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Novel Type of Carbon-Supported Catalysts

I. Preparation and Characterization

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ABSTRACT

The exposure of $\text{CoO}/\text{Al}_2\text{O}_3$ catalysts to carbon monoxide leads, after reduction to cobalt metal, to the formation of filamentary carbon in addition to a less reactive form of deposited carbon. The filament diameters were determined by scanning electron microscopy. The carbon content was determined by temperature-programmed oxidation. The carbon filament diameter increased with increasing exposure temperature, whereas the total carbon deposition decreased at higher temperatures. $\text{CoO}-\text{MoO}_3/\text{Al}_2\text{O}_3$ catalysts exposed to carbon monoxide also showed carbon deposition, but no filaments were formed, so carbon deposition on these catalysts took place via a different route. The filament-containing catalysts are referred to as tulip-field catalysts.

INTRODUCTION

It is known that the hydrodesulphurization (HDS) activity of supported metal sulphide catalysts increases in the order alumina < silica < carbon [1–3]. This effect was found for supported Co, Ni, Mo and W sulphides [3], Fe and Cr sulphides [4] and for supported Co–Mo and Fe–Mo sulphides [5]. Also, the activity of the hydrodeoxygenation (HDO) of dibenzofuran and the hydrodenitrogenation (HDN) of quinoline appeared to be higher on carbon-supported metal sulphide catalysts [3]. These differences were explained in terms of metal–support interactions. With alumina-supported catalysts, owing to a strong interaction of the metal sulphide with alumina, part of the metal does not participate in the reaction.

A higher catalytic activity of carbon-supported reduced iron catalysts compared with alumina-supported iron catalysts was found in the Fisher–Tropsch synthesis [6]. To the best of our knowledge, no extensive study has been reported in which the activities of carbon-supported metal oxide catalysts have

been compared with those of alumina-supported metal oxides. In terms of activity, carbon-supported catalysts are preferred. Unfortunately, carbon has some disadvantages compared with alumina and silica. In addition to a low bulk density, most of the carbon supports have either extensive microporosity or poor mechanical strength, which makes commercial applications less attractive. One way in which this problem was overcome was the development of carbon-covered alumina (CCA) [7–10]. The essence of this type of catalyst is the coverage of an alumina support with carbon by pyrolysis of hydrocarbons, followed by pore volume impregnation of the CCA with a metal salt solution. In this way the mechanical strength of alumina is combined with the carbon support characteristics with respect to activity. CCA's show higher activity for HDS compared with alumina-supported catalysts, but have lower activity than activated carbon-supported catalysts. One of the problems of using this method is the partial, non-uniform coverage of the alumina; after impregnation, part of the metal salt is situated on the carbon and part on the alumina surface [10].

A second approach to combine the favourable characteristics of carbon and alumina is to deposit carbon between the active transition metal phase and the alumina via the formation of carbon filaments on reduced alumina-supported metal oxide catalysts. The generally accepted mechanism for the formation of carbon filaments consists of a metal carbide formation–dissociation cycle. Atomic carbon ($C-\alpha$ in the nomenclature of McCarthy and co-workers [11,12]) is formed by dissociation of carbon monoxide on the metal surface and dissolves in the metal with the formation of a metal carbide [13,14]. After saturation with carbon, diffusion through the metal particle takes place. At the metal–support interface the metal carbide decomposes and the carbon precipitates in the form of a graphitic filament that lifts the particle from the support [15–17]. The diameter of the filaments is believed to be a function of the temperature of the filament formation [18] and the metal particle diameter [13,19]. Identical activation energies for filament growth and carbon diffusion through metal led to the conclusion that diffusion of the carbon through the metal particle is the rate-determining step [15,20,21]. As a consequence, more atomic carbon is formed at the surface of the metal particle than is removed by diffusion. Eventually, this will lead to complete coverage of the metal particle and the filament formation will stop [22,23]. The formation of carbon filaments has been reported on nickel [11,13,19,24–26], iron [13,21,26], cobalt [18,24] and vanadium [27] on both metal foils and supported metal systems. It has also been shown that carbon filaments could be grown on molybdenum foils [27].

An advantage of these so called “tulip-field” catalysts over CCA's is the potential regenerability. After removing the carbon deposits by gasification, the remaining alumina-supported metal oxide can be resubmitted to carbon mon-

oxide treatment. The mechanism for filament formation shows a great similarity to the mechanism proposed for catalytic graphitization [28]. Here a metal carbide particle consumes the disordered carbon in front and transports the carbon (by diffusion) to the rear of the particle, where the carbon precipitates in the form of an ordered graphitic structure. A global classification of the activity of transition metals for catalytic graphitization indicated a high activity for Ni, Fe and Co (923–1373 K) and Mo, W, Pt and Ta (1273 K) [29–32].

