Catalysis Letters Vol. 101, Nos. 3–4, June 2005 (© 2005)
DOI: 10.1007/s10562-005-4888-0

Fischer–Tropsch synthesis: Deactivation of promoted and unpromoted cobalt–alumina catalysts

Tapan K. Das*, Gary Jacobs, and Burtron H. Davis
Center for Applied Energy Research, 2540 Research Park Drive Lexington, KY 40511

Received 23 June 2004; accepted 19 January 2005

The loss in activity of Pt-promoted and unpromoted 25 wt% Co–Al_2O_3 catalysts has been compared under identical conditions except for adjustment of the space velocity to give the same initial CO-conversion. Both catalysts underwent a 200 h period of rapid, initial decline in CO conversion and then a slower, linear decline during the next 1000 h. Pt-promotion did not alter the cobalt dispersion (or average particle size) from that of the unpromoted catalyst but did increase the amount of cobalt that was reduced. When compared not by time-on-stream, but by the moles of Co converted per unit weight of catalyst, both the Pt-promoted and unpromoted catalysts decline in activity at the same rate.

KEY WORDS: Co-Al_2O_3 catalysts; Pt promoter; catalyst aging; deactivation; Fischer–Tropsch synthesis; water.

1. Introduction

Cobalt catalyst for the Fischer–Tropsch synthesis are now receiving commercial applications for gas-to-liquids (GTL) conversions. It has been well established that the catalytic activity of the cobalt catalyst depends directly upon the number of surface cobalt atoms as determined by chemisorption, i.e., by hydrogen chemisorption. Thus, the turnover number (TON) remains constant as the cobalt dispersion increases up to about 12%, the highest attained dispersion following reduction of the cobalt catalyst [1]. Since the TON is constant with dispersion, approaches to increase the productivity include increasing dispersion and/or increasing the fraction of cobalt that is reduced to the metal. The addition of promoter metal(s), mainly noble metals, has been widely utilized to increase the fraction of cobalt that is available for surface catalysis.

The noble metal could increase the extent of reduction by dissociating hydrogen which then spills over to reduce the cobalt oxide to cobalt metal. If this is the case, one would expect the cobalt dispersion to show a significant increase when the noble metal was present compared to that of the unpromoted catalyst. However, it has been found that while the promoter metal may increase the fraction of cobalt reduced to the metal by a factor of two or even greater, there is only a slight decrease in the size of the individual cobalt crystallite [2]. One might anticipate that to reduce the cobalt that strongly interacts with the support by spillover hydrogen atoms would lead to smaller cobalt particles than the ones produced from the easily reduced cobalt oxide particles. However, for the alumina, silica and titania supported catalysts the dispersion of cobalt was nearly the same whether the noble metal was present or not; the major difference was that when the noble metal was present the percentage reduction of cobalt was much higher [2]. It therefore appears that the cobalt atoms formed by spillover hydrogen are mobile and diffuse to produce cobalt clusters which grow to a size that is primarily determined by the reduction temperature so that both the easily reduced cobalt oxide and the more difficult to reduce cobalt that interacts with the support form a common size cobalt particle.

One may expect the cobalt that is most difficult to reduce would be the easiest to re-oxidize. One would also expect the more difficult-to-reduce cobalt would be present in smaller crystal sizes, and this is the case when the average particle size is calculated based upon the total cobalt in the sample. However, when the cobalt particle size is based on the cobalt that is reduced, both samples have the same average particle size. Preliminary data indicate that the promoted catalyst had a higher initial activity but also had a more rapid loss of catalytic activity so that eventually the promoted catalyst had a lower activity than the unpromoted catalyst [3]. In the present study, a common base catalyst was used as the unpromoted and the Pt-promoted catalyst. In addition, prior conversion data was used so that the unpromoted cobalt–alumina catalysts could be utilized with the same conditions, except for space velocity, as the Pt-promoted catalyst, so that the initial conversion would be essentially the same. Thus, both catalysts would be exposed to the same initial partial pressure of water as well as the reactants. This should then allow the aging rate to be defined under identical initial reaction conditions.

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*To whom correspondence should be addressed.

2. Experimental

The catalyst was prepared on 150 $m^2 g^{-1}$ Condea Vista Catalox B γ-Al_2O_3 support. The Co/Al_2O_3 catalyst with a loading of 25% was prepared by a slurry impregnation method. In this method, which follows a procedure in a Sasol patent [4], the ratio of the volume of loading solution used to the weight of alumina was 1:1, such that approximately 2.5 times the pore volume of solution was used to prepare the catalyst. Two impregnation steps were used to load 12.5% of Co by weight in each step. Between each step the catalyst was dried under vacuum in a rotary evaporator at 333 K with the temperature being slowly increased to 373 K. After the second impregnation/drying step, the catalyst was calcined in air for 10 h. The promoter was added by the incipient wetness impregnation technique and the precursor utilized for noble metal addition was tetraammineplatinum (II) nitrate. After Pt addition, the sample was dried and calcined again, with the same conditions as before.

