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Controlled gas-phase preparation and HDS activity of $Re_2(CO)_{10}$/alumina catalysts

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Re/Al_2O_3 catalysts were prepared from a carbonyl precursor by controlled gas-phase deposition with all conditions accurately monitored by a computer-programmed CVD reactor. The catalysts were made in an inert atmosphere. Growth of the rhenium concentration was studied with different preparation procedures and with different times and temperatures of deposition. Rhenium loading of the catalysts varied between 0.3 and 12.8 wt%. The activity of the catalysts was tested in thiophene hydrodesulfurization reaction and the results suggest good activity in low rhenium loading. The portion of n-butane among the reaction products was high for the catalysts with high rhenium content.

Keywords: controlled gas-phase preparation, fluidized-bed reactor, ALE, rhenium carbonyl, $Re_2(CO)_{10}$, alumina, hydrodesulfurization, HDS

1. Introduction

Rhenium-based supported catalysts have been used in metathesis [1–8], reforming [9–12], hydrogenation [13] and various hydrotreating processes [14–19] such as hydrodesulfurization. Good activity and selectivity of Re_2O_7/Al_2O_3 catalysts has made them one of the most widely used metathesis catalysts [20]. In the systematic study made by Pecoraro and Chianelli [15] rhenium was found to be active in the hydrodesulfurization of dibenzothiophene. Other studies as well have demonstrated the activity of supported rhenium catalysts in HDS reaction [16,19].

Impregnation is by far the most common technique for preparing supported rhenium catalysts [1,2,4,21]. Ammonium perrhenate NH_4ReO_4 [1,2,7,8,16,17,22], perrhenic acid $HReO_4$ [23–27] and Re_2O_7 [3,19,28–30] are the most frequently applied metallic precursors. Alternatively Re_2O_7/Al_2O_3 catalysts have been prepared by the sol–gel method, with use of $Al(OiPr)_3$, perrhenic acid and water [5].

To some extent supported rhenium catalysts have also been prepared by vapor deposition. Alumina-supported catalysts have been made by a stationary bed technique, with use of a pre-evacuated reactor cell for dosing the $Re_2(CO)_{10}$ precursor [31–33]. A similar technique has been used in the preparation of $Re_2(CO)_{10}$ supported on Na-Y zeolite [34]. However, the gas-phase technique has also been used for preparation of the zeolite-supported $Re_2(CO)_{10}$ catalysts [9,35]. Sublimation of $Re_2(CO)_{10}$ onto supercages of the zeolite was discovered to be a very effective way to deposit the rhenium. The catalytic activity has been better than reported for similar rhenium catalyst prepared by impregnation [9].

Vapor deposition of metallic precursors on oxide and zeolite surfaces is an effective and flexible way to prepare highly dispersed metal catalysts. Because solvents are not needed a clean metal surface can be achieved with no contamination from the liquid phase. The spectroscopic characterization is easier since the catalysts are structually well-defined [36].

Metal carbonyls are good precursors for the vapor deposition [37–40] mainly because they sublime at low temperatures. The main advantage is that low-valent metal particles can be obtained on the surface without the need for high deposition temperature [41]. The reaction between metal carbonyl and the surface is an oxidate addition due to the zero-valent character of the precursor. Controlled metal contents can be achieved and the catalysts obtained are active in thiophene HDS reaction [42].

In the present work we aim to demonstrate the use of vapor deposition techniques for the preparation of hydrodesulfurization catalysts from a rhenium carbonyl precursor. The deposition method and the control of rhenium content are described as well as the spectroscopic characterization of the decarbonylation process. The catalyst is treated with hydrogen sulfide and tested for activity and selectivity in hydrodesulfurization catalysis of thiophene. The performance of the catalyst is compared with a standard industrial catalyst.

2. Experimental

2.1. Reagents and support pretreatment

Aluminum oxide (Aldrich, manufacturer values, Brockmann I, standard grade, neutral and activated, 150 mesh,

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58 Å, surface area 155 m^2/g) was used as support material. $Re_2(CO)_{10}$ was the metallic precursor and no further purification was performed. Nitrogen (AGA, 99.999%) was used as carrier gas during the preparation and partial decarbonylation procedure. Total decarbonylation was carried out in hydrogen flow (AGA, 99.999%).

The support was heated at 500 °C in vacuum for 10 h to remove physisorbed water from the pores of the support. Afterwards the support was transferred to a nitrogen glove box and the rest of the preparation procedure was conducted without exposure to air or moisture.

