $\text{Re}_2(\text{CO})_{10}$  particles at low rhenium loading and four peaks at high coverage [34]. Supported by the literature [6,35] we concluded that in the first stage of the desorption the bimetallic rhenium molecule dissociates to  $\text{Re}(\text{CO})_3$  and further heating leads to the desorption of the final three carbonyls. The results support the suggestion that, after the desorption process, rhenium is in monometallic form on the surface and after oxidation the most likely phase is  $\text{ReO}_4$ .

Molar ratio and dispersion results indicate that when the metal loading is low (1 wt.%) the dispersion of the metal is good. Nearly all rhenium atoms are available on the surface. As expected, increase in rhenium loading diminishes the dispersion of the particles. Samples A to F were prepared without any decarbonylation process and dispersion was decreased to 43% (11.1 wt.% rhenium sample).

Evidently, carbonyls create steric hindrance during the preparation procedure and limit the metal dispersion as the metal loading increases. To avoid this hindrance, we applied successive deposition and decarbonylation.  $\text{PCO}_2$  results for partially and totally decarbonylated rhenium/alumina catalysts suggest that dispersion as well as other investigated properties are better for catalysts with decarbonylation treat-

Table 1  
Uptake of oxygen by rhenium/alumina catalysts at 250°C

Catalyst code	Rhenium (wt.%)	$\text{O}_2$ sample (mmol/g)	Molar ratio ( $\text{O}_2/\text{Re}$ )	Dispersion (%)	Metallic surface area of rhenium ( $\text{m}^2/\text{g}$ )	Active particle diameter (nm)
A	1.0	0.11	2.0	100	211	1.3
B	3.0	0.23	1.4	72	151	1.9
C	3.7	0.28	1.4	72	151	1.9
D	8.3	0.48	1.1	53	112	2.6
E	8.9	0.43	0.9	46	96	3.0
F	11.1	0.52	0.9	43	91	3.2
PDC	10.4	0.56	1.1	54	113	2.6
TDC	12.7	0.67	1.4	68	142	2.1

ments. Partial decarbonylation technique leaves average three carbonyl groups per one rhenium atom and this still creates some hindrance. Steric limitations are removed only by applying total decarbonylation between the preparation cycles and then the dispersion of the metal increases.

Dispersion of the metal was better with gas-phase adsorption method compared to impregnation method. The present results suggest that our successive deposition-total decarbonylation cycles even further enhance the dispersion of rhenium.

Rhenium oxide particle size increases with the rhenium content and some of the metal is inevitably buried within larger rhenium oxide stacks. As well, some layers of rhenium carbonyls may form at high metal loadings if the carbonyls are not removed from the surface. Total decarbonylation between the deposition cycles helps to prevent some of the above problems.

According to the XRD spectra, no crystalline rhenium oxide phase was present on the surface and this further indicates that the rhenium oxides are well-dispersed in the surface.

### 3.2. Temperature-programmed reduction (TPR)

TPR patterns of the Re/Al<sub>2</sub>O<sub>3</sub> catalysts are presented in Fig. 1. The profiles on the left side (A–C)

were recorded for catalysts prepared by single deposition pulse technique, and those on the right, PDC and TDC for catalysts prepared by multiple deposition pulses with, respectively, partial and total decarbonylation between each pulse. Catalyst D was prepared with three deposition pulses without decarbonylation step.

At low rhenium loading (A), the temperature of the reduction maximum is 300°C. The temperature decreases with increase in rhenium content (to 274°C for catalyst B and 254°C for catalyst C). Furthermore we can distinguish a minor shoulder for catalyst C at near 315°C.

The main peak in patterns A–C seems to become narrower with increasing rhenium loading. At low metal loading oxidised rhenium particles are in strong interaction with the alumina surface and the interactions weakens with increase in the metal content. The decrease in the reduction temperature support this suggestion.