The gasification of carbon catalysed by nickel takes place via a comparable, although reverse version of the above-mentioned mechanism. The carbon on the outer surface of the nickel particle is removed by reaction with carbon dioxide or water. This induces a concentration gradient over the particle, leading to consumption of carbon at the opposite side of the particle [33,34].

The production of synthetic diamonds is also performed in the presence of Group VIII metals (Fe, Ni, Co, Pt, Pd, Mn, Cr or Ta). The mechanism involves the formation and dissociation of carbides in the metal-carbon melts [35].

Normally, the formation of carbon filaments is classified as “deactivation”. However, some examples have been reported in which carbon filament-supported metal particles are thought to be responsible for increased activity [36,37]. The object of this study was to prepare and characterize tulip-field catalysts. Part II will describe the activity of these catalysts for carbon monoxide oxidation, nitric oxide reduction and thiophene hydrodesulphurization.

EXPERIMENTAL

Materials

The alumina support was a high purity γ -alumina (Ketjen 000-1.5E CK 300; specific surface area 195 m²/g; particle size 100–200 μ m). Analytical-reagent grade $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Merck) were used. All gases were of HP quality, and dried over conventional gas-purification columns.

Catalyst preparation

$\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts were prepared by pore-volume impregnation of ca. 5 g of dried alumina (18 h at 385 K in static air) with a solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in demineralized water. Subsequently, the catalyst was dried in air, starting at 325 K for 60 min. Every 60 min the temperature was raised by 30 K until the final temperature (385 K) was reached. The catalyst remained at 385 K for a further 18 h before calcination at 775 K for 2 h in a flow of air. Cobalt-containing catalysts were prepared by pore-volume impregnation of $\gamma\text{-Al}_2\text{O}_3$ or $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ with a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in demineralized water, followed by identical drying and calcination procedures as

for $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$. The metal content was 10% (w/w) CoO and 10.4% (w/w) MoO_3 . The average pore radius, as determined the nitrogen BET method, was 4.0 nm.

Filament formation

A schematic diagram of the apparatus is shown in Fig. 1. Six quartz reactor tubes (I.D. 4–5 mm) could be operated simultaneously. The feed [10% (v/v) carbon monoxide in nitrogen] was mixed by a set of flow controllers and divided over six reactors by a second set of flow controllers. Normally, five reactors were filled with ca. 70 mg of sample and the sixth reactor was used as a blank. The samples were heated under nitrogen to the reaction temperature (675, 740, 770 and 840 K). Subsequently, 10% (v/v) of carbon monoxide was added to the nitrogen (total flow-rate, $1.1 \mu\text{mol/s}$ of carbon monoxide) for a period of 30 or 60 min and, after interruption of the carbon monoxide supply, the samples were cooled to room temperature under nitrogen and stored for characterization and activity measurements. It should be stressed that reduction of the oxidic catalyst took place with the carbon monoxide-containing feed, without a separate reduction step.

Scanning (SEM) and transmission electron microscopy (TEM)

SEM

The samples were mounted with double-sided tape on aluminium stubs and covered with a gold–palladium layer by sputtering (2 min, 25 mA, 1.2 kV, Polaron 3000 Sputter-coater). Electron micrographs were taken in the top stage of an ISI DS 130 scanning electron microscope (electron beam voltage 25 kV). From the micrographs the filament diameter was determined.

Fig. 1. Schematic diagram of the apparatus used for carbon deposition with carbon monoxide.

TEM

The samples were suspended in 2-propanol and deposited on carbon film-coated 400-mesh copper grids. Micrographs were taken at 60 kV in a Philips EM-300 transmission electron microscope.

Temperature-programmed oxidation (TPO)

The sample was placed between two quartz-wool plugs in a quartz reactor tube (I.D. 4–5 mm). The temperature of the sample was increased linearly from room temperature to 1075 K (heating rate 5 K/min). The feed consisted of 20% (v/v) oxygen in helium (2.5 $\mu\text{mol/s}$ of oxygen). The product mixture was led over a copper (II) oxide column (1115 K) in order to convert carbon monoxide into carbon dioxide. Subsequently, the reaction products (carbon dioxide and water) were trapped in a 5A molecular sieve column. The oxygen content of the remaining mixture was monitored continuously by means of a thermal conductivity detector.

By means of a sampling valve, placed directly after the carbon monoxide converter and before the product trap, small aliquots of the product mixture were injected on to a gas chromatograph to determine the carbon dioxide produced.

Calibration of the detector was performed by oxidizing V_2O_3 , Mo and Mo_2C . The last compound was also used for calibration of the gas chromatograph.

