ELSEVIER

Catalysis Today 24 (1995) 181–187

CATALYSIS TODAY

Catalyst deactivation in liquid- and gas-phase hydrogenation of acetylene using a monolithic catalyst reactor

Staffan Asplund *, Charlotte Fornell, Anna Holmgren, Said Irandoust

Department of Chemical Reaction Engineering, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Abstract

The deactivation of a monolithic Pd/α-alumina catalyst in the selective hydrogenation of acetylene in the presence of excess ethylene has been studied. The deactivation behavior of the monolithic catalyst in the gas-phase hydrogenation was compared to that of the liquid-phase hydrogenation. It was shown that the deactivation behavior was different in the two systems. It was concluded that in the gas-phase hydrogenation the rate of the deactivation is strongly dependent on the operating conditions. In the liquid-phase hydrogenation, both the catalytic activity and the ethylene selectivity declined during the first 60 h of operation and then stabilized. This was not observed in the gas phase. Here, the activity and the selectivity passed through a maximum. Temperature programmed analyses of spent catalysts from liquid and gas phase processes revealed that the amount and nature of the species adsorbed on the catalyst surfaces are different for these two types of processes. In the case of a gas phase process, the amount of oligomers formed on the catalyst surface was much higher. In the liquid-phase hydrogenation, these compounds showed a lower H/C ratio and were adsorbed more strongly in comparison to those from the gas phase process.

1. Introduction

The complete removal of small amounts of acetylene present in feeds of ethylene produced from the steam cracking of naphtha or propane is of commercial interest. Acetylene deteriorates the polymerization catalyst used in the manufacturing of polyethylene from ethylene. Therefore, it is desirable to selectively hydrogenate acetylene with minimum ethane production.

In any acetylene hydrogenation, some polymerization compounds (referred to as green oil) are formed on the catalyst, causing many serious problems such as catalyst fouling and plugging of piping. Green oil will also affect both the ethylene selectivity and the acetylene conversion [1–3]. It is therefore of crucial importance to control the green oil formation in every existing hydrogenation plant.

The conventional process is a catalytic hydrogenation of the gaseous stream. In this process, temperature runaway phenomena, causing several critical problems such as hot spots, can occur. Also, addition of CO is necessary to suppress the formation of ethane. The commercial catalysts for acetylene hydrogenation are based on palladium supported on low surface area alumina, with a metal content of 0.01–0.1 wt.-%. The catalyst load is limited by the smallest size of the pellets that gives an acceptable pressure drop.

Recently, a new technology in which the hydrogenation is performed in the presence of a liquid phase has been developed by the Institut Français du Pétrole [2]. In this process the liquid phase, circulating in a closed loop, continually removes

* Corresponding author.

SSDI 0920-5861(95)00023-2

the green oil by washing the catalyst. The high heat capacity of the liquid serves to reduce the temperature rise, thereby improving the stability of the catalyst. The acetylene content of the feed is reduced to a low level without addition of carbon monoxide. However, when the acetylene content is lowered, the selectivity of this process becomes poor. Therefore, the desired level of acetylene concentration is achieved by a subsequent hydrogenation, which is carried out as a conventional gas phase process with carbon monoxide present. Both these hydrogenation processes are carried out in packed-bed reactors. In the presence of a liquid phase, an even flow distribution is also required to keep the catalyst particles wetted.

Edvinsson et al. [4] have suggested the use of a monolithic catalyst for the liquid-phase hydrogenation of acetylene. In this type of reactor, the solid catalyst forms the walls of a number of small, parallel channels. The geometry of these channels allows a large, specific external surface. The gas and liquid phase form a sequence of separated plugs giving low mass-transfer resistances and pressure drop. The monolithic catalyst reactor does not exhibit considerable scaling-up effects, which facilitates the design [5].

The objective of this work is to compare the gas and the liquid phase processes with respect to the deactivation using a monolithic catalyst.