Prior to the BET measurement, the sample was slowly ramped to 433 K and evacuated for 4 h to approximately 6.7 Pa. Pore size distributions (PSD) of the catalysts were quantified by the Barrett, Joyner, Halenda (BJH) desorption model [5], which provides a relationship where the amount of adsorbate lost during a desorption step gives the average size of the pore emptied during that desorption step. Experimentally, the desorption branch was employed by the BJH method.

The catalyst activation was conducted first *ex situ* and then *in situ*, according to the following procedure. The catalyst (about 15 g; actual weight accurately known) was placed in a fixed bed reactor and pure hydrogen was introduced at a flow rate of 60 NLh^{-1} (ca. 3000 GHSV) (298 K, 0.1 MPa); the reactor temperature was increased from room temperature to 373 K at a rate of 120 K h^{-1}, then increased to 623 K at a rate of 60 K h^{-1} and kept 623 K for 16 h. The catalyst was transferred under the protection of helium to the CSTR to mix with 300 g of melted Polywax (P.W.) 3000. The catalyst was then reduced *in-situ*. The hydrogen was introduced to the reactor at atmospheric pressure with a flow rate of 30 NLh^{-1} (ca. 1500 GSHV) (298 K, 0.1 MPa). The reactor temperature was increased to 553 K at a rate 120 K h^{-1} and maintained at this activation condition for 24 h.

The FTS reactor system has been described earlier [6]. After the activation period, the reactor temperature was decreased to 453 K and synthesis gas mixture ($2H_2$/1CO) was introduced to increase the reactor pressure to 2.0 MPa. The reactor temperature was then increased to 503 K at a rate of 10 K h^{-1}. During the entire run, the reactor temperature was 503 K and the pressure was 2.0 MPa. Separate mass flow controllers were used to add H_2 and CO at the desired rate to a mixing vessel that was preceded by a lead oxide–alumina containing vessel to remove iron carbonyls. The mixed gases entered the CSTR below the stirrer operated at 750 rpm. Products were continuously removed from the vapor and passed through two traps, one maintained at 373 K and the other at 273 K. The contents of 273 K and 373 K traps were combined, the hydrocarbons and water fractions separated, and then analyzed by GC. The uncondensed vapor stream was reduced to atmospheric pressure through a pressure letdown valve. The flow was measured with a bubble-meter and composition quantified using an on-line GC. The accumulated reactor liquid products were removed every 24 h by passing through a 2 μm sintered metal filter located below the liquid level in the CSTR. The reactor wax sample was analyzed by a high-temperature GC to obtain a carbon number distribution for C_{20}–C_{80}.

The space velocity was adjusted to produce essentially the same conversion (48% CO conversion) for both catalysts. For the unpromoted catalyst this was 3 SL h^{-1} g^{-1}_{cat} and for the Pt-promoted catalyst it was 8 SL h^{-1} g^{-1}_{cat}. As the run progressed the space velocity was adjusted so that the flow to both catalysts was essentially the same (2 SL h^{-1} g^{-1}_{cat}).

3. Results and discussion

The surface area of the support was 150 $m^2 g^{-1}$ and following impregnation to load 25 wt% Co the surface area was found to be 103 $m^2 g^{-1}$. Correcting the weight of the catalyst for the loading of cobalt oxide indicates that the measured surface area of the cobalt–alumina catalyst should be 106 $m^2 g^{-1}$, in good agreement with the measured value, showing that the added cobalt did not significantly alter the surface available to the gas phase. Characterization following reduction of the catalyst at 623 K was accomplished by hydrogen adsorption for the uncorrected data (table 1) and following reoxidation to obtain the percentage of cobalt that was reduced to the metal to calculate the corrected data (table 1).