RESULTS

Owing to the gold–palladium sputtering procedure, necessary for SEM image formation, the observed diameter of the carbon filaments included the gold–palladium layer. Comparison of the micrographs of a $\text{Co}/\text{Al}_2\text{O}_3$ sample treated with carbon monoxide at 770 K after one and two sputter procedures indicated that gold–palladium layers of approximately 10 nm were formed. All the SEM results were corrected accordingly. Figs. 2 and 3 show transmission electron micrographs of carbon monoxide-treated $\text{Co}/\text{Al}_2\text{O}_3$ (1 h at 675 K and 1 h at 740 K, respectively). A metal particle is situated on top of the carbon filaments.

In Fig. 4 the average carbon filament diameter is plotted versus the carbon monoxide treatment temperature. It can be seen that a higher carbon monoxide treatment temperature resulted in larger filament diameters. The carbon monoxide treatment temperature also influenced the morphology of the filaments. After carbon monoxide treatment at 675 K a large number of short, thin filaments were formed. With increasing carbon monoxide treatment temperature the number of filaments decreased, whereas the diameter of the filaments increased, from 12.5 nm after carbon monoxide treatment at 675 K to 50 nm after treatment at 840 K. No filaments were found on carbon monoxide-treated $\text{Co-Mo}/\text{Al}_2\text{O}_3$, although carbon deposition did take place.

Fig. 2. Transmission electron micrograph of carbon monoxide-treated $\text{Co}/\text{Al}_2\text{O}_3$ (1 h at 675 K). The length of the bar is 50 nm.

Fig. 3. Transmission electron micrograph of carbon monoxide-treated $\text{Co}/\text{Al}_2\text{O}_3$ (1 h at 740 K). The length of the bar is 50 nm.

Fig. 4. Filament diameter as a function of the carbon monoxide treatment temperature of $\text{Co}/\text{Al}_2\text{O}_3$.

Fig. 5. TPO patterns (carbon dioxide production) of carbon monoxide-treated $\text{Co}/\text{Al}_2\text{O}_3$.

TABLE 1

Total carbon content of carbon monoxide-treated $\text{Co}/\text{Al}_2\text{O}_3$ (TPO)

Catalyst composition: 10% (w/w) CoO .

CO treatment		carbon content (%, w/w)
Temperature (K)	Time (min)	
675	30	4.7
675	60	6.5
740	60	8.2
770	60	6.6
840	30	3.5

In Fig. 5 the TPO patterns (carbon dioxide production) of the carbon monoxide-treated $\text{Co}/\text{Al}_2\text{O}_3$ catalysts are shown. The patterns are normalized with respect to the amount of catalyst used for the TPO experiments. Therefore, the areas under the curves, which correlates directly with the amount of carbon dioxide produced, can be compared.

All patterns showed a shoulder at 590 K and a main peak at 670–710 K. The temperature of the main peak tended to shift to higher temperatures with increasing carbon monoxide treatment times and higher carbon monoxide treatment temperatures. In the TPO pattern of $\text{Co}/\text{Al}_2\text{O}_3$ treated with carbon monoxide at 770 K an additional (weak) shoulder on the high-temperature side of the main peak was found.

These two peak patterns indicated the presence of two types of carbon. The

Fig. 6. TPO patterns (carbon dioxide production) of carbon monoxide-treated Co-Mo/Al₂O₃.

TABLE 2

Total carbon content of carbon monoxide-treated Co-Mo/Al₂O₃ (TPO)

Catalyst composition		CO treatment		Carbon content (% w/w)
CoO (% w/w)	MoO ₃ (% w/w)	Temperature (K)	Time (min)	
10	10.4	675	30	0.9
10	10.4	675	60	7.1
10	10.4	840	30	3.7
10	10.4	840	60	8.9

relative amount of the most reactive form of carbon (shoulder) decreased with increasing temperature. The total amounts of carbon are listed in Table 1.

TPO (carbon dioxide production) patterns of carbon monoxide-treated Co-Mo/Al₂O₃ are depicted in Fig. 6. Carbon monoxide treatment at 675 K for 30 min resulted in a single maximum at 610 K. Prolonging the reaction time to 60 min caused an additional maximum at 680 K. Exposure to carbon monoxide at 840 K for either 30 or 60 min resulted in carbon dioxide production maxima at 640 K (shoulder) and 800–805 K. The amounts of carbon are listed in Table 2.

