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Passivation of a Co–Ru/γ-Al_2O_3 Fischer–Tropsch catalyst

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Abstract

Passivation of highly dispersed metal catalysts after reduction is necessary prior to exposure to air due to the exothermicity of metal oxidation. This exothermicity can result in a significant increase in temperature of the catalyst resulting in catalyst degradation and a potential fire hazard. This paper reports the results of a study of passivation of Ru-promoted Co/alumina. Passivations using CO and $CO + H_2$ mixtures were compared to the standard method of passivation using small concentrations of O_2. Passivation by $CO + H_2$ resulted in a lower temperature rise upon exposure to air than oxygen passivation. Passivation using $CO/H_2 = 10$ resulted in a catalyst whose catalytic activity for CO hydrogenation was able to be recovered after exposure to air by re-reduction similar to after oxygen passivation. CO passivation yielded a catalyst that was not able to be as well recovered upon re-reduction, probably due to the formation of graphitic carbon. Exposure of the CO/H_2 passivated catalyst to air for at least 90 min actually made it easier to recover the original activity upon re-reduction. This is probably related to the oxidation of the carbidic passivation layer during air exposure. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Passivation; O_2 passivation; CO passivation; Cobalt catalysts; Fischer–Tropsch synthesis

1. Introduction

One of the most-studied hydrogenation reaction systems is that of Fischer–Tropsch synthesis [1–3]. Among the catalysts used for this reaction, cobalt is the one that attracts most of current attention for the indirect conversion of natural gas due to its high activity, high selectivity for long chain paraffins, and low water gas shift activity. It is well known that the reduced form of the metal is the active site for this reaction [4], thus an activation of the catalyst prior to reaction by reduction is required. For various reasons, it is often useful to reduce the catalyst ex situ. Due to the high oxidizibility of cobalt metal upon exposure to air and the high exothermicity of this reaction, the catalyst may be degraded by sintering and may constitute a fire hazard. Passivation is required to protect the surface of the reduced catalyst from rapid oxidation. It is common to passivate metals or materials by creating a layer of oxide on the surface, which will decrease the activity of the oxidation thus a decrease in the generated heat. As an example of this application, aluminum, very reactive to air, is coated with a layer of oxide in order to make it inert [5]. In the case of metals, passivation is typically achieved by introducing slowly a low concentration of oxygen to the reduced metal to form a thin layer of oxide. A recent Exxon patent suggests that passivation with CO or CO/H_2 is effective [6]. The mentioned work suggested the idea of examining the passivation with CO/H_2 of cobalt catalysts and its effect on the reactivity. This paper reports on the results of an investigation into the

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effectiveness of passivation with O_2, CO, or CO/H_2 a Co–Ru/γ-Al_2O_3 Fischer–Tropsch catalyst.

2. Experimental

The catalyst, 20 wt.%Co–0.5 wt.%Ru/γ-Al_2O_3, used for this study was prepared by incipient wetness impregnation. The Al_2O_3, vista B, was calcined at 500 °C during 10 h prior to utilization. Its BET surface area was ca. 200 m^2/g and average particle size was ca. 60 μm. Cobalt nitrate and the ruthenium nitrosyl nitrate were dissolved in de-ionized water and co-impregnated in γ-Al_2O_3 to form 20 wt.%Co–0.5 wt.%Ru/γ-Al_2O_3. The catalyst was dried at 110 °C for 12 h and calcined in air at 300 °C for 2 h. The average Co particle size based on hydrogen chemisorption at 100 °C was ca. 218 Å.

