

Processes occurring during deactivation and regeneration of metal and metal oxide catalysts

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Abstract

Catalyst deactivation is a complex area that often does not receive the attention that it deserves. In this paper a series of examples are considered showing poisoning, carbon laydown and restructuring resulting in catalyst deactivation. The catalyst systems examined include base catalysts, metal hydrogenation catalysts, metal and metal oxide dehydrogenation catalysts. Methods of regeneration, thermal, reductive and oxidative, are also considered and their efficacy and suitability discussed with respect to the different catalytic systems.

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1. Introduction

Disappointingly as it is to catalyst users, catalysts do not maintain their activity and selectivity permanently. All catalysts deactivate and become less effective with time. The timeframe however, can vary dramatically from a few seconds to many years (Table 1). Interestingly a short life does not necessarily mean that the catalyst will not be used. Various processes operate with short lifetime catalysts but use regular regeneration to give a long period between new catalyst charges. In most cases deactivation will be observed as a general loss in activity but changes in selectivity can also be seen. In large-scale plants the catalyst volume will take into account slow deactivation (Fig. 1) and increasing temperature may be used to compensate for slight deactivation over an extended period but changes in selectivity as temperature is increased must also be considered. As always economics drives the industrial application and activity and selectivity may be traded against catalyst life to bring a catalyst change-out in line with a plant shutdown.

The reasons for catalyst deactivation can be grouped under three headings:

- (i) Poisoning
- (ii) Coking or carbon laydown
- (iii) Sintering/restructuring.

In this paper the effect of these causes of catalyst deactivation will be examined over a series of metal and metal oxide catalysts. Methods of regeneration will be considered in terms of their suitability and effectiveness.

2. Results/discussion

2.1. Deactivation in base catalysis

Research into solid base catalysis can be traced back to a study by Ipatieff and Pines in 1955 [1], when they showed that alumina-supported metallic sodium was active for alkene isomerisation. Since then the area has hardly flourished. Indeed as research and development into the area of solid acids blossomed, solid bases were largely a forgotten backwater. However in recent years the advantages of the solid base has become more apparent and research interest is now increasing, although it is still small compared with research into solid acid systems. These catalysts offer the potential for high activity and novel selectivity in a wide range of reactions, from large-scale, gas-phase refinery processes to small-scale, liquid-phase fine chemical applications.

Many of the materials are simple oxides or mixed oxide systems that are easy to handle and prepare. Often they exhibit high activity at low temperatures eliminating by-product reactions and hence giving high selectivity. However activation can require high temperature treatment and once active the systems are sensitive to a variety of deactivating agents.

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Table 1
Deactivation processes for various catalytic reactions

Reaction	Conditions	Catalyst	Life (years)	Process affecting life	Catalyst property
Ammonia synthesis	450–550 °C, 200–300 atm	Fe with promoters	5–10	Sintering	Activity
Methanation CO + H ₂	250–350 °C, 30 atm	Supported nickel	5–10	Slow poisoning	Activity
Ethyne hydrogenation	30–100 °C, 50 atm	Supported palladium	5–10	Slow sintering	Activity/selectivity
Desulphurisation	300–400 °C, 30 atm	Supported CoMoSulphide	2–8	Slow coking, metal poisoning	Mass transfer, pressure drop
Methanol to formaldehyde	600–700 °C, 1 atm	Silver granules	0.3–1	Poisoning, Fe	Selectivity
Reforming	460–525 °C, 8–50 atm	Supported platinum	0.01–0.5	Coking, regeneration	Mass transfer
Catalytic cracking	500–560 °C, 2–3 atm	Zeolites	0.000002	Very rapid coking	Mass transfer