2.2. Catalyst preparation

Catalysts were prepared by a controlled chemical vapor deposition (CVD) technique in a fluidized-bed reactor connected to a nitrogen glove box. The system includes controlled temperature zones, a circulation pump and gas flow controllers. The preparation scheme has been reported earlier [37].

As soon as the reactor and chemisorption temperature was achieved the metallic precursor was led to the reactor and deposition began. The nitrogen flow carries $Re_2(CO)_{10}$ through the support material, where adsorption occurs.

The catalysts were prepared by three methods. In the first method, adsorption occurred during a single deposition pulse. Temperature was 90, 115 or 120 °C. The shortest deposition time was 4 h and the longest 17 h. In the second method, after a single deposition pulse (115 °C and 6 h) catalysts were partially decarbonylated (PDC) in the same reactor at 200 °C (nitrogen flow), and the preparation continued with five identical deposition–partial decarbonylation cycles. In the third method, catalysts were totally decarbonylated (TDC) under hydrogen flow at 450 °C after each deposition pulse (115 °C and 6 h) in a special reduction tube outside the glove box [37]. Five deposition–total decarbonylation cycles were performed.

2.3. Catalyst characterization

Rhenium loadings were determined by a combined atomic absorption spectrometry (AAS)–energy dispersive X-ray fluoresence technique (EDXRF). Samples of catalysts with different metal contents were dissolved by heating in acidic solvent. AAS standards ($KReO_4$, 99.99%) were prepared by using the guide from the instrument manufacturer (Varian, Spectr AA-400). N_2O–acetylene flame was applied. AAS was used to determine rhenium loading of these catalysts.

Metal contents of all catalysts were measured by EDXRF. The system included a Si–Li detector and the source of the radiation was CD-109 radioisotope. Measurement time was 100 s and 0.15 keV resolution was achieved. The solid catalyst was placed between two thin mylar sheets and was measured three times, after each measurement the sample holder was turned $\sim 120^\circ$ to achieve the most accurate results. AAS results were used for the EDXRF calibration.

A Nicolet Impact 400 D FTIR (with diffuse reflectance apparatus and mercury–cadmium–tellurium detector) located below the glove box was used to confirm that the deposition was successful.

The sulfur content of the catalysts was determined with an elemental analyzer (CE instrument EA 1110) after sulfidation (10% H_2S in hydrogen, AGA) treatment.

2.4. HDS activity measurements

Activity of the catalysts was measured in thiophene (Aldrich, 99%) HDS reaction. Tests were made in the batch reactor described in our previous study [42]. Prior to the reaction, catalysts were sulfided at 2.0 bar pressure (10% H_2S in hydrogen) at 370 °C for 2 h. The amount of the rhenium catalyst in the test was 0.2 g (0.003–0.117 mmol rhenium). Less of the commercial CoMo/alumina catalyst was used (0.05 g, 0.085 mmol metal) so that the amount of metal moles would be at similar molar level. The reactor was cooled after sulfidation and flushed with nitrogen (AGA, 99.99%). Prior to thiophene transfer the system was evacuated. HDS reaction was performed at 4 bar hydrogen pressure (AGA, 99.99%) at 340 °C for 2 h. The reaction products were analyzed by gas chromatography (HP, 5890 series II, FID detector, and 60 m HP 1 column).

3. Results and discussion

3.1. Preparation and rhenium loading

Table 1 shows the preparation conditions and rhenium loading of the catalysts. The metal content of the single pulse catalysts varied between 0.3 and 8.3 wt%. Use of low temperature (90 °C) allowed the preparation of catalysts with low metal loading. Since commercial reforming catalysts often contain only a small amount of rhenium (0.3 wt%) [43], it is important to understand how to prepare rhenium catalysts with low metal content.

Rhenium content increased when the temperature was raised to 115 °C. Further temperature increase (to 120 °C) caused more rapid sublimation and a part of the $Re_2(CO)_{10}$ was recovered in the colder parts of the reactor. Metal content up to 8.3 wt% was nevertheless achieved.

Saturation level (calculated maximum coverage would be about 25 wt%) was not achieved. Evidently steric hindrance limits the adsorption of the precursor to a part of the support surface due to the large size of the molecule. At 17 h reaction time the amount of the rhenium was more than three times what it was at 10 h. Figure 1 shows the metal content as a function of deposition time after a single deposition pulse at 115 °C.