The catalyst was reduced in situ in a differential fixed bed reactor in H_2 at 350 °C for 10 h using a ramp of 1 °C/min. The amount of catalyst used, around 20 mg, was diluted in α-Al_2O_3 (40 mg) to avoid an increase of temperature in the catalytic bed due to the exothermicity of the reaction. Following the reduction, several pretreatments were studied. The catalyst was passivated with 1.93% O_2/He (20 cm^3/min) during 1 h at room temperature, or with CO/He (20/30 cm^3/min), or CO/H_2/He (20/2/28 cm^3/min) for 1 h of time at 250 °C. Following passivation, the catalyst was exposed to a flow of air of 20 cm^3/min at room temperature prior to reaction. Different exposure times were studied in the case of CO/H_2 passivation. In order to determine the impact of passivation on the catalyst, the activity of the catalyst for CO hydrogenation was tested after each pretreatment. The reaction was performed at 220 °C and 1.8 atm. The feed composition was of $CO/H_2/He = 2/20/78\ cm^3/min$. All the gases used were of ultra high purity and were further purified. The exit lines from the reactor were heated and maintained at 120 °C to avoid condensation of hydrocarbons.

3. Results and discussion

3.1. Effect of passivation on ΔT during exposure to air

As mentioned previously, the oxidation reaction of cobalt metal generates a lot of heat. Before investigating the effect of passivation of Co–Ru/γ-Al_2O_3 on FTS, the increase of temperature after passivation of the reduced cobalt upon exposure to air was examined. For this purpose, 2 g of catalyst were reduced under standard reduction conditions and then passivated with either O_2 or CO/H_2 and exposed to a flow of air. Fig. 1 shows the increase of temperature that occurred during the exposure to air of reduced cobalt, O_2-passivated Co, and CO/H_2-passivated Co. It is clear that CO/H_2 passivation was more efficient in protecting the catalyst from a high increase in temperature.

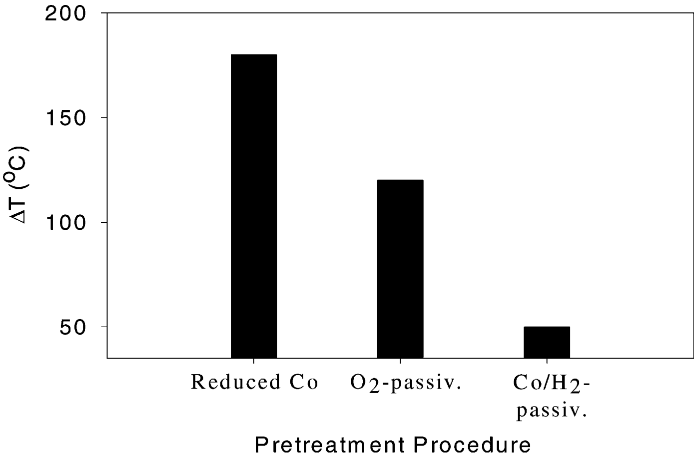

Fig. 1. Effect of passivation on the increase of temperature of Co catalyst during air exposure.

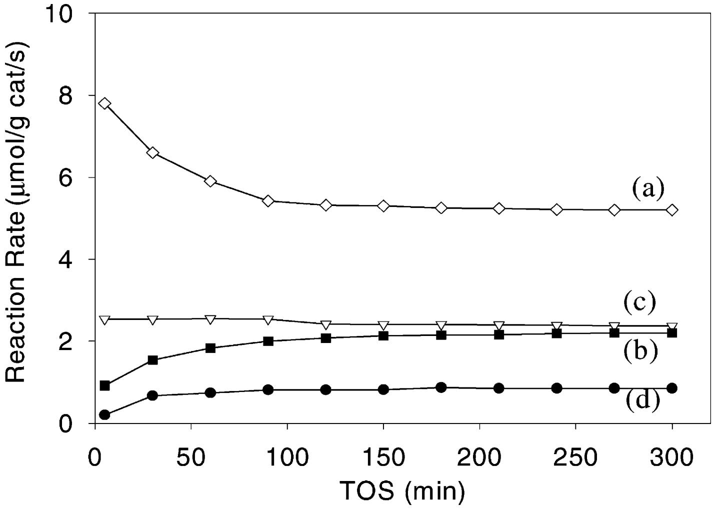

Fig. 2. Effect of O_2 passivation, CO passivation and CO/H_2 passivation on the activity of the catalyst: (a) freshly reduced catalyst; (b) passivation with O_2; (c) passivation with CO; (d) passivation with CO/H_2.