2. Experimental methods

2.1. Equipment

The setup used for the gas-phase hydrogenation (GPH) experiments is shown in Fig. 1. The gas composition was analyzed by a gas chromatograph (Varian 3300) equipped with a 25 m Al_2O_3/KCl PLOT column (Chrompack). A TCD detector was used for hydrogen whereas a FID detector measured the hydrocarbon components. An internal recycle (Berty) reactor was used for the GPH experiments (Autoclave Engineers). Before conducting any deactivation or kinetic experiments the system was checked for non-idealities following the procedure described by Bos et al. [6]. The equipment used in the liquid-phase hydrogenation (LPH) experiments has been described in detail by Edvinsson et al. [4]. It consisted of a monolithic reactor operated in batch mode with external recirculation.

2.2. The catalyst

The catalyst was prepared by impregnation of an α-Al_2O_3 monolith with $PdCl_2$ following the incipient wetness method. After impregnation the catalyst was dried at room temperature for 16 h, calcined in air at 573 K for 1 h and reduced in

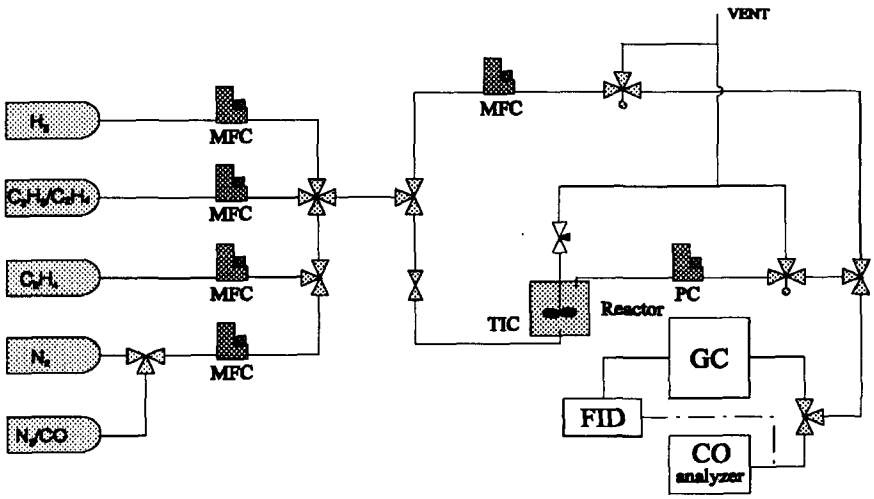

Fig. 1. The setup used for the gas-phase hydrogenation experiments.

Table 1
Catalyst properties

Wall thickness	0.2 mm
Pore volume	0.20 cm^3/g
Cell density	110 cells/cm^2
BET surface	8 m^2/g
Average pore diameter	80 nm
Pd dispersion	0.05–0.10

hydrogen at 573 K for 2 h. Prior to use the catalyst was re-reduced at 423 K for 3 h in situ. The catalyst characteristics are summarized in Table 1.

2.3. Analysis of the spent catalyst

The carbonaceous residues accumulated on the catalyst surface were characterized by temperature programmed hydrogenation (TPH) and temperature programmed oxidation (TPO). In the TPH experiments 0.02 g of catalyst was heated from room temperature to 620 K at a rate of 4 K/min in a stream of hydrogen (10 nml/min). In the TPO measurements 0.10 g of the spent catalyst was heated from room temperature to 1100 K at a rate of 10 K/min. The gas flow rate was 60 nml/min (1.7 vol.-% oxygen in nitrogen).

Further information was obtained through the regeneration experiments, performed as follows. A catalyst sample was put in the gas phase reactor and exposed to the following treatments: (1) H_2 at 523 K, 2 h; (2) air at 573 K, 2 h followed by treatment 1; (3) air at 673 K, 2 h followed by treatment 1; (4) air at 743 K followed by treatment 1. After each step a reactant stream was fed to the system and when conditions were stable (after about 1 h) catalyst performance was measured at a specified gas composition (0.3% C_2H_2, 1.2% H_2, 30% C_2H_4 and nitrogen to balance).