DISCUSSION

The electron micrographs revealed that an increase in carbon monoxide exposure temperature caused an increase in filament diameter (Fig. 4). Similar results were reported by Baker and Harris [17] for filaments grown from ethylene on a cobalt-covered mesh. They found maximum diameters after ethylene exposure at 998 K. A further increase in the exposure temperature caused a decrease in both the filament diameter and the filament yield. In this work the filament diameter was a maximum after carbon monoxide treatment at 840 K and the total carbon yield was a maximum after carbon monoxide treatment at 740 K. Two explanations can be suggested for this increase in diameter. First, the particle diameter might increase at higher temperatures owing to sintering phenomena, and second, at lower temperatures filaments are preferentially formed by the smaller metal particles [19] and therefore only relatively thin filaments are found on the electron micrographs. Bernardo and Lobo [38] found maximum carbon deposition at 773 K on cobalt foils from acetylene in the presence of hydrogen. Other studies confirmed the decrease in total carbon deposition at higher temperatures [25].

From temperature-programmed gasification (TPG) experiments with carbon dioxide [24] and hydrogen [11,12,24] on carbon monoxide-treated Co/Al₂O₃ and Ni/Al₂O₃, it was found that the relative amount of filamentary carbon decreased with increasing temperature. At higher temperatures a less reactive form of carbon deposit was formed (C- ϵ) [11,12]. A similar trend was observed in the TPO patterns in this study. The relative amount of the reactive form of carbon deposits (low-temperature shoulder in the TPO patterns) decreased with increasing carbon monoxide treatment temperature. The shoulder on the high-temperature side of the main peak in the TPO pattern after carbon monoxide treatment at 770 K might be the result of the formation of a more ordered form of graphitic carbon at this temperature. Considering the graphitic character of filamentary carbon [39], the temperature of oxidation is low. Pure graphite starts to react with oxygen at 720 K (oxidation maximum at 1020 K) [40]. This difference is an indication of the catalytic activity of cobalt metal on the carbon-oxygen reaction. The formation of filamentary carbon through the decomposition of metal carbides is thermodynamically limited to a maximum temperature [12,41,42]. Because the equilibrium of the carbon monoxide dissociation reaction shifts to the carbon monoxide side at higher temperatures, the amount of filamentary carbon is limited.

The weight percentages carbon were determined from the TPO (carbon dioxide production) patterns. The accompanying amounts of oxygen consumed exceeded the amount of carbon dioxide produced. The extra oxygen consumption is needed for oxidation of the metal. This means that CoO is reduced by carbon monoxide to Co, after which the formation of filaments commences. It also indicates that, even after exposure of the coked catalysts

to air at room temperature, at least part of the metal remained in the reduced state. This was confirmed by the TPG experiments with carbon dioxide where, after (catalytic) gasification of the filamentary carbon, the metal is oxidized [24].

Co-Mo/Al₂O₃ behaved differently to Co/Al₂O₃. Although a maximum in the production of carbon dioxide was found at 610 K after carbon monoxide exposure at 675 K, no filaments were detected by SEM. Apparently, the conditions needed for filament formation were not met. Temperature-programmed reduction experiments [43] with hydrogen showed that on Co-Mo/Al₂O₃ with comparable Co and Mo contents and calcination temperatures, part of the Co is present as Co₃O₄ crystallites. These crystallites are easily reduced by hydrogen [44]. It is to be expected that carbon monoxide is also capable of reducing the crystallites. This would mean that the condition for filament formation, i.e. the presence of metallic particles, is probably fulfilled. Apparently, the molybdenum oxide or molybdenum acts as a barrier for precipitation. This is in agreement with the observation that small amounts of MoO₃ acts as an inhibitor for filament formation on supported metal alloys [34,45].

The oxidation of the carbon deposit on Co-Mo/Al₂O₃ took place at higher temperatures than the oxidation of filamentary carbon on Co/Al₂O₃. This is further indication of a different carbon deposition mechanism on Co-Mo/Al₂O₃.

In the preparation of optimum tulip-field catalysts, a maximum metal surface area and short carbon filaments are favourable. Considering the first factor, it is to be expected that small filament diameters (with metal particles on top) will yield maximum metal surface areas. Therefore, carbon filaments should be made at the lowest carbon monoxide treatment temperature possible. Second, there is no need for long carbon filaments. The metal particle need only be separated from the alumina support and this can be achieved by using short carbon monoxide treatment times.

CONCLUSIONS

By varying the temperature of carbon monoxide treatment it was possible to influence the average filament diameter on Co/Al₂O₃ catalysts. Minimum diameters were obtained at the lowest temperature employed in this study. In addition to filamentary carbon, also a less reactive form of carbon was deposited. At higher temperatures the latter form became more abundant, whereas the total carbon content decreased. No filaments were formed on Co-Mo/Al₂O₃. Therefore, carbon deposition on Co-Mo/Al₂O₃ took place via a different route.

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