3.2. *Catalyst activity after passivation (without exposure to air or re-reduction)*

The results of variation in activity with time-on-stream of the O_2-passivated catalyst, CO-passivated catalyst and CO/H_2-passivated catalyst are shown in Fig. 2. The results are compared to those for the freshly reduced catalyst. They indicate, as expected, a clear decline in the activity of the passivated catalysts. However, the mechanism of deactivation during passivation was different for the three cases. Obviously, passivation with O_2 deactivated the catalyst due to the formation of a layer of oxide on the Co surface of the catalyst. Passivation with CO partially deactivated the catalyst, although not as much as in the case of O_2 passivation. The decrease in the activity was due to carbon deposited by the Boudouard reaction ($2CO \rightarrow C + CO_2$). The carbon formed may have been carbidic (C_α), or graphitic carbon. Since the temperature of pretreatment used does not favor the formation of graphite, it was unlikely that it was the main species formed. The necessary temperature for graphite formation is as high as 350 °C [7]. Graphitic carbon deactivates irreversibly the catalyst given that it is relatively inert to hydrogen. It has been found that, in the absence of H_2, surface carbon formed on Ru is mainly C_α [8]. This carbidic carbon would react easily with hydrogen to form methane [8–10]. Though the C_α may be very reactive with H_2, the complete recovery of the active sites in this study was not possible at 220 °C. Relatively high initial rate have been due to fast removal of carbidic carbon. This difficulty to completely regenerate the catalyst even after 300 min in a CO/H_2 mixture with a high concentration of H_2 probably relates to graphitic carbon formation.

As was the case for both O_2 passivation and CO passivation, there was a significant decline in the activity of the CO/H_2-passivated catalyst. However, the mechanism of deactivation must have been different. Deactivation of the catalyst was probably the result of formation of a layer of a partially hydrogenated carbonaceous species on the surface of the catalyst that decreased the amount of available active sites by covering them. This carbonaceous layer may have consisted of a variety of species. Nakamura et al. [10] detected the presence of CH_x while pretreating the catalyst with CO in the presence of a small amount of H_2. Other species that may be present is C_β, a less reactive form of carbon [8]. It has been determined that C_β has the structure of an alkyl group [11] and can be formed by polymerization of CH_x species [8]. The formation of carbidic carbon cannot be excluded.

The rate of reaction increased with the time-on-stream for both O_2-and CO/H_2-passivated catalyst. The increase in the activity may be explained by the fact that the reactants (CO/H_2) partially reduced the layer of cobalt oxide that was formed during O_2 passivation. For the CO/H_2-passivated catalyst, the results may be interpreted by the fact that the reactants, mainly H_2, reduced the layer of carbonaceous species on the surface by hydrogenating it to products. The recovery of the activity for O_2 and CO/H_2 passivation was not even asymptotic to the steady-state activity of the reduced catalyst. Unlike for O_2 and the CO/H_2 passivations, CO-passivated catalyst decreased slightly in activity from its initial relatively high value with time-on-stream.

