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Novel Type of Carbon-supported Catalysts

II. Activity Measurements

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ABSTRACT

The exposure of $\text{CoO}/\text{Al}_2\text{O}_3$ catalyst to CO at elevated temperatures leads, after reduction of CoO to cobalt metal, to the formation of filamentary carbon, on top of which a metal particle is situated. In this way a carbon-supported metal catalyst on an alumina base can be prepared. These catalysts were tested for CO oxidation, NO reduction and thiophene hydrodesulphurization and the activity was compared with that of untreated $\text{CoO}/\text{Al}_2\text{O}_3$ catalysts. In all reactions the CO-treated $\text{CoO}/\text{Al}_2\text{O}_3$ showed a higher activity. CO-treated $\text{CoO}-\text{MoO}_3/\text{Al}_2\text{O}_3$, on which no filamentary carbon was formed, showed a "normal" deactivation behaviour.

INTRODUCTION

Carbon-supported metal sulphides show a higher catalytic activity than alumina-supported catalysts in several reactions. Therefore, efforts have been devoted to the development of carbon-supported analogues of commercially applied alumina-supported catalysts. The application of carbon-supported metal sulphides has been shown to be successful for hydrodesulphurization (HDS) [1-4], hydrodeoxygenation (HDO) [1] and hydrodenitrogenation (HDN) [1]. The activity of carbon-supported metal sulphides was higher for both mono- and bimetallic systems.

In principle, carbon-supported catalysts can be divided into two groups: (i) metal oxides and sulphides supported on one of the various forms of carbon; normally these carbons are activated carbons made from wood, coal, peat or other naturally occurring materials by thermal treatment and, by choosing the appropriate preparation conditions, a suitable pore structure can be obtained [5,6]; and (ii) metal oxides and sulphides supported on a thin layer of carbon that is deposited on the surface of a porous alumina (carbon-covered alumina,

CCA); the carbon is deposited by pyrolysis of hydrocarbons at elevated temperatures on alumina [7–10] and subsequently the metal component is added by conventional impregnation procedures.

In this study a third group of carbon-supported catalysts is introduced, viz., metal particles supported on carbon, which in turn is situated on alumina. Starting off with metal oxide/alumina catalysts, the carbon is catalytically deposited by CO treatment between the in situ reduced metal particle and the alumina. These catalysts have been called tulip-field catalyst. The mechanism of formation [11–13] and the method of preparation have been described elsewhere [14]. In this way, monometallic tulip-field catalyst could be prepared. It is worth mentioning that these catalysts are in principle regenerable. After removing the carbon by oxidation, a second CO treatment will yield new carbon filament-supported metal particles.

Tulip-field catalysts and CCAs combine the favourable mechanical characteristics of the alumina support with the beneficial effect of the carbon support on catalytic activity.

Activity data for activated carbon-supported catalysts and carbon-covered alumina-supported catalysts have been published [1–4,8] but, to our best knowledge, no such data for tulip-field catalysts have been reported so far. It was therefore decided to investigate the catalytic activity of tulip-field catalysts in some reactions in which a high activity might be expected, such as CO oxidation, NO reduction and thiophene HDS. The activity was compared with that of the parent (untreated) catalysts. Also, the NO reduction activity of CO-treated Co–Mo/Al₂O₃ catalysts was measured, although, as was shown previously, no filamentary carbon was formed during CO treatment [14].

EXPERIMENTAL

Catalysts

The preparation and characterization of the catalysts were described earlier [14]. The parent catalysts were 10 wt.-% CoO/ γ -Al₂O₃ and 10 wt.-% CoO–10.4 wt.-% MoO₃/ γ -Al₂O₃, prepared by pore volume impregnation of γ -Al₂O₃ with aqueous solutions of Co(NO₃)₃·6H₂O and (NH₄)₆Mo₇O₂₄·4H₂O, followed by calcination in air at 775 K for 18 h. After CO treatment of Co/Al₂O₃ at various temperatures and reaction times, the total carbon content varied from 3.5 to 8.2 wt.-%, whereas for Co–Mo/Al₂O₃ the carbon content varied from 0.9 to 8.9 wt.-%. Treatment of Co/Al₂O₃ with CO resulted primarily in the reduction of CoO to Co, followed by the formation of filamentary carbon. Exposure of these tulip-field catalysts to air at room temperature did not reoxidize the metal, as was confirmed by temperature-programmed oxidation (TPO) [14,15] and temperature-programmed reduction (TPR) [15].

Temperature-programmed NO reduction

About 50 mg of catalyst were placed in U-shaped quartz reactor tube. The temperature of the sample was increased linearly from 300 to 1075 K at 5 K/min. The feed consisted of 2000 ppm of CO and 2000 ppm of NO in helium. The molar flow-rates were $4 \cdot 10^{-2}$ $\mu\text{mol/s}$ of NO and CO. The total pressure was 1 bar. The CO, NO, CO₂ and N₂ contents in the product mixture were determined by gas chromatography (GC).

Temperature-programmed CO oxidation

The apparatus used was identical with that described for filament formation [14]. A 50-mg amount of catalyst was exposed to a gas mixture consisting of 1000 ppm of CO and 500 ppm of O₂ in N₂. The molar flow-rates were $1.4 \cdot 10^{-2}$ $\mu\text{mol/s}$ of CO and $0.7 \cdot 10^{-2}$ $\mu\text{mol/s}$ of O₂. The sample was heated from 300 to 1075 K at 2 K/min. The product stream was analysed for CO and CO₂ (after methanation) by means of a GC equipped with flame ionization detection.

Thiophene HDS

Activities for thiophene HDS were measured in a microflow reactor operated at 673 K at atmospheric pressure. About 200 mg of catalyst were presulphided in situ with a mixture of 10% hydrogen sulphide in hydrogen at atmospheric pressure (total molar flow-rate, 45 $\mu\text{mol/s}$). The temperature was increased from 300 to 675 K in 1 h, followed by an isothermal period of 2 h. The feed consisted of 6.2% thiophene in hydrogen. The thiophene conversion after 2 h was used as an activity characteristic. The products were analysed by on-line GC.

RESULTS

Tulip-field catalysts showed a higher activity than the parent catalyst for NO reduction (Fig. 1). Clearly the preparation conditions (CO treatment temperature and time) are important. The highest activity was found for the catalyst treated with CO for 60 min at 675 K. In Table 1 the temperatures at which 50% ($T_{50\%}$) and 100% NO conversion ($T_{100\%}$) were achieved are given.

In Fig. 2 the NO conversion of "fresh" and CO-treated Co-Mo/Al₂O₃ catalyst is plotted versus the temperature. The CO-treated Co-Mo/Al₂O₃ sample was less active compared with the parent Co-Mo/Al₂O₃. At 975 K, only for the untreated catalysts 100% NO conversion was attained.

The CO oxidation activities of the CO-treated Co/Al₂O₃ catalysts are shown in Figs. 3 and 4. In Table 2 the temperatures at which 50% ($T_{50\%}$) and 100%

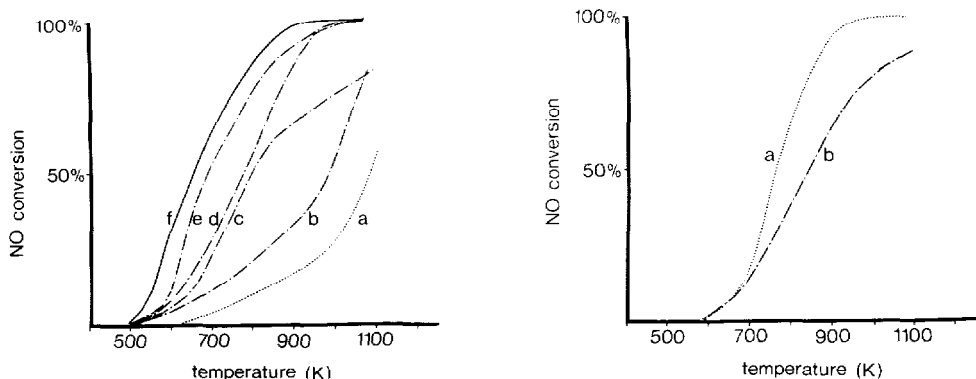


Fig. 1. NO conversion as a function of the reaction temperature. (a) Untreated Co/Al₂O₃; (b) Co/Al₂O₃ after 60 min CO at 770 K; (c) Co/Al₂O₃ after 30 min at 840 K; (d) Co/Al₂O₃ after 30 min CO at 675 K; (e) Co/Al₂O₃ after 60 min CO at 675 K; (f) activated carbon-supported Co.

Fig. 2. NO conversion as a function of the reaction temperature. (a) Untreated Co-Mo/Al₂O₃; (b) Co-Mo/Al₂O₃ after 30 min CO at 675 K.

TABLE 1

NO reduction activity data

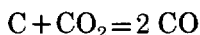
Catalyst composition		CO treatment		$T_{50\%}^a$ (K)	$T_{100\%}^b$ (K)
CoO (wt.-%)	MoO ₃ (wt.-%)	Time (min)	Temperature (K)		
10	10.4		Untreated	760	975
10	10.4	30	675	840	—
10	—		Untreated	1080	—
10		30	675	780	1000
10		60	675	690	1000
10		60	770	990	—
10		30	840	800	—

^aTemperature at which 50% NO reduction takes place.

^bTemperature at which 100% NO reduction takes place.

CO oxidation ($T_{100\%}$) were achieved and temperatures at which the carbon filaments started to react (T_f) are given.

CO oxidation started at 350–375 K for all catalysts. The CO-treated catalysts attained 100% CO conversion at much lower temperatures than the untreated catalyst. The most active catalyst was that treated with CO at 770 K. The tulip-field catalysts at ca. 800–900 K showed CO production accompanied by CO₂ consumption, owing to gasification of the carbon filaments. Obviously, they are gasified with CO₂ according to the reaction



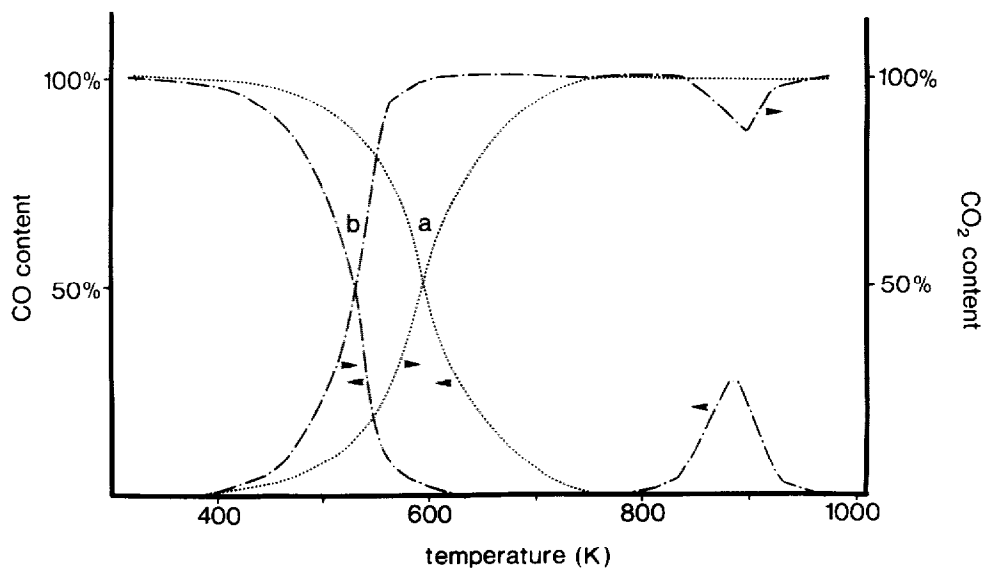


Fig. 3. Temperature-programmed CO oxidation; CO and CO₂ contents of the product mixture as a function of the reaction temperature. (a) Untreated Co/Al₂O₃; (b) Co/Al₂O₃ after 30 min CO at 675 K.

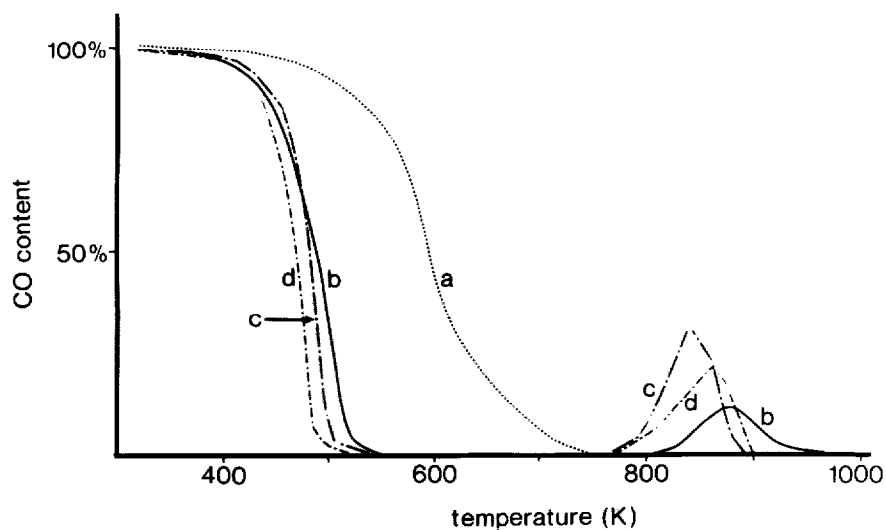


Fig. 4. Temperature-programmed CO oxidation; CO content of the product mixture as a function of the reaction temperature. (a) Untreated Co/Al₂O₃; (b) Co/Al₂O₃ after 30 min CO at 840 K; (c) Co/Al₂O₃ after 60 min CO at 675 K; (d) Co/Al₂O₃ after 60 min at 770 K.

TABLE 2

CO oxidation activity data

Catalyst composition (wt.-% CoO)	CO treatment		$T_{50\%}^a$ (K)	$T_{100\%}^b$ (K)	T_i^c (K)
	Time (min)	Temperature (K)			
10		Untreated	595	765	—
10	30	675	535	620	800
10	60	675	485	525	760
10	60	770	470	515	750
10	30	840	490	550	800

^aTemperature at which 50% conversion is reached.^bTemperature at which 100% conversion is reached.^cTemperature at which the carbon filaments start to react.

TABLE 3

Thiophene HDS activity data

Catalyst composition (wt.-% CoO)	CO treatment		Thiophene conversion (%)
	Time (min)	Temperature (K)	
10		Untreated	1.1
10	60	740	1.9
10	30	770	1.2
10	60	840	1.9

In Table 3 the HDS activities of some catalysts are given. The activity is presented as percentage thiophene conversion. Also for thiophene HDS the tulip-field catalysts showed a higher activity than catalysts not treated with CO.

DISCUSSION

NO reduction

The untreated Co-Mo/Al₂O₃ catalyst was more active than the CO-treated catalysts for NO reduction. Taking into account the fact that no filaments were observed by scanning electron microscopy of the CO-treated catalysts [14], although carbon deposition did take place, it is likely that the carbon deposit covered the active sites. In fact, this is the behaviour that is generally observed in catalysis; carbon deposition acts as a poison.

With CO-treated Co/Al₂O₃ catalysts, on which carbon filaments with a cobalt particle on top are formed, the activity was higher than that of the un-

treated catalysts for all the reactions studied. In addition to the carbon supported effect, leading to increased activity, two other explanations can be suggested. First, CO treatment during preparation resulted in the reduction of CoO to cobalt metal. The metal-carbon interaction stabilizes the reduced state. This statement was confirmed by temperature-programmed gasification with CO₂ [TPG (CO₂)] of tulip-field catalysts. Only after gasification of filamentary carbon, catalysed by nickel and cobalt metal, was the metal itself oxidized [15]. Therefore, if the metallic state is preferred to the oxidic state, a higher catalytic activity for tulip-field catalysts is to be expected.

Second, it is known that filament formation can cause fragmentation of a metal particle. For instance, CO treatment of metal foils resulted in the formation of filamentary carbon with a metal particle on top [16-18]. Therefore, it is possible that as a result of CO treatment the cobalt surface area is increased, leading to an enhanced activity. Comparing the NO reduction activity of tulip-field Co/Al₂O₃ catalysts with that of active carbon-supported Co catalysts, almost similar activities were obtained. The strongest increase in activity was found after CO treatment at 675 K, whereas CO treatment at 770 K gave rise to only a relatively small enhancement of the activity. Both catalysts contained comparable amounts of carbon, the major difference being the filament diameter. As was shown, the filament diameter increases with increasing CO treatment temperature [14]. Apparently, the better dispersion obtained by low-temperature CO treatment is the governing parameter.

CO oxidation

CO treatment of Co/Al₂O₃ resulted in 100% CO conversion at lower temperatures than for the untreated Co/Al₂O₃ (Table 2). The highest activity was obtained after CO treatment at 770 K. Similar activities were obtained after CO treatment at 675 and 840 K, indicating that the filament diameter itself is not the most important parameter. For instance, it is possible that only part of the cobalt is lifted from the surface. The effect of the CO treatment temperature on the CO oxidation activity is much less pronounced than that on the NO reduction activity. Apparently, the differences in CO oxidation activity due to different pretreatment temperatures are strongly diminished, perhaps owing to the removal of encapsulating carbon. This suggests that only in a CO-O₂ atmosphere is part of the Co activated. In addition to the shift in $T_{100\%}$, it was also observed that for CO-treated Co/Al₂O₃ a much smaller temperature interval was needed between 0% and 100% conversion. All tulip-field catalysts showed a dip in CO consumption accompanied by an increase in CO₂ production, starting at 750 K. This was caused by gasification of the carbon filaments with CO₂. The temperature is in good agreement with the gasification temperature found for TPG (CO₂) of similar catalysts [15]. This peak was ascribed

to the metal-catalysed gasification of filamentary carbon. The second form of carbon deposit is gasified (non-catalytically) at higher temperature.

As previously stated, it proved impossible to prepare carbon filaments on Co-Mo/Al₂O₃ by CO treatment, which makes the application of the described preparation technique for hydrotreatment catalysts, which normally are alumina-supported Ni-Mo or Co-Mo, impossible. As is known from the literature, Co/Al₂O₃ has a lower HDS activity than Co-Mo/Al₂O₃ or Ni-Mo/Al₂O₃ catalysts. However the HDS activity of tulip-field Co/Al₂O₃, although still very low, is considerably higher than that of the parent Co/Al₂O₃ catalysts. Vissers et al. [4] reported a 7-fold increase in thiophene HDS activity from alumina-supported Co to carbon-supported Co. This is a much greater increase in HDS activity than those found in this study. It is not yet clear why the activity of tulip-field catalysts is much more enhanced for CO oxidation and NO reduction than thiophene HDS.

A potential application in HDS might be based on CO-treated Fe/Al₂O₃. This would yield an inexpensive, disposable catalyst for hydrotreating coal-derived liquids and heavy oils.

CONCLUSIONS

It is possible to increase the CO oxidation, NO reduction and the thiophene HDS activity of Co/Al₂O₃ catalysts by CO treatment. CO treatment of Co-Mo/Al₂O₃ resulted in a lower NO reduction activity, because the carbon deposit covered the catalyst. No filamentary carbon was formed on these catalysts. Therefore, this preparation method is not applicable to Co-Mo/Al₂O₃-type catalysts. There is no straightforward relationship between the carbon filament diameter and the CO oxidation and NO reduction activity.

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