The behaviour of $Re_2(CO)_{10}$ on alumina differs noticeably from the behaviour of $W(CO)_6$. In the case of tungsten, 2 wt% metal content was achieved during 5 h deposition and further increase in deposition time brought about only minor increase in the metal loading [37]. The rhenium

Table 1
Preparation methods for $Re_2(CO)_{10}/Al_2O_3$ catalysts.

Catalyst	Sublimation pulses	Temperature (°C)	Time (h)	Decarbonylation	Rhenium content (%)
Single pulse					
A	1	90	4	250 °C, 3 h	0.3
B	1	115	6	210 °C, 4 h	0.9
C	1	115	6	–	1.0
D	1	115	10	–	1.0
E	1	115	14	–	2.0
F	1	115	17	–	3.7
G	1	120	17	–	8.3
Multiple pulses					
H	2	115	17	–	11.1
I	2	115	6 + 4	210 °C, 4 h	3.0
J	3	110	4	210 °C, 4 h	4.1
K	2	115 + 125	17 + 18	–	8.9
PDC	5	115	6	5 × 200 °C, 5 h	10.4
TDC	5	115	6	5 × 200 °C, 5 h	12.7

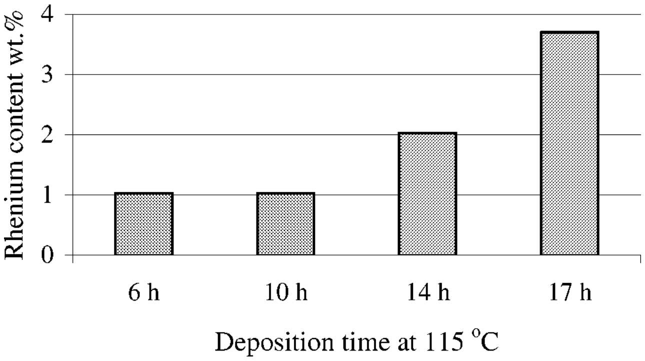

Figure 1. Rhenium content on alumina as a function of deposition time at 115 °C.

content, in turn, remained at more or less steady level during the first 10 h and then increased (figure 1). The difference may due to the higher deposition temperature required in the case of the rhenium precursor.

As noted above, the ten carbonyl groups of the rhenium precursor create steric crowding on the alumina surface, which hinders the adsorption of further $Re_2(CO)_{10}$. However, metal loading can be increased in a controlled manner by removing a part of the carbonyl groups from the surface before re-introducing the precursor. Figure 2 shows the growth of the rhenium content during five deposition–decarbonylation pulses. The step between the first and the second pulses increases the rhenium loading most, evidently because there is then more space for rhenium precursors to chemisorb on the surface.

IR spectra suggest the presence of carbonyl groups after decarbonylation at 200 °C. Bands at 1921 and 2035 cm^{-1} suggest the formation of rhenium tricarbonyl, as Escalona Platero et al. [33] have proposed. Three carbonyl groups still create steric hindrance, but to much lesser extent, and the rhenium precursor has space to adsorb on the surface. After five successful cycles the metal loading was 10.4 wt%.

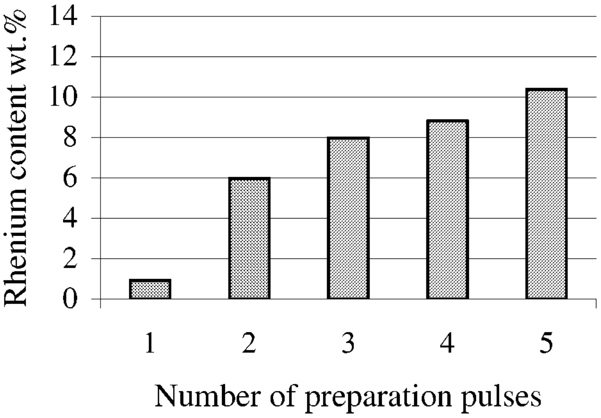

Figure 2. Rhenium content on alumina during five deposition–partial decarbonylation cycles at 115 °C.

The advantage of applying partial decarbonylation is that three carbonyl groups isolate rhenium particles sufficiently from one another so that the formation of larger rhenium particles is avoided. A good level of dispersion of the metal is thereby assumed.