Table 1
Dispersion and average diameter of cobalt in the promoted and unpromoted catalyst

Sample	Uncorr. dispersion, %	Uncorrected av. D, nm	% reduction	Corrected dispersion, %	Corrected av. D, nm
25%Co–Al_2O_3	3.7	28.2	42	8.7	11.8
0.5%Pt–25%Co–Al_2O_3	7.0	14.7	71	9.4	11.0

Considering only the uncorrected data shown in table 1, the presence of the Pt-promoter appears to greatly increase the dispersion and to decrease the average diameter of the cobalt particles. The uncorrected data are based on the total amount of cobalt present in the catalyst. However, when these values are corrected to include only the cobalt reduced to the metallic state in the calculations, the dispersion and average particle diameter are essentially the same for the two catalysts. On the corrected basis, the Pt-promoter has the effect of increasing only the fraction of cobalt that is reduced to the metallic state and does not alter significantly either the dispersion or the average cobalt particle diameter from that of the unpromoted catalyst. While this may seem surprising, this effect has been observed for different loadings of cobalt on a common support and for cobalt on three different supports: alumina, silica and titania [2]. Thus, based on the amount of cobalt reduced, the two catalysts used in this study have essentially the same cobalt crystallite size.

One view of Pt-promotion would be that hydrogen dissociates on a Pt site and spills over to reduce cobalt in addition to that which is reduced in the unpromoted catalyst. This would require that the dispersion become higher and the average cobalt diameter become smaller than in the unpromoted catalyst if it is assumed that the major fraction of the cobalt that is reduced in the unpromoted catalyst exists as Co_3O_4 particles. If the Co_3O_4 particles that are reduced in both catalysts are the same size, they should reduce to the same extent in the unpromoted catalyst as in the Pt-promoted catalyst, and produce cobalt metal particles of the same size, as is observed experimentally. It is therefore concluded that the Pt is catalyzing the reduction of cobalt species that are in addition to those reduced in the unpromoted catalyst, and these should be more difficult to reduce. As noted, the more difficult to reduce cobalt should produce smaller cobalt metal particles but, as shown in table 1, this is not the case. Therefore, it is concluded that in the case of promotion by Pt, the more difficult to reduce cobalt must, rather than form smaller particles, sinter to produce a cobalt metal particle size distribution that depends upon the reduction temperature, and not on the extent of reduction.

The initial CO conversions of the promoted and unpromoted catalysts were essentially the same (figure 1). Both catalysts showed a rapid, initial decline in CO conversion and this is typical of earlier results from other laboratories [e.g., [7]]. While there is a large error in measuring the rate of this initial decline, it is approximately 1.3% CO conversion/week for the unpromoted and 17% CO conversion/week for the Pt-promoted catalyst. As we have observed previously [8], the initial decline in activity of the promoted cobalt catalyst may be more rapid than the unpromoted one so that eventually the unpromoted catalyst has a higher CO conversion than the promoted one. This is the case for the data in figure 1 up to 1000 h if the difference in space velocity is ignored. Thus, while the promoted catalyst has a higher catalytic activity, it loses its activity at a rate that is more rapid than observed for the unpromoted catalyst.

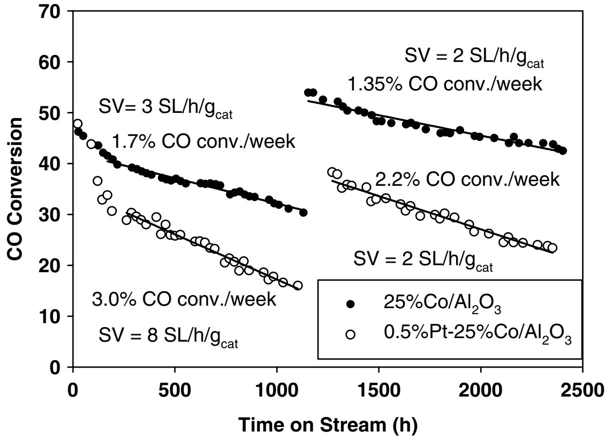

Figure 1. CO conversion with time-on-stream for 25 wt% Co–Al_2O_3 (●) and 0.5 wt% Pt-25 wt% Co–Al_2O_3 (○) catalysts as same conditions (2.02 MPa, 220 °C, $H_2/CO = 2$) except for space velocity as indicated in the figure.

The rapid decline in activity lasts for about 200 h for both catalysts. Following this rapid decline, there then begins a slower, linear decline in activity during a period of about 1000 h. For the unpromoted catalyst the decline is 1.7% CO conversion/week and for the Pt-promoted catalyst it is more rapid at 3.0% CO conversion/week. After about 1200 h, the space velocity was adjusted to 2.0 SL h^{-1} g^{-1}_{cat} so that the catalysts could be compared under identical conditions. As shown in figure 1, the unpromoted catalyst now has a higher activity that the Pt-promoted catalyst. In addition, the Pt-promoted catalyst declines in activity more rapidly than the unpromoted catalyst (1.35% CO conversion/week versus 2.2% CO conversion/week, respectively) at this lower space velocity.