The slight shoulder for catalyst C indicates changes in the reduction behaviour with high metal loading. Larger particles may form with increasing metal content, although XRD results suggests that no crystalline phase exist in the surface. Catalyst D was prepared with three deposition pulses but with no decarbonylation step between the pulses. Metal content increased by only 3 wt.%, but changes in the reduction pattern

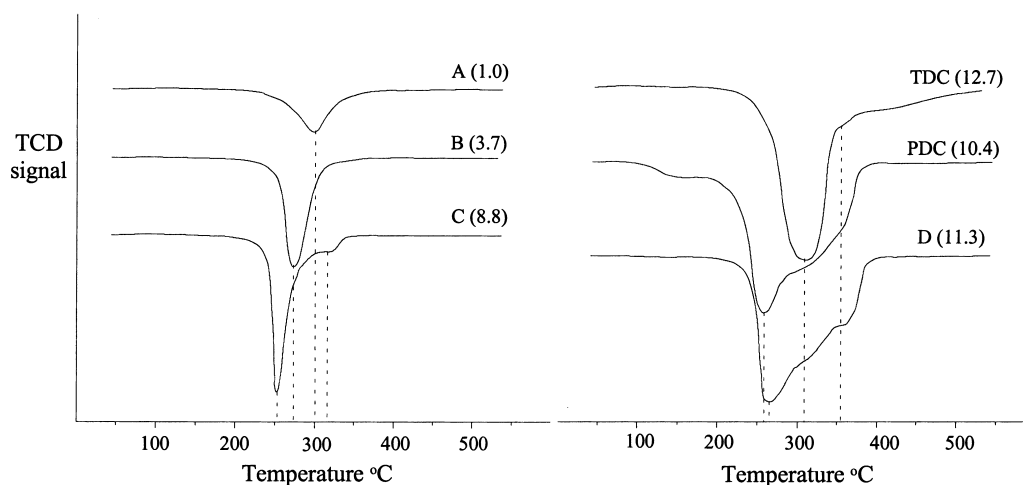


Fig. 1. TPR profiles of rhenium/alumina catalysts with different metal loading. Catalysts A–C were prepared with a single deposition pulse, catalysts TDC and PDC with multiple pulses with intervening total and partial decarbonylation, respectively. Catalysts D was prepared with three deposition pulses and no decarbonylation. Metal loading is shown in parentheses.

Table 2  
Uptake of hydrogen by rhenium/alumina catalysts during TPR experiment

Rhenium (wt.%)	Amount of Re sample (mmol/g)	H <sub>2</sub> consumption (ml/g) sample (STP)	H <sub>2</sub> sample (mmol/g)	Molar ratio (H <sub>2</sub> /Re)
1.0	0.05	5.3	0.24	4.3
3.0	0.16	11.2	0.50	3.1
3.7	0.20	12.1	0.54	2.7
8.3	0.44	18.2	0.81	1.8
8.9	0.47	18.9	0.84	1.8
11.1	0.59	20.0	0.89	1.5
PDC	0.57	28.3	1.26	2.2
TCD	0.66	42.2	1.88	2.8

was marked. The reduction begins in nearly the same temperature region as with catalyst C, but the much broader profile suggests that the reduction behaviour is no longer uniform.

The profile for PDC is closely similar to that for catalyst D. Partial decarbonylation under nitrogen atmosphere between the preparation pulses did not significantly change the reduction behaviour. Distinct changes are observed, however, when all the carbonyls are removed during the preparation cycles. The TPR profile is much narrower indicating much more uniform reduction behaviour.

Temperatures of the peak maximum were lower in our work than was from the literature data. One explanation is our method of preparation. The catalyst precursor contained no impurities since all steps were carried out in gas-phase. Arnoldy et al. [25] have reported that impurities and additives change the reduction behaviour. Furthermore, we obtain well-dispersed metal particles on the surface by gas-phase preparation from zero-valent precursors and this may decrease of the temperature of the reduction maximum.