Decarbonylation during 6 h at 450 °C (H_2 flow) removes all carbonyl groups from the metal particles, so that there is no steric hindrance during the next deposition pulse. IR was used to confirm the absence of the carbonyl groups. Figure 3 shows the metal loading during five deposition–decarbonylation cycles. Rhenium content increased in nearly equal steps and after five pulses 12.8 wt% rhenium loading was achieved. The results suggest the possibility of achieving further increase in the loading with more than five cycles and longer reaction times.

The CVD technique allows the deposition of rhenium on alumina without major impurities, and dispersion of the metal particles usually is good. CVD has been successfully used to prepare $W(CO)_6$/alumina catalysts in controlled manner [37] and it has been used to produce homogeneously distributed chromia particles on the alumina surface [44].

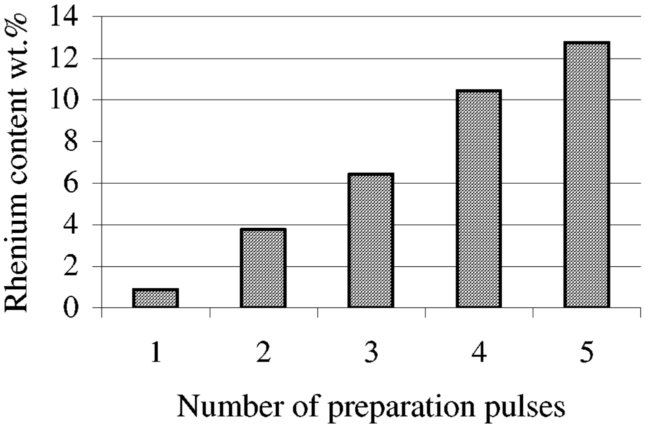

Figure 3. Rhenium content on alumina during five deposition–total decarbonylation cycles at 115 °C.

Table 2
HDS activity results for rhenium/alumina catalysts.

Catalyst code	Rhenium (wt%)	Conversion of thiophene (%)	Conversion/metal (mol/mol)
A	0.3	42.7	359.6
B	0.9	45.9	120.2
I	3.0	72.3	54.1
F	3.7	73.6	46.6
J	4.1	74.1	41.7
G	8.3	80.5	22.1
K	8.9	82.4	21.7
H	11.1	80.1	17.3
Commercial CoMo	3.9/10	69.0	20.4

3.2. HDS activity

The conversions of thiophene with rhenium catalysts at various metal loadings are given in table 2. As can be seen, even at low rhenium loading catalysts are active in thiophene HDS reaction. Conversion of thiophene increases with increase in the metal content up to 8.9 wt% but after this loading there is no further increase. This may indicate that the maximum amount of active sites has already been achieved.

Relative molar ratio (conversion of thiophene divided by the amount of metal) is nearly twenty times as great for the catalysts with low rhenium loading as it is for the commercial CoMo/alumina catalyst. This is in good agreement with earlier studies where rhenium sulfide was found to be two to twenty times as active as molybdenum catalysts [16]. As the rhenium content increases, the molar conversion drops to the level of the commercial catalyst.

The good molar ratio results suggest that the highly active species are formed in low metal loading and as the metal content increases similar relative activity cannot be obtained. Since the precursor includes the Re–Re bond it may be that the interaction between these atoms persists on the surface. However, at low metal content the rhenium particles are small and the most of the rhenium sites are available for the HDS reaction. Due to growth of the rhenium content particle size increases, so dispersion of the sulfided rhenium particles is lost and the relative conversion decreases.

Table 3
Degree of sulfidation of the rhenium catalysts.

Catalyst code	Rhenium (wt%)	Rhenium (mmol)	Sulfur (mmol)	Sulfur/rhenium ratio
A	0.3	0.26	0.68	2.6
B	0.9	0.81	1.98	2.4
I	3.0	2.22	5.39	2.4
F	3.7	3.04	6.48	2.1
G	8.3	6.86	13.45	2.0
K	8.9	5.81	10.85	1.9
H	11.1	9.26	16.80	1.8

According to Arnoldy et al. [16] interaction between the support and rhenium becomes weaker with increasing rhenium content which enhances the HDS activity of the catalysts. They suggest that, at low rhenium loading, the activity of alumina- and silica-supported catalysts can be attributed to the promotion of the carrier sites promoted by low-valent rhenium species. The decrease in the activity at high loading is due to the presence of ReS_2 crystallites on the surface.