The previous comparisons have been made by the activity changes with time-on-stream. Because the Pt-promoted catalyst is more active, it has converted a larger number of CO during the period of time in which the comparison is made. A more reasonable comparison can be made on the basis of the number of moles of CO that are converted rather on the basis of time-on-stream. When the comparison is made on the basis of number of moles of CO converted, the two catalysts show a similar rate of decline in CO conversion, both during the period of initial, rapid decrease and then during the slower, linear rate of decline (figure 2).

The data reported here is for a lower loading of cobalt for a typical FTS catalyst. At this level Pt has a major impact on the amount of Co that is reduced. At a higher loading (ca. 25% Co) the noble metal will not have as great an impact on the fraction of Co that is reduced. It appears, based on this limited data, that the

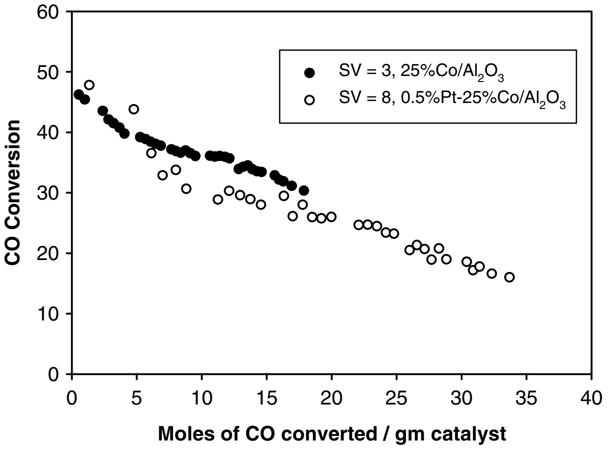

Figure 2. CO conversion compared on cumulative CO converted rather than time-on-stream (2.02 MPa, 220 °C, $H_2/CO = 2$).

decision to use the noble metal as a promoter will be primarily an economic choice based on increased product yield versus cost of the noble metal.

Since the cobalt particle size is the same in the two catalysts, the Pt-promoted catalyst will contain 1.7 times as many cobalt particles as the unpromoted catalyst. The apparent rate of decline in CO conversion on the time scale (figure 1) is greater for the Pt-promoted catalyst; however, if we consider that the Pt-promoted catalyst is converting more CO it should deactivate more rapidly. Thus, the ratio of the rate of decline of the Pt-promoted catalyst to that of the unpromoted catalyst during the slower, linear rate decline period is 1.8, essentially the same as the 1.7 ratio for the greater number of particles on the promoted catalyst.

In summary, the cobalt metal particle sizes in the Pt-promoted and unpromoted catalysts are essentially the same. Based upon the CO conversion versus time curves, it could be concluded that the Pt-promoted catalyst ages more rapidly than the unpromoted catalyst. This activity decline would be consistent with the view that has been advanced that the smaller cobalt particles in the noble metal promoted catalysts re-oxidize more rapidly than the larger ones that are present in the unpromoted catalyst. However, the data show that the cobalt metal particle sizes are the same in both catalysts so that a more rapid re-oxidation of the promoted catalyst cannot account for the difference in the decline in activity. Likewise, since both catalysts were exposed to the same conditions except for space velocity to produce a common initial CO conversion, the differences in activity decline cannot be due to the catalysts being exposed to a different atmosphere in the reactor. When the catalysts are compared, not on a time basis, but on the basis of moles of CO converted, a common curve describes the activity decline for the two catalysts very well. It is therefore concluded that the promotion by Pt merely increases the fraction of cobalt that is reduced to the metal but does not alter the aging properties of the cobalt catalyst.

References

[1] E. Iglesia, Appl. Catal. A: Gen. 161 (1997) 59–78.
[2] G. Jacobs, T.K. Das, Y. Zhang, J. Li, G. Racoillet and B.H. Davis, Appl. Catal. A: Gen. 233 (2002) 233.
[3] J. Li, X. Zhan, Y. Zhang, G. Jacobs, T. Das and B.H. Davis, Appl. Catal. A: Gen. 228 (2002) 203.
[4] R.L. Espinoza, J.L. Visagie, P.J. van Berge, F.H. Bolder, U.S. Patent 5,733,839 (1998).
[5] E.P. Barrett, L.G. JOyner and P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373.
[6] J. Li, L. Xu, R.A. Keogh and B.H. Davis, Catal. Lett. 70 (2000) 127.
[7] P.J. van Berge and R.C. Everson, Stud. Surf. Sci. Catal. 107 (1997) 207–212.
[8] G. Jacobs, Y. Zhang, T.K. Das, J. Li, P.M. Patterson and B.H. Davis, Stud. Surf. Sci. Catal. 139 (2001) 415.