3. Results

There are many ways to define catalyst activity and selectivities in a system with parallel as well as consecutive reactions. In this work the catalyst activity will be given as the turn over frequency (TOF) for acetylene, defined as:

$$\text{TOF} = \frac{\text{acetylene consumption rate (molecules/s)}}{\text{number of exposed Pd sites}}$$

The catalyst performance will be further characterized by the ethane selectivity, S_{26}, defined as follows:

$$S_{26} = \frac{\text{rate of ethane formation}}{\text{rate of acetylene consumption}}$$

S_{26} represents the undesired ethane formation but it should be noted that this is not the only unwanted reaction. A fraction of the acetylene is also consumed in the formation of dimers and higher hydrocarbons, in part retained on the catalyst.

A number of different deactivation experiments, lasting for about 100 h each, have been performed in the GPH as well as the LPH. Experimental conditions for the various runs are listed in Table 2. Initially we performed a set of comparative deactivation experiments (I and II), try-

Table 2
Experimental conditions

Run	C_2H_2, mole fraction	H_2, mole fraction	Conditions	Cat. wt. increase (%)
I	0.03–0.006	0.06–0.02	Liquid phase, a sequence of batches (4–8 h each depending on activity)	1
II	0.03–0.006	0.06–0.02	Gas phase, a sequence of ramp changes in C_2H_2 and H_2 (4.8 h each)	16
III	0.003	~0.014	Gas phase, C_2H_2 conversion constant	19
IV	0.024	~0.066	Gas phase, C_2H_2 conversion constant	22
V	0.024	~0.014	Gas phase, C_2H_2 conversion constant	16

Conditions equal in all experiments: Overall pressure: 20 bar (liquid phase); 10 bar (gas phase). Temperature: 313 K. C_2H_4, mole fraction: 0.30 (dilution gas:nitrogen). Solvent (liquid phase): n-heptane.

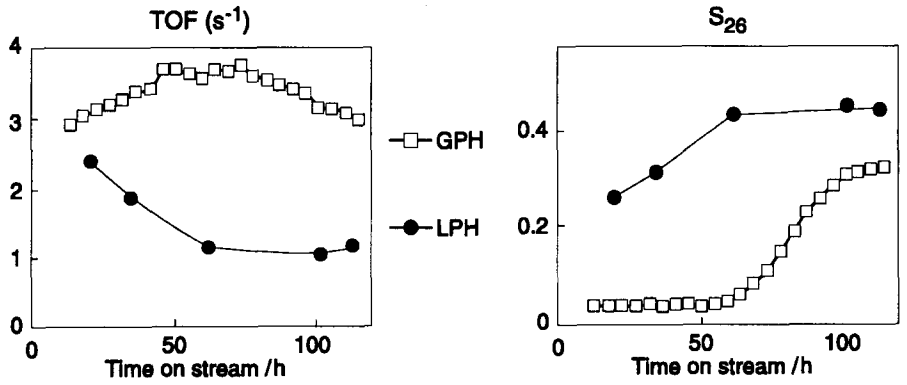

Fig. 2. Deactivation runs I (LPH) and II (GPH).

ing to use the same conditions in both systems. These experiments consisted of a sequence of batch runs. In the LPH experiments fresh solvent was used in each batch. The results are shown in Fig. 2. Note that the TOF and selectivities reported in these cases are average values over the whole conversion range. The results are clearly surprising since the LPH is greatly affected by deactivation, especially in the beginning. After 50–60 h of operation the catalyst in the LPH seems to stabilize while the catalyst performance in the GPH starts to decline rapidly.