Results of elemental analysis are shown in table 3. The calculated sulfur/rhenium molar ratio gives indications about the extent of sulfidation. With low metal loading catalysts, the molar ratio is nearly 2.5 and increasing metal content inevitability causes some steric hindrance leading to the decrease of the molar ratio.

3.3. Selectivity for n-butane

The product distribution of the rhenium catalysts is shown in table 4. The main product is n-butane and the portion increases with the metal content. This is illustrated in figure 4 where n-butane selectivity is plotted as a function of rhenium loading.

Commercial HDS catalysts are designed to be highly selective and our results for the commercial catalysts verified this. The maximum n-butane selectivity of rhenium-based catalysts (89.2%) achieved with the 8.9 wt% sample is comparable with the selectivity of the commercial catalysts.

As is clear from figure 4, selectivity increased with the rhenium content. For catalysts with low metal loading the portion of other products than n-butane increased. Growth in the metal content led to a change in the equilibrium in the reaction and more n-butane was formed as the result.

At low metal loading, rhenium particles are well dispersed and isolated on the surface. The progress of the HDS reaction demands dissociated hydrogen atoms and if hydrogen is not easily available, the selectivity of n-butane decreases.

The dissociation takes place probably at the rhenium surface. Furthermore, if the double-bonded, cracked or branched hydrocarbons formed at the start of the reaction are able to find hydrogen atoms nearby, the reaction will

Table 4
Distribution of main products (mol%) in the thiophene HDS reaction.

Product	Catalyst code								
	A	B	I	F	J	G	H	K	Commercial
1-butene	3.8	3.9	3.3	2.6	3.0	1.3	1.3	1.3	0.1
n-butane	19.8	23.4	49.9	57.7	57.0	70.5	73.0	69.6	80.1
trans-2-butene	11.4	11.0	10.0	7.9	8.3	4.7	4.3	4.8	0.2
Ethyl acetylene	7.0	7.0	6.3	4.4	5.3	2.8	2.6	2.8	0.5
Thiophene	57.7	54.7	29.3	27.1	26.2	20.2	18.1	20.9	17.7
Other	0.3	0	1.2	0.3	0.2	0.6	0.6	0.06	1.4

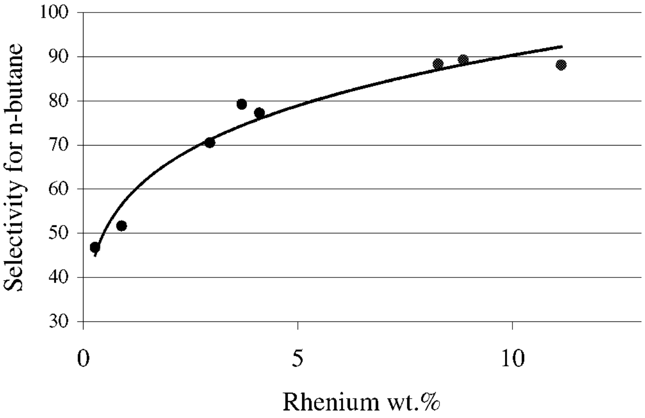

Figure 4. The portion of n-butane among the reaction products.

continue towards the n-butane. As rhenium loading increases, rhenium particles become larger and their neighbour particles are closer making it easier for the newly formed hydrocarbons to find hydrogen nearby.

4. Conclusions

A method was developed to control the rhenium content during the deposition on an alumina surface. Single-pulse deposition and multiple-pulse technique, both allow increase of the rhenium loading to a desired level. Partial and total decarbonylation steps between the deposition cycles proved to be particularly important intermediary stages in increasing metal content still further through gas-phase preparation. Well dispersed metal particles can be achieved on the surface.

The prepared catalysts were active in thiophene HDS reaction. The activity of the catalysts was even at low rhenium loading good and the relative molar ratio was nearly twenty times that for a commercial CoMo/alumina catalyst. As the metal loading increased, the relative activity of the catalysts decreased to the level of the commercial catalyst. The results encourage us to use low rhenium content in further experiments or to prepare HDS catalysts in which rhenium is a promoter.

The selectivity of the rhenium-based catalysts varied with metal loading. The concentration of n-butane among the products increased with rhenium content and the catalysts with high rhenium content were highly selective for n-butane. The good selectivity at higher rhenium loading may be due to the capability of rhenium to dissociate hydrogen in the surface.

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