3.3. Passivated-catalyst activities after exposure to air (without re-reduction)

In order to estimate the effectiveness of passivations with O_2 and CO/H_2, the catalysts were exposed to a flow of air for 90 min after being passivated. Fig. 3 gives the activity variation of the passivated catalysts with time-on-stream, after exposure to air. The freshly reduced catalyst was used as a reference. The initial activity of the O_2-passivated catalyst was low (near zero) compared to the CO/H_2-passivated one. The O_2-passivated catalyst was obviously further oxidized when exposed to air producing the decrease in initial activity from 0.93 to 0.02 μmol/g-cat/s. The layer of oxide formed on the reduced catalyst during O_2 passivation decreased the rate of oxidation during exposure to air but did not prevent it. For comparison with a fully oxidized catalyst, the calcined catalyst was tested under reaction conditions and its activity compared to the activity of the O_2-passivated catalyst and to the O_2-passivated and exposed to air catalyst (Fig. 4). The calcined cobalt catalyst, containing most of the cobalt in Co_3O_4, had basically no activity, even after 24 h TOS of exposure to the reactants stream. These results suggest that O_2 passivation oxidized the cobalt available on the surface of the catalyst. The layer of cobalt oxide formed on the reduced Co surface during O_2 passivation can be gradually removed under reaction conditions. The O_2 introduced during passivation after reduction was insufficient to oxidize all the metal present in the catalyst. It has been found that a short exposure to air of a reduced catalyst is sufficient to form an oxide layer on the metal surface that has the form of CoO [12]. Whereas the O_2-passivated catalyst exposed to air had a very low initial activity, comparable to that of the calcined catalyst, after 3 h of reaction the activity increased to 2 μmol/g-cat/s, similar to that of the O_2-passivated catalyst for the same TOS.

A very interesting behavior of the CO/H_2-passivated catalyst was noticed since the activity of the catalyst increased when exposed to air after passivation. The carbonaceous layer must have prevented the catalyst from significant oxidation.

The activity of the catalysts increased with TOS for the reasons mentioned earlier, reduction by the reactants of the oxide layer formed in the case of O_2

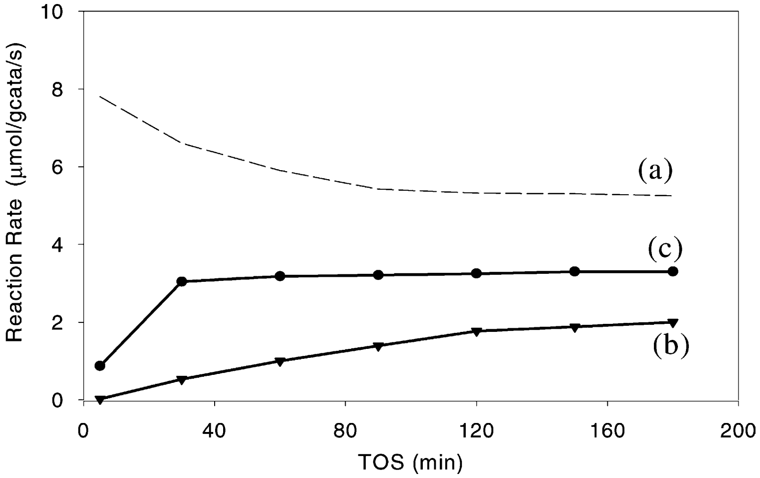

Fig. 3. Activity of the passivated catalysts after exposure to air: (a) freshly reduced catalyst; (b) passivation with 1.93% O_2/He; (c) passivation with CO/H_2.

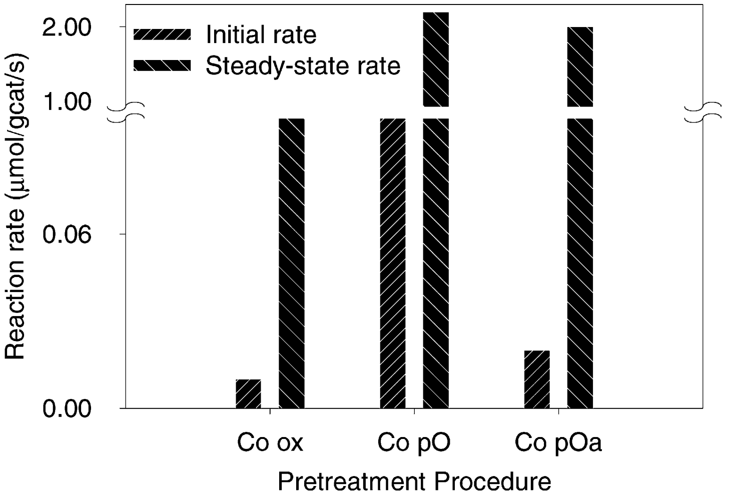

Fig. 4. Comparison of the calcined catalyst (Co ox), the O_2-passivated catalyst (Co pO), and the O_2 passivated and exposed to air catalyst (Co pOa).