The catalysts from these experiments were analyzed by TPH and TPO. The outcome of these measurements is given in Fig. 3; note also the catalyst weight increase given in Table 2. It is clear that in the LPH, the solvent washes the catalyst very effectively giving much less carbon deposited on the catalyst. It is also clear that the type of retained coke differs between the two cases. The main part of the deposits formed in the GPH can be removed easily in hydrogen below 500 K, but most of the deposits formed in the presence of a liquid must be burnt off at high temperatures. The H/C ratio is also much lower for the latter coke.

The used catalysts were further characterized by means of a regeneration experiment (see above). In this experiment the performance of both catalysts was measured in the gas phase, so the obtained differences are attributed to the deactivation only. The result, shown in Fig. 4, is in good agreement with the TPH and TPO data. It is evident that the coke formed in the LPH is much more strongly bound to the surface and that this form of deposits affects the ethane selectivity more than the coke formed in the GPH.

Deactivation runs III–V were all performed in the gas phase, the difference between them being

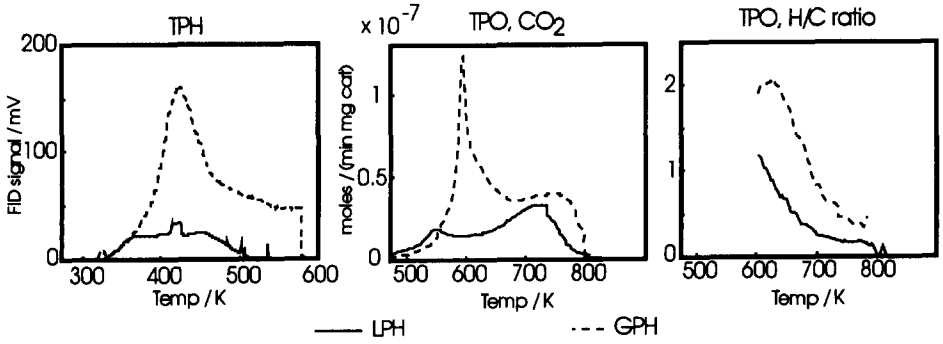

Fig. 3. TPH and TPO analysis of the spent catalyst from deactivation runs I (LPH) and II (GPH).

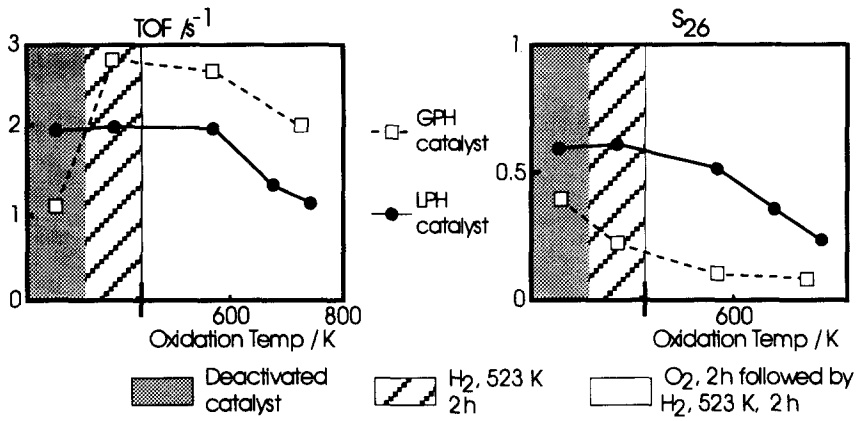

Fig. 4. Regeneration of the spent catalyst from deactivation runs I (LPH) and II (GPH).

