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# Deactivation of a Co-Precipitated Co/$Al_2O_3$ Catalyst

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The effects of reaction temperature, feed ratio, space time, and CO percentage in feed on the deactivation conditions of a co-precipitated 36 wt% Co/$Al_2O_3$ catalyst in CO hydrogenation were investigated. Environmental-SEM-EDX and temperature-programmed reduction (TPR) studies were performed on used catalysts to investigate the effect of reaction conditions on catalyst deactivation. Intensive coke deposition on the catalyst was observed at a reaction temperature of about 573 K. Increasing the $H_2$/CO ratio also increased the catalyst activity. Methane formed as the main product at high $H_2$/CO ratios. Although catalyst activity did not change significantly during the 9-h reaction period at all conditions, a maximum of 6.8% C deposition was observed with increasing $H_2$/CO, and this caused a 2% decrease in the total surface area of the used catalyst. Space time and CO percentage in the feed had less influence on catalyst decomposition.

**Key Words:** Fischer-Tropsch synthesis, catalyst deactivation, cobalt-alumina catalysts, CO hydrogenation, co-precipitation.

## Introduction

The CO hydrogenation product spectrum includes a great variety of products. The wide range of conditions brings with it a wide range of products, such as paraffins, olefins, and alcohols, depending on the catalysts used and the process conditions.[1] Co-based catalyst systems seem to be especially suitable due to their high activity and selectivity, low water-gas shift activity, and comparatively low price. Co catalysts are often used with $Al_2O_3$ as support because of its favorable mechanical properties.[2] A series of papers have also been published concerning CO hydrogenation reactions over Co-based catalysts with different supports.[3–5]

Decreasing the deactivation rates of these catalysts for Fischer-Tropsch synthesis has been an important challenge facing the development of alternative resources to crude oil.[6] The loss of the catalytic activity by coke deposition is an important fact, both economically and technologically. Co/$Al_2O_3$ catalysts have been studied several times over the years, not only for their activity in CO hydrogenation, but also for their deactivation conditions during reactions.[7–11]

Our main concern here was the investigation of deactivation conditions (reaction temperature, $H_2$/CO ratio, space time, and CO percentage in feed) of co-precipitated 36 wt% Co/$Al_2O_3$ catalysts in CO hydrogenation reactions. The catalysts were chosen in this study based on the results of previous studies.[2,11–13]

An extensive study was previous conducted on the development of co-precipitated Co/$Al_2O_3$ catalysts for the production of lower hydrocarbons by CO hydrogenation and 36 wt% Co/$Al_2O_3$ was found to exhibit optimum performance.

## Experimental

The reactions were verified with a 36 wt% Co/$Al_2O_3$ catalyst prepared by the co-precipitation of the hydroxides of Co and Al from the corresponding nitrates reacting in a basic solution. The detailed preparation procedure is given elsewhere.[12]

Reaction experiments were performed in a stainless steel fixed-bed micro-reactor system controlled to ± 0.5 K by a Shimaden FP-21 programmable temperature controller equipped with a K-type sheathed thermocouple placed in a tube furnace. All extrapure reactants (i.e. $H_2$and CO), inert diluent (He), and reducing gas ($H_2$) were fed from pressurized gas cylinders. Feed and product composition were determined by on-line GC analysis. The feed and product gases were analyzed for CO, $CO_2$, and $C_1$-$C_3$ hydrocarbons by an on-line Shimadzu GC-8APT temperature programmable gas chromatograph connected to a Shimadzu CR-4A data processor.

The catalyst samples were reduced in situ at 648 K and 101 kPa under a hydrogen stream of 100 $cm^3\ min^{-1}$ for 8 h and flushed with helium under the same conditions, followed by switching to reaction conditions. Experiments were carried out to investigate the deactivation conditions of a co-precipitated 36 wt% Co/$Al_2O_3$ catalyst used for the production of $C_1$-$C_3$ hydrocarbons by CO hydrogenation. For this aim, 4 different temperatures (509-573 K), 3 $H_2$/CO ratios (1-3), 3 space times (5.5-17 mg min/mL), and 3 CO percentages in feed (10%-33.33%) were chosen as variable parameters.