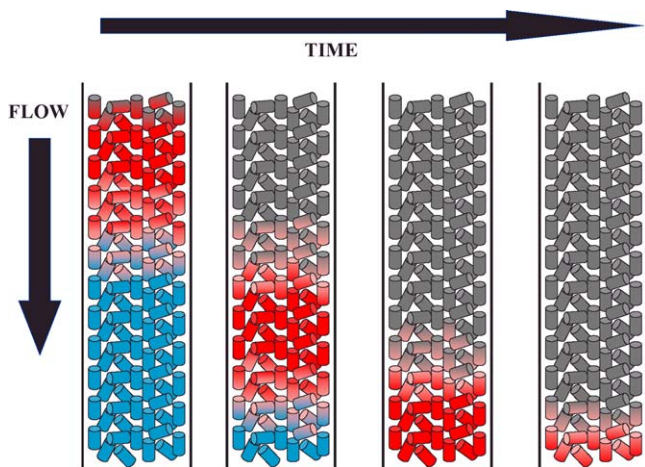


Fig. 1. A schematic representation of a catalyst deactivation front moving through a fixed bed reactor.

The isomerisation of propadiene to propyne can be catalysed at 293 K by K₂CO₃/alumina. The catalyst activation procedure is one of 16 h at 873 K in flowing nitrogen. Once activated the catalyst is highly active at ambient temperatures with a LHSV of 40 at 12 barg. Early experiments showed that the catalyst rapidly lost activity when subjected to a commercial feed. The feed was analysed and low levels of water were detected. The effect of water on the catalyst is shown in Fig. 2. At low levels there is a

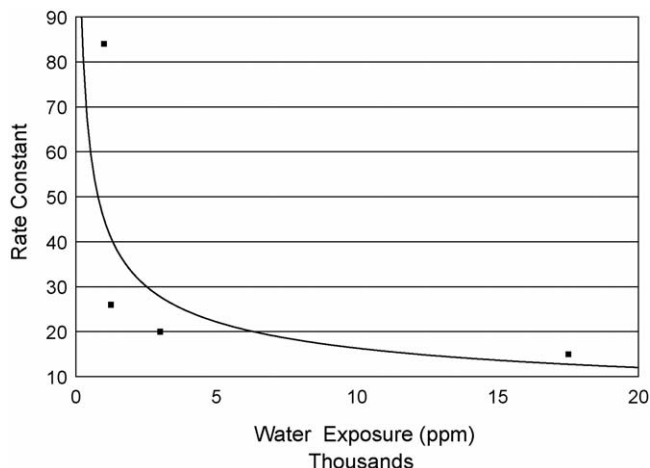


Fig. 2. The effect of water on the rate constant for base catalysed alkyne isomerisation.

dramatic loss in activity as the catalyst is deactivated; at higher levels the deactivation effect is much less. This is a classic example of poisoning where a low level of activity is left even at high poison levels. It is likely that the effect of water is to convert strong base sites such as K₂O into weaker bases such as KOH. This would reduce the pK_a from over 35 to a value closer to 25 and hence reduce the effectiveness of the catalyst. In Fig. 3 the effect on the life of the catalyst of adding a pre-bed of molecular sieve, alumina and a combination can be seen. The water is removed by the molecular sieve and by the alumina but the combination is more effective indicating that there were unknown poisons other than water in the feedstream. Even with feedstream clean up the catalyst still slowly lost activity due to trace levels of impurities (Fig. 4) and it was clear that the ability to regenerate the catalyst would be necessary. The regeneration methodology used was the same as the initial activation and using that methodology the catalyst could be regenerated with little or no loss in effectiveness (Fig. 5). However the question arose as to whether lower temperature regeneration was possible. Fig. 6 shows the effect of reducing the temperature of regeneration. As long as the temperature is above 773 K full activity can be restored but if a temperature of 673 K is used then there is irreversible loss in activity.

This need for high temperature regeneration is a significant drawback in the implementation of new base catalysts of this type. Few reactors that operate at 293 K would normally be rated

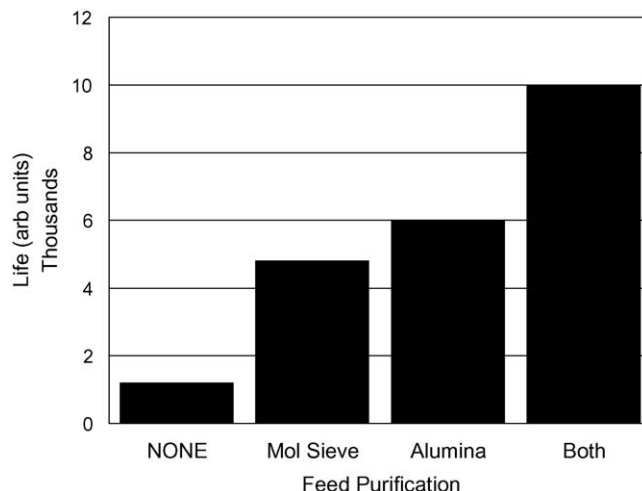


Fig. 3. The effect removing feedstock impurities on catalyst life.

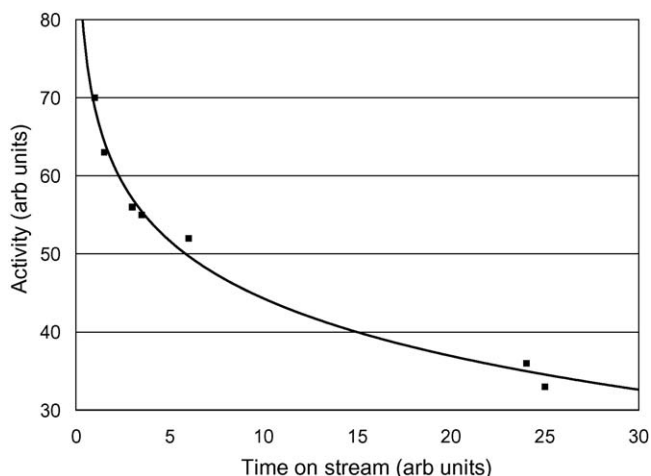


Fig. 4. Activity decay with time for alkyne isomerisation over a base catalyst.

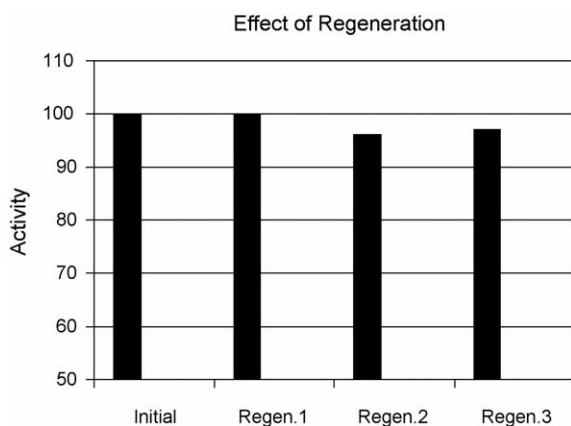


Fig. 5. Effect of repeated regenerations on catalyst activity.

for operation at 873 K, also the plant infrastructure needed to heat the reactor under intrinsically safe conditions is non-trivial. Before base catalysts of this type enter mainstream catalysis applications minimising deactivation and obtaining more energy efficient regeneration methodologies will be required.

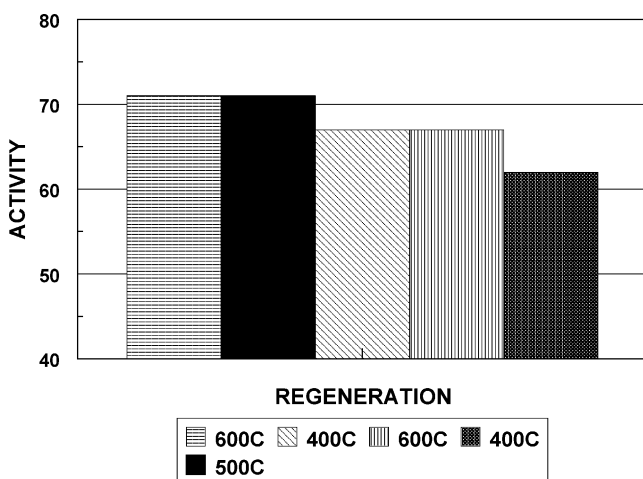


Fig. 6. Effect of regeneration temperature on regaining full activity.

2.2. 1,3-Butadiene hydrogenation over copper/silica

It has long been known that during the hydrogenation of unsaturated hydrocarbons carbonaceous material is deposited on the catalyst surface [2]. The nature of this material, which over time can result in catalyst deactivation, can give insights into the main catalytic reaction. The hydrogenation of 1,3-butadiene was studied over a reduced 5% w/w Cu/silica catalyst. The reaction was performed in a continuous flow microreactor at 373 K. A sequence of reactions was performed on each catalyst. The first reaction used a 1,3-butadiene to hydrogen ratio of 1:4; the catalyst was then used at a further three 1,3-butadiene: hydrogen ratios of 1:2, 1:1 then 1:4 again. The catalyst was on-stream for approximately 2 h before the 1,3-butadiene feed was removed from the feedstream. Once the 1,3-butadiene was removed from the feedstream, the catalyst was held under flowing hydrogen at 373 K until no hydrocarbon could be detected in the effluent of the reactor. Fig. 7 shows the conversion/selectivity against time for the initial run at a 1:4 ratio followed by the hydrogen. Although there is no significant deactivation observed at a 1:4 butadiene: hydrogen ratio, this does not mean that carbonaceous material is not being deposited. When the gas flow is switched to hydrogen, retained surface species are desorbed as butane and butenes. In Fig. 8 the isomeric ratio of the butenes is shown for each reaction ratio and for hydrogen regeneration. It can be seen that the ratio of the isomers removed by the hydrogen treatment is not the same as the ratio observed during reaction, nor is it a gas-phase equilibrium distribution. Indeed the surface ratio is the same for both 1:4 and 1:2 ratios although the reaction isomer ratio does change. Similarly when the 1:4 ratio is repeated the reaction ratio has changed significantly from the initial 1:4 test, however the surface isomer ratio returns to the value observed from the initial test. These results indicate that the surface deposit and the hydrogenation/isomerisation reaction are not in rapid equilibration. The surface species is influenced by the reaction gas ratio but much less than the reaction itself. Finally, with the isomer ratio formed from hydrogenation of the surface species being beyond gas-phase equilibrium limits, we can propose that equilibration of the surface species is slow and that the trans isomer may hydrogenate more slowly than the others.

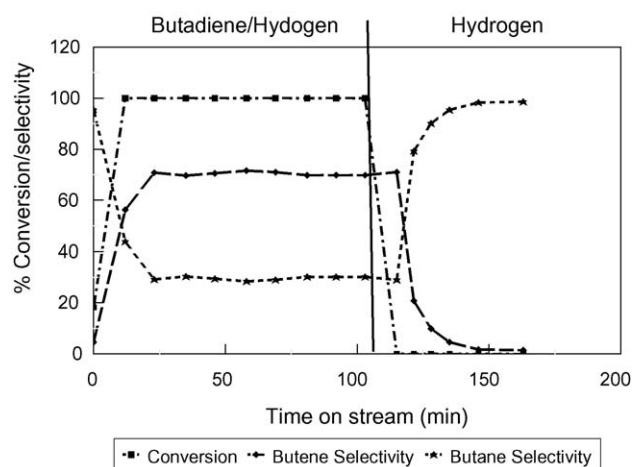


Fig. 7. Reaction profile for butadiene hydrogenation over Cu/silica at 373 K.

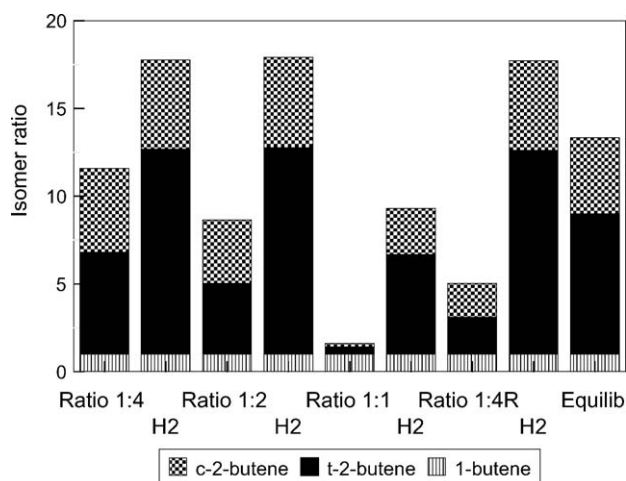


Fig. 8. Isomer profiles for butadiene hydrogenation reaction at different butadiene: hydrogen ratios and during hydrogen cleaning of surface.

Understanding the nature and reaction chemistry of the surface species is a key part of understanding the catalytic process in its entirety. In the above example the reaction kinetics and the surface species kinetics are different and although the hydrogen clean up removed surface species it did not totally regenerate the catalyst. This is an aspect that we shall look at further.

2.3. Furan hydrogenation over Pd/support

Early studies in the literature of furan hydrogenation [3,4] indicated that there is a problem of catalyst deactivation as both palladium black and Pd/C were found to deactivate rapidly. A tendency to decomposition (and hence deactivation) has also been seen in studies of furan adsorption on palladium [5,6]. At low coverages in ultra-high vacuum conditions over Pd single crystals decomposition to CO and C₃H₃ has been observed followed by coupling of the C₃H₃ unit to give benzene [6,7]. Under high temperature hydrogenation reaction conditions fracture of the furan has also been observed to give carbon monoxide and C-3 molecules [8]. In a detailed study the deactivation of supported palladium was examined using pulse-flow techniques, infrared spectroscopy, isotope exchange, temperature programmed oxidation and temperature programmed reaction spectrometry (TPO/TPRS) [9]. Contrary to expectations no decomposition to carbon monoxide and a C₃H₃ moiety was observed. However there was significant deactivation and carbon laydown. Infra-red spectroscopic analysis of the surface residue identified strongly bound furan and dissociatively adsorbed THF. The ratio of these species on the surface was dependent upon the H₂/furan ratio. At high ratios the retained surface species was close to THF, whereas at low ratios the retained species was a mixture of furan and THF. After a short period on line regeneration of the catalyst with hydrogen removed THF and, at higher temperatures, methane (Fig. 9). The low-temperature THF peak at 378 K was found to have an activation energy of ~29 kJ mol⁻¹ and can be assigned to hydrogenation from the surface of dissociatively adsorbed THF. The second evolution of THF at 498 K

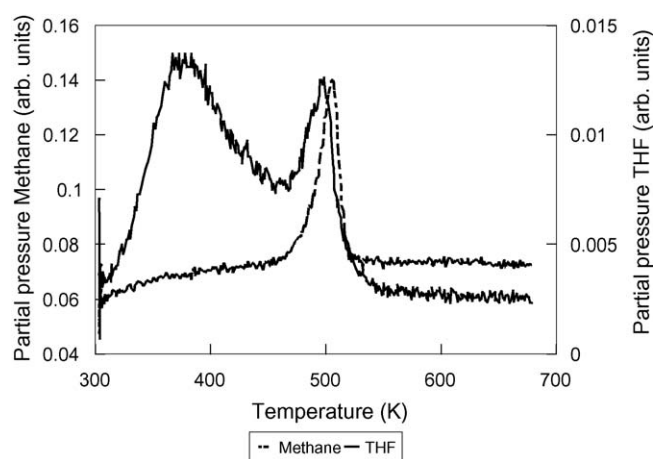


Fig. 9. Profile of species produced during temperature programmed reaction with hydrogen over Pd/zirconia after pulses of furan/H₂.

has a desorption activation energy of ~138 kJ mol⁻¹ and can be assigned to hydrogenation of a more dehydrogenated form of adsorbed THF. The evolution of methane is observed as a single well-defined peak at 505 K. The production of methane at 505 K indicates that hydrogenolysis of furan/THF is initiated only at around 500 K. This desorption has an activation energy of ~258 kJ mol⁻¹ in keeping with a hydrogenolysis reaction. Regeneration could also be performed using oxygen (Fig. 10). Using oxygen required higher temperatures but gave confidence that all carbon had been removed, whereas often a hydrogen treatment does not remove all surface deposits. In this case however both regeneration sequences returned the catalyst to the same state, even though it was not the original one. Indeed no matter the regeneration methodology the catalyst's initial state is one that is unique and cannot be regenerated. In general the retained species from low-temperature hydrogenation reactions is closely related to the starting reactant but this is only in the initial stages. Retained species are not static, but change with time. After an extended period of furan hydrogenation, TPO removed almost no surface material and extraction of the catalyst confirmed that the original furan/THF type moieties on the surface

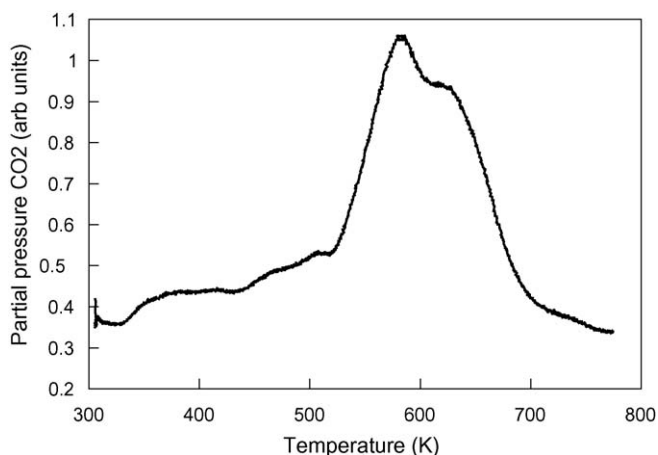


Fig. 10. Profile of species produced during temperature programmed reaction with oxygen over Pd/zirconia after pulses of furan/H₂.

had aged into coke with a low H:C ratio that was resistant to hydrogenation.

2.4. Alkane dehydrogenation

The dehydrogenation of light alkanes has been known as a catalytic process for a significant number of years [10]. The dehydrogenation of propane to propene, $C_3H_8 \rightleftharpoons C_3H_6 + H_2$, is highly endothermic ($\Delta H = +110 \text{ kJ mol}^{-1}$) and is equilibrium limited, hence typical operating conditions for commercial reactors lie in the range 0.3–3 atm and 823–923 K. The catalytic processes fall into two categories, those based on platinum as the active phase [11] and those based on chromia as the active phase [12]. However in both cases the catalytic process is complex with a series of competing reactions occurring simultaneously including significant carbon laydown resulting in catalyst deactivation. Both catalyst systems require frequent regeneration to maintain activity and the heat liberated from the regeneration may be used to balance the endothermic nature of the principal reaction. Regeneration of the catalyst is periodic and by oxidation. This means that the catalysts undergo repeated oxidation and reduction. In both systems the catalysts are in a reduced state during reaction, then oxidised during the regeneration then re-reduced for reaction. As may be expected this type of high temperature regeneration can be aggressive and may bring other deactivation problems to the fore. For example, sintering of the metal or metal oxide due to reductive/oxidative cycling is an issue that can effect the catalysts over a longer time frame, while with chromia-based systems the degree of reduction may change with the number of cycles. The designs of commercial reactors for this process take different approaches both to managing the deactivation and to the regeneration. Of specific interest in the present context are the timeframes of the cycles and the catalysts that are used for a given cycle sequence.

In the Lummus/Houdry CATOFINTM Process [13] the heat of regeneration is fuel supplemented and used to regeneratively heat the endothermic dehydrogenation reaction by cycling the feeds through a series of 3–4 fixed, adiabatic beds, over a 15–25 min period. In the classic process, the regenerating (heating) gas is fed in the same direction as the process gas, which leads initially to a higher temperature at the feed than the exit. With time on-stream, a temperature front will move through the bed as the front of the bed is cooled by the endothermic reaction. In the UOP OLEFLEXTM Process [11,14], deactivation suppression is by hydrogen co-feed. Heating is by fired interheaters between adiabatic moving beds. Catalyst cycle times are 3–5 days. Each adiabatic reactor has a decreasing temperature in the direction of flow, with a step increase in temperature between each bed.

Two significant differences between the processes are the time between regenerations and the nature of the catalyst. In the Houdry process the catalyst is based on chromia whereas in the UOP process the catalyst is based on platinum. When a Pt/alumina catalyst is subjected to short cycle times (~15 min) its selectivity and yield are poor for a large number of cycles (Fig. 11a), even after 3000 cycles its still is not generating a yield near equilibrium. However using a chromia catalyst, equi-