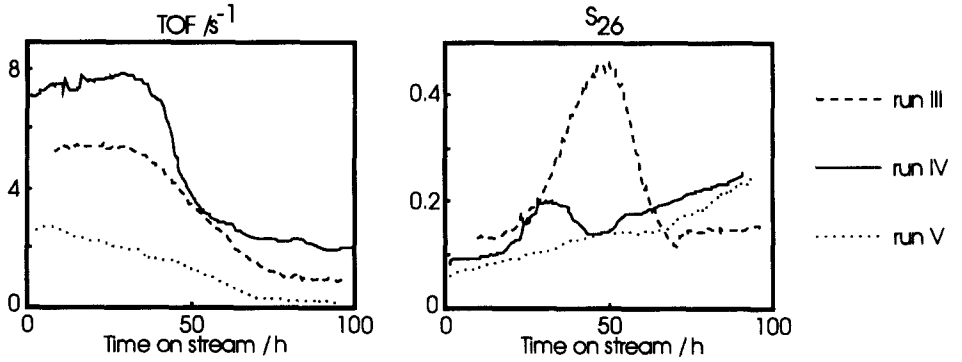

Fig. 5. Deactivation runs III–V. Gas phase hydrogenation at different conditions.

the acetylene and hydrogen mole fractions. In these runs the residence time was automatically adjusted to keep the acetylene conversion constant in spite of the deactivation. The activity and ethane selectivity variations for all three experiments are given in Fig. 5. Obviously, operating conditions have a dramatic influence on the deactivation rate as well as the selectivity variations resulting from the deactivation. The results can be compared with those of Sárkány et al. [1], who have found that upon deactivation the TOF remains constant but the ethane selectivity increases. It should be noted, however, that the acetylene pressure used in the present work is about 20 to 100 times higher than in their study. This means that the deactivation in our case is likely to be more rapid, and indeed if one considers only the first 20–40 h of experiments III and IV, the results agree very well with those of Sárkány et al. [1]. In experiment V (low H_2/C_2H_2 ratio) a different behavior is observed since in this case the TOF starts to decrease immediately, and the ethane selectivity increases continuously. It is interesting to note that this is very similar to the run performed in the liquid phase, suggesting that the hydrogen availability at the catalyst surface is reduced in the presence of a solvent.

The spent catalysts from these experiments appeared very different. The catalysts used in experiments III and IV, were covered with liquid greenish residues (green oil) whereas the catalyst from run V (low H_2/C_2H_2 ratio) was covered with

dark, dry 'carbon'. The catalysts from runs III and V were characterized by means of regeneration experiments. The coke formed at lower acetylene concentration (run III) was easily removed from the catalyst, which was almost completely recovered after the hydrogen treatment (523 K, 2 h). The coke formed at a higher acetylene concentration (run V) on the other hand was very hard to remove, and it had a severe effect on the ethane selectivity.

4. Discussion

From the above results we find it reasonable to explain the difference with respect to deactivation between the GPH and the LPH by means of mass transfer considerations. Obviously, the mass transfer properties of the system are different when a solvent is added. The GPH experiments have revealed that changes in reactant concentrations can have a crucial influence on the deactivation. Preliminary investigations have shown that no external mass transfer limitations are present. The intra-particle concentration gradients were computed from a simple model of the monolith. In this model, the monolith wall was regarded as an isothermal, semi-infinite slab with reaction mixture on both sides. The reactions considered were those of a consecutive reaction scheme where acetylene was hydrogenated to ethylene and ethylene to ethane. The kinetic equations used were strictly empirical and obtained from kinetic experiments using fresh catalysts. These experiments were performed in the gas phase. In the mass transfer calculations, we assumed the same kinetics for the GPH and the LPH. Solubilities etc. are given in Edvinsson et al. [4].

The calculations showed that the GPH is not limited by mass transfer. For the LPH on the other hand, the hydrogen concentration in the centre of the wall is reduced to about 60% of the bulk concentration. Even though this profile has a relatively small effect on the rate of the main reactions, the decreased H_2/C_2H_2 ratio might well explain the increased formation of strongly bound coke.