Table 2 shows the hydrogen consumption and molar ratios (H<sub>2</sub>/Re) for Re/Al<sub>2</sub>O<sub>3</sub> catalysts. H<sub>2</sub>O was

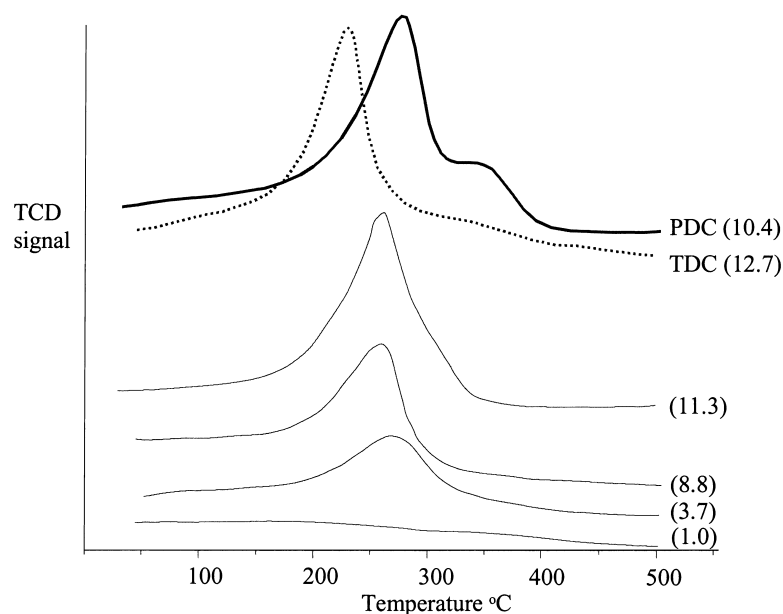


Fig. 2. TPO profiles of reduced rhenium/alumina catalysts with different metal loading (PDC and TDC, see Fig. 1).

formed during the TPR experiment and the molar ratios verify the trend found in the PCO<sub>2</sub> results.

### 3.3. Temperature-programmed oxidation (TPO)

Experiments were performed to determine the oxidation temperature of the catalysts. TPO profiles of the reduced Re/Al<sub>2</sub>O<sub>3</sub> are presented in Fig. 2. The maximum temperature of the profile varies with the rhenium loading. At low rhenium loading (A), no oxygen consumption is observed at all. Probably the interaction between reduced rhenium particles and the surface is so strong that the oxidation is somehow restricted. Chadzynski et al. [17] observed a similar phenomenon.

Increase in rhenium content weakens the interaction and oxidation becomes possible (catalyst B, at 268°C), and further increase in the metal loading decreases the temperature of the oxidation maximum (catalyst C at 265°C and catalyst D at 265°C).

Larger differences are observed between the PDC and TDC catalysts. The TPO profile of the TDC catalyst, which was prepared with total decarbonylation steps between each preparation pulse, is very similar to the patterns discussed above. On the other hand, the catalyst with partial decarbonylation produced a broad profile with the main peak and a clear shoulder. Furthermore, the temperature of the oxidation maximum was higher (main peak at 277°C and shoulder at 340°C). In this case, the oxidation process is complex with several steps.

## 4. Conclusions

PCO<sub>2</sub> results suggest that the rhenium carbonyl precursors create steric hindrance on the surface causing the dispersion to decrease with increasing rhenium loading. Loss of the dispersion can be avoided by applying pulse technique with a decarbonylation step between each preparation pulse. Total decarbonylation in hydrogen flow was found to be the best method of increasing metal content without losing the dispersion of the metal. In our reactor arrangement, the metal content can grow in a controlled manner and at the same time well-dispersed metal particles are obtained.

Increase in rhenium loading as well as changes in the preparation procedure effected clear changes in the

TPR profiles. With catalysts with low metal content, profiles consisted of one clear peak, and with increase in the rhenium content the temperature of the reduction maximum decreased. Furthermore, new shoulders appeared in the profiles and peaks became broader. The distance between two oxidised rhenium centres shortened, so that the interactions between two rhenium neighbours became stronger and the reduction behaviour became to more complex. Application of total decarbonylation caused more uniform reduction behaviour.

Catalysts with low metal loading (1 wt.%) gave a flat line in TPO tests. Interactions between rhenium oxide and the support were so strong that no oxidation was observed. Response in the TPO patterns was obtained with increase in rhenium content. As in TPR profiles, the maximum of the oxidation temperature decreased with increasing rhenium loading, but the change was only slight. The shape of the patterns changed when a different preparation procedure was applied. With total decarbonylation steps, metal particles well-dispersed and homogeneous as indicated by the greater uniformity of the TPO profile of the TDC catalyst than of the PCD catalyst.

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