passivation and removal of the carbonaceous species or the new species formed after exposure to air in case of CO/H_2 passivation.

3.4. Passivated-catalyst activities after exposure to air and re-reduction

After exposure to air, the passivated catalysts were re-reduced under standard reduction conditions. From Fig. 5, we can see that the O_2-passivated, the CO/H_2-passivated, and the fresh catalysts had almost similar activities. Passivation of the catalyst by various means did not deactivate it irreversibly.

The passivation of the catalyst with O_2 deactivated slightly the catalyst. The small decrease in activity of the O_2-passivated catalyst may have been due to the formation of irreducible cobalt species during re-reduction. Zhang et al. [13], found a decrease in

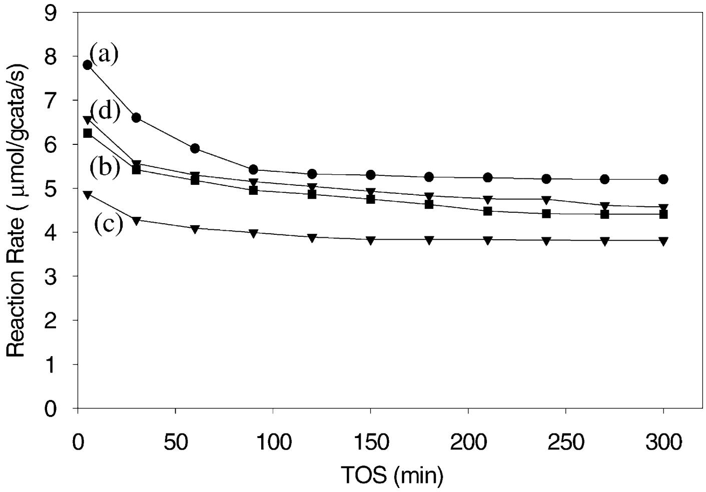

Fig. 5. Effect of re-reduction of the passivated catalyst on the activity: (a) freshly reduced catalyst; (b) O_2-passivation; (c) CO-passivation; (d) CO/H_2-passivation.

Table 1
Effect of reduction on the CO/H_2-passivated catalyst

CO/H_2-passivated catalyst[a]	Initial rate (μmol/g-cat/s)	S–S rate (μmol/g-cat/s)	CH_4 selectivity
Without exposure to air	5	3.5	52.0
With exposure to air[b]	6.6	4.8	56.5

[a] CO/H_2 = 10.
[b] Time of exposure: 90 min.

the reducibility of the catalyst due to the presence of water vapor during catalyst reduction. During reduction, a small fraction of Co^{2+} diffused into the tetrahedral vacancies of γ-Al_2O_3 [14].

The activity of the CO-passivation catalyst was not fully recovered. The partial irreversible deactivation of the CO-passivated catalyst may have been due to the presence of a large amount of carbidic carbon in the catalyst even after exposure to air and its conversion to graphite during re-reduction at high temperature.