Table 3
Performance of the catalyst treated with hexadecane, compared to fresh and deactivated catalyst. All data taken at the same reaction conditions

	Fresh catalyst	Deactivated catalyst	Catalyst filled with $C_{16}H_{34}$
TOF/s^{-1}	5.3	0.9	0.75
S_{26}	0.13	0.15	0.24

It is not trivial to explain the role of the carbon deposited on the catalyst for this system. Clearly the effect is much more complicated than a simple blocking or poisoning of the active sites. Previous authors claim that the coke plays an active role in the hydrogenation of ethylene, either by providing adsorption sites for ethylene or by promoting hydrogen spill over from the metal sites to the support, thus increasing the hydrogen availability and the ethane formation [1,7–9]. We believe that this could be the role of the strongly bound coke formed under certain circumstances. This form of deposits interacts strongly with the surface and is highly unsaturated, possibly containing reactive groups that could be active in the hydrogen transfer. Moreover, the effect on the catalyst selectivity is dramatic even for small amounts of deposits.

According to our results the more weakly bound coke formed in the gas phase has a very different effect, and we propose that it acts as an inert liquid, affecting mainly the intra-particle transport properties. The large catalyst weight increase observed after about 100 h on stream (up to 20%) corresponds to filling the whole pore volume with a suitably sized hydrocarbon like hexadecane. This was verified by filling up the pores of a small sample of the catalyst with pure hexadecane. The performance of this catalyst was compared to that of the spent catalyst from experiment III (0.3% C_2H_2, 1.2% H_2). As seen in Table 3, the agreement is striking. A similar experiment was performed by Sárkány et al. [1], but surprisingly enough they found the hexadecane to have no effect at all.

5. Conclusions

This study has shown that the recently developed LPH process for selective acetylene hydrogenation is surprisingly sensitive to deactivation in spite of the fact that the solvent removes most of the hydrocarbon deposits from the catalyst. The reason for this is the formation of a strongly bound, highly unsaturated coke that increases the rate of ethylene hydrogenation. The coke formed in the presence of a solvent is more unsaturated and more difficult to remove than the one formed at corresponding pure gas phase conditions. This difference can be explained on the basis of intraparticle mass transfer limitations.

In the traditional gas phase process the rate of deactivation as well as the type of coke formed is strongly dependent on the operating conditions. At low hydrogen availability (at least when $H_2/C_2H_2 < 1$) highly unsaturated species are formed that adsorb strongly on the catalyst surface. These species have a dramatic and very destructive effect on catalyst performance. At higher hydrogen availability large amounts of liquid oligomers are formed, which are easily removed from the catalyst. The effect of the latter deposits is complicated but can possibly be explained as a mass transfer effect.

An important conclusion is that there is no direct relation between the amount of coke on the catalyst and its effect on the activity and selectivity.

Acknowledgements

Financial support by the Swedish National Board for Industrial and Technical Development is gratefully acknowledged.

References

[1] A. Sárkány, L. Guczi and A.H. Weiss, Appl. Catal., 10 (1984) 369.
[2] M.L. Derrien, Stud. Surf. Sci. Catal., 27 (1986) 613.
[3] J.T. Wehrli, D.J. Thomas, M.S. Wainwright, D.L. Trimm and N.W. Cant, Stud. Surf. Sci. Catal., 68 (1991) 203.
[4] R.K. Edvinsson, A.M. Holmgren and S. Irandoust, Ind. Eng. Chem. Res., 34 (1995) 94.
[5] S. Irandoust, B. Andersson, E. Bengtsson and M. Siverström, Ind. Eng. Chem. Res., 28 (1989) 1489.
[6] A.N.R. Bos, E.S. Bootsma, F. Foeth, H.W.J. Sleyster and K.R. Westerterp, Chem. Eng. Process, 32 (1993) 53.
[7] S. Leviness, V. Nair and A.H. Weiss, J. Mol. Catal., 25 (1984) 131.
[8] J.M. Moses, A.H. Weiss, K. Matusek and L. Guczi, J. Catal., 86 (1984) 417.
[9] A.H. Weiss, S. Leviness, V. Nair, L. Guczi, A. Sárkány and Z. Schay, Int. Congr. Catal., (8th Proc.), 5 (1984) 591.