Deactivated catalysts were characterized by total surface area (TSA) measurements, and temperature-programmed oxidation and reduction (TPO, TPR) experiments. Scanning electron microscopy (SEM) analyses were performed on deactivated catalysts to obtain a better understanding of C deposition. The TSA of Co/$Al_2O_3$ catalysts after reactions was measured with a Micromeritics Flowsorb II 2300 by $N_2$ adsorption from $N_2-$He mixtures at liquid nitrogen temperature, using a multi-point technique and the BET equation. A Mettler Toledo TGA/SDTA851$^e$ thermo gravimetric analysis system was used for temperature-programmed studies (TPR, TPO) of the thermal characterizations of the used catalysts. Used catalyst samples were tested using environmental scanning electron microscopy (ESEM) to obtain information on their deactivation properties.

## Results and Discussion

In order to study the effect of temperature on catalyst activity and deactivation conditions, experiments were conducted on the 36 wt% Co/$Al_2O_3$ catalyst at 4 different temperatures (508-573 K), a constant $H_2$/CO ratio of 2, and with a feed stream containing 20 mol% CO. The results presented in Figure 1 indicate that the production rates for methane and $C_2$-$C_3$ hydrocarbons attained their maximum levels at a reaction temperature of 508 K, as previously reported.[13]

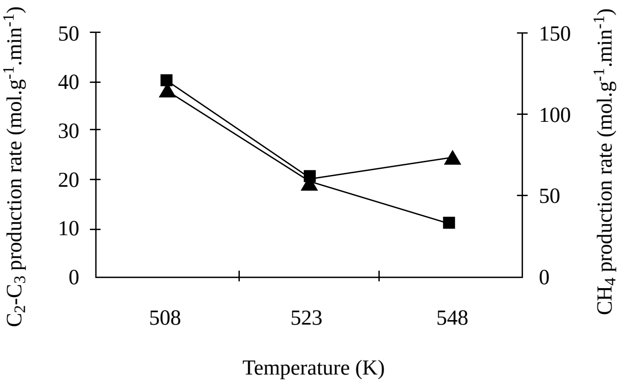

**Figure 1.** The effect of temperature on production rates ($CH_4$ production rate, $C_2$-$C_3$ production rate).

The results presented in Figure 2a and b indicate that CO conversion attained its maximum level at a reaction temperature of 573 K, but after 3 h, because of coke formation and deposition, the catalyst lost its activity. It should be noted that at 508 K the catalyst showed low, but stable activity for 9 h on the stream experiment.

A decrease in TSA and increase in deposited coke, 7% and 94 wt%, respectively, were observed for the catalyst used for the reaction performed at 573 K, compared to the reactions at lower temperatures. As a result of rapid activity loss of the catalyst, coke deposition blocked the pores and an instantaneous pressure rise occurred in the reactor.

As a result of TPR experiments, which were performed in a reducing atmosphere of a 4% $H_2$-96% Ar mixture on used catalysts, an endothermic peak was observed for all used catalysts. An example TGA-DTA graph of these experiments (for the catalysts used at the 523 K reaction) is shown in Figure 3. The endothermic peak can be explained by the distinction of water formed during the reaction or the decomposition of low molecular weight carbonaceous components. After TPR experiments, 68 wt% of carbonaceous components was removed from the catalyst used in the 523 K reaction. Figure 4a and b show the SEM images of this catalyst before and after TPR experiments, respectively. Brighter metallic particles, which mean clean surfaces, were observed in the SEM photograph shown in Figure 4b, compared to the SEM photograph shown in Figure 4a.

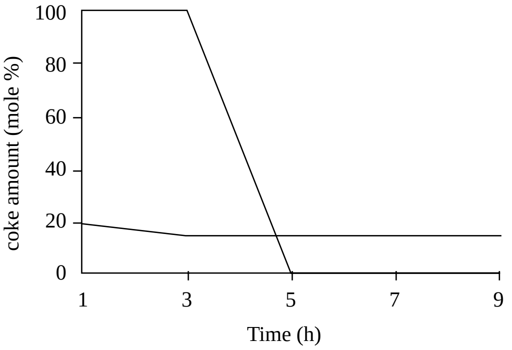

**Figure 2a.** The effect of temperature on CO conversion ($H_2$/CO = 2, W/F = 5.5, 15% CO). 508 K and 573 K.

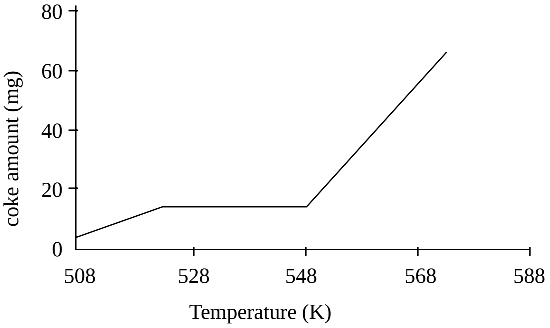

**Figure 2b.** Coke amount, determined with TPR tests, deposited on used catalysts.

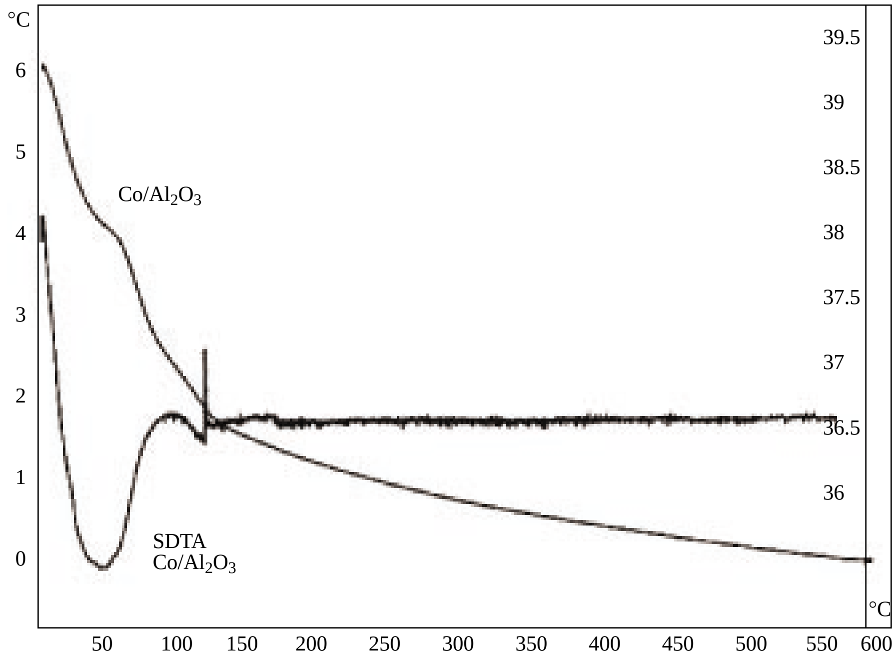

**Figure 3.** TGA-DTA graph of the catalyst used for the CO hydrogenation reaction at 523 K ($H_2/CO = 2$, W/F = 5.5 $mg_{cat}$.min/mL, CO% in feed gas = 20).

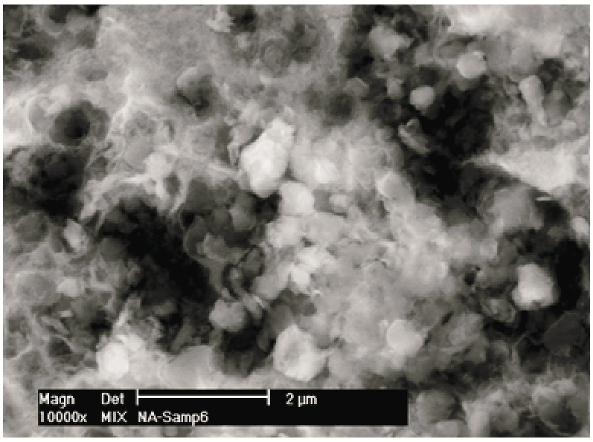

**Figure 4a.** SEM image before TPR (used catalyst at 523 K).

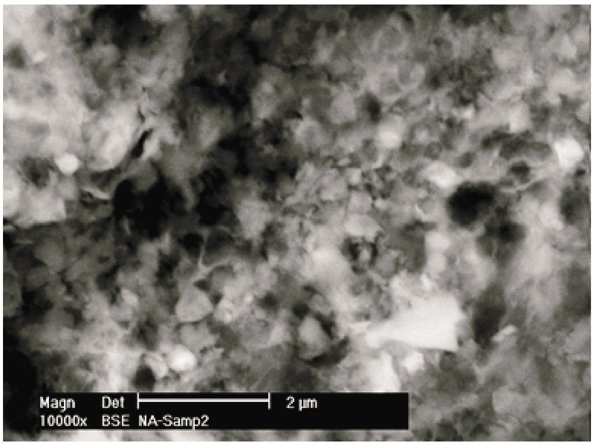

**Figure 4b.** SEM image after TPR (used catalyst at 523 K).

In order to investigate the effect of $H_2/CO$ ratios in feed on the production rates of hydrocarbons and catalyst deactivation properties, experiments were conducted with $H_2/CO$ feed gas of ratios between 1 and 3 and at a constant reaction temperature of 523 K. The CO conversion and the individual production rates of $CO_2$, $CH_4$, and $C_2$-$C_3$ hydrocarbons given in Table 1 showed that $CH_4$ and $CO_2$ production rates increased at higher $H_2/CO$ ratios. In the case of $H_2/CO = 3$, 98 wt% of hydrocarbons in the product stream was methane.

**Table 1.** CO conversion and production rates of hydrocarbons at 3 different feed ratios (523 K, 5.5 mg min/ml, 20% CO in feed).

| $H_2$/CO | CO conversion (mole %) | $CO_2$ production rate ($\mu$mol/$g_{cat}$.min) | $CH_4$ production rate ($\mu$mol/$g_{cat}$.min) | $C_2$-$C_3$ production rate ($\mu$mol/$g_{cat}$.min) |
|---|---|---|---|---|
| 1 | 4.4 | 3.9 | 3.6 | 4.7 |
| 2 | 15.0 | 25.7 | 58.7 | 20.4 |
| 3 | 96.3 | 413.6 | 2064.9 | 0.7 |

By increasing the $H_2$/CO ratio, coke deposition on the catalyst increased and the highest value of coke deposition was observed on the catalyst tested at $H_2/CO = 3$, as shown in Figure 5. Additionally, a 2% decrease was observed in TSA of this used catalyst compared to the fresh one.

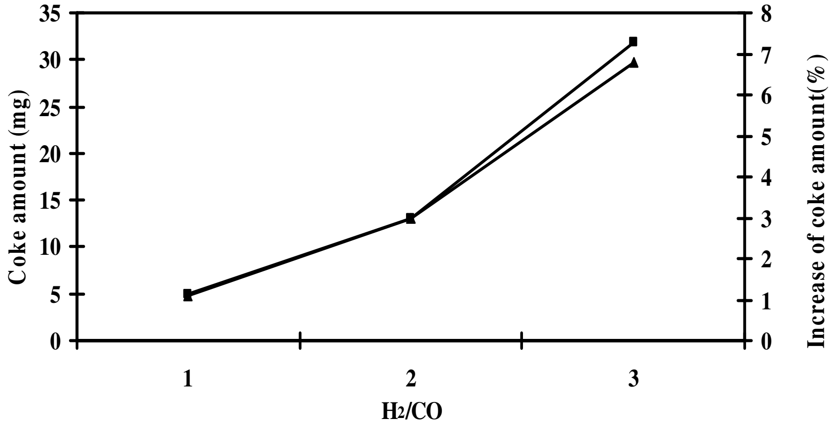

**Figure 5.** The effect of the $H_2$/CO ratio on the amount of coke deposited on the catalysts. (▲ increase in coke (%), ■ coke amount (mg))

To study the effect of the W/F (catalyst weight/feed flow rate) ratio on catalyst deactivation conditions, experiments were conducted at 3 different W/F ratios (5.5, 11.5, 17.0), and at a constant $H_2$/CO value of 2, temperature of 523 K, and a minimum 20% CO in feed. According to the results obtained from these experiments, CO conversion increased by increasing the space time, as shown in Figure 6. At low space times, stable activity and selectivity were obtained for 9 h. Increasing the W/F ratio caused a decrease in catalyst activity, as a function of time, due to coke formation. As shown in Table 2, an increase in methane selectivity and a decrease in $C_2$-$C_3$ hydrocarbons selectivity were observed at high W/F ratios. Furthermore, the amount of carbonaceous compounds deposited on the used catalyst increased from 17% to 35% by increasing the W/F ratio from 5.5 to 17 mg.min/mL.

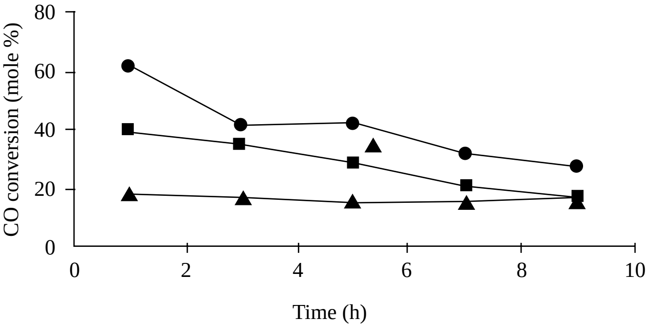

**Figure 6.** CO conversion versus reaction time at different space times (523 K, $H_2$/CO = 2, 20% CO in feed). (▲ 5.5 mg.min/mL; ■ 11.5 mg.min/mL; ♦ 17 mg.min/mL.)

**Table 2.** $C_2$-$C_4$ and $CH_4$ selectivities at different W/F ratios (523 K, $H_2$/CO = 2, 20% CO in feed).

| W/F ratio | $C_2$-$C_3$ selectivity (mol%) | $CH_4$ selectivity (mol%) |
|---|---|---|
| 11.5 | 0.46 | 0.39 |
| 17 | 0.38 | 0.45 |

In order to study the effect of CO percentage in feed gas, experiments were conducted at 3 different percentages (10%, 20%, and 33%), at a constant temperature of 523 K, $H_2$/CO ratio of 2, and space time of 5.5 mg.min/mL. The results presented in Table 3 indicate that increasing the CO percentage in feed gas caused a decrease in activity of the catalyst due to coke formation, but increased $C_1$-$C_3$hydrocarbon selectivity. Higher molecular weight hydrocarbon selectivities at lower CO percentages in feed gas were also observed.

**Table 3.** Conversion and selectivity values at different CO percentages in feed gas at a constant temperature (523 K, space time 5.5 $mg_{cat}$.min/mL, and $H_2$/CO ratio 2).

| CO % in feed gas | CO conversion (mol%) | $C_1$-$C_3$ selectivity (mol%) | High molecular weight HC selectivity (mol%) | $CO_2$ selectivity (mol%) |
|---|---|---|---|---|
| 10 | 36.2 | 36.0 | 40.0 | 24.0 |
| 20 | 25.8 | 55.0 | 32.0 | 13.0 |
| 33 | 20.3 | 58.0 | 20.0 | 22.0 |

## Conclusions

Deactivation conditions (reaction temperature, $H_2$/CO ratio, space time, and CO percentage in feed) of Co/$Al_2O_3$ catalysts with metal loadings of 36 wt% catalysts were investigated in CO hydrogenation reactions. The results show that: (i) CO conversion attained its maximum levels at a reaction temperature of 573 K, (ii) increasing the temperature decreased methane and $C_2$-$C_3$ production rates, and the minimum $C_2$-$C_3$ production rate was observed at 548 K, but the catalyst lost its activity in a very short time at 573 K, (iii) $CH_4$ and $CO_2$ production rates increased at higher $H_2$/CO ratios, and (iv) the effect of space time and CO percentage in feed has less influence on catalyst activity.

## Acknowledgment

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