The loss of active sites in the case of the CO/H_2-passivated catalyst may have been due to several reasons. During reduction, the carbonaceous layer was probably partially removed in the form of hydrocarbons; the remaining carbonaceous material could have been converted to graphitic carbon which caused permanent loss of surface active sites. Samorjai and Zaera [15] have found that an organic layer on a surface of a metal is readily removed with hydrogen if it is in the form of $C_nH_{1.5n}$, while, if in the form of $C_{2n}H_n$, it is not able to be removed even in the presence of an excess of H_2. Those results are consistent with the activity results for the CO/H_2-passivated catalyst re-reduced before and after exposure to air (Table 1). The exposure of the catalyst to air helped in recovering a slightly larger amount of the active sites than the one that was not exposed to air probably by reaction of O_2 with the carbonaceous material to form species easier to remove with H_2.

3.5. Effect of time of air exposure of the CO/H_2-passivated catalyst

The CO/H_2-passivated catalyst was exposed to air for different lengths of time in order to verify that the layer in fact protected the surface of the catalyst. The results for activity with time-on-stream for different exposure times are shown in Fig. 6. The freshly

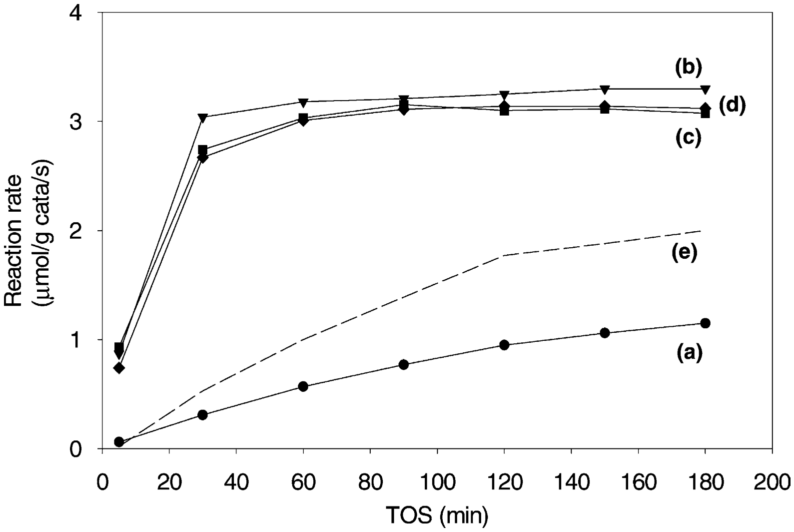

Fig. 6. Effect of exposure time to air of the CO/H_2-passivated catalyst: (a) 30 (b) 90 (c) 180 (d) 360 min; (e) O_2 passivation (90 min).

reduced catalyst was again used as a reference. The activity of the catalyst increased with time of exposure to air from 30 to 90 min. There was no significant change in activity after 90 min of exposure to air. The results suggest that when exposed to air, the carbonaceous layer reacts with oxygen in the air to form species that are stable at room temperature such as perhaps surface cobalt carbonates. Thirty minutes of exposure of the catalyst to air is too short time to oxidize the carbon on the surface of the catalyst. Removal of the carbonaceous layer under reaction conditions is not easy, thus the low activity. A long exposure time to air oxidizes the carbon on the surface facilitating the recovery of the activity. It is easier to remove the carbon oxide from the surface of the catalyst than to reduce the oxide layer formed during O_2 passivation or the carbonaceous layer.

4. Conclusions

This study has provided a better understanding of Co passivation and the use of CO as a passivating agent. CO/H_2 passivation was more effective in protecting the catalyst from a high increase in temperature upon exposure to air compared to O_2 passivation.

Re-reduction of the catalyst after O_2 or CO/H_2 passivation and exposure to air resulted in recovery of most of the original activity. However, re-reduction after CO passivation and exposure to air did not lead to a recovery of the original activity of the catalyst, possibly due to the conversion of carbidic carbon, formed during passivation, to graphitic carbon at the higher temperature used for re-reduction.

CO/H_2 passivation created a layer of carbonaceous species on the surface of the catalyst. It preserved the surface of the catalyst from rapid oxidation upon exposure to air. The exposure to air helped in facilitating the recovery of most of the active sites during re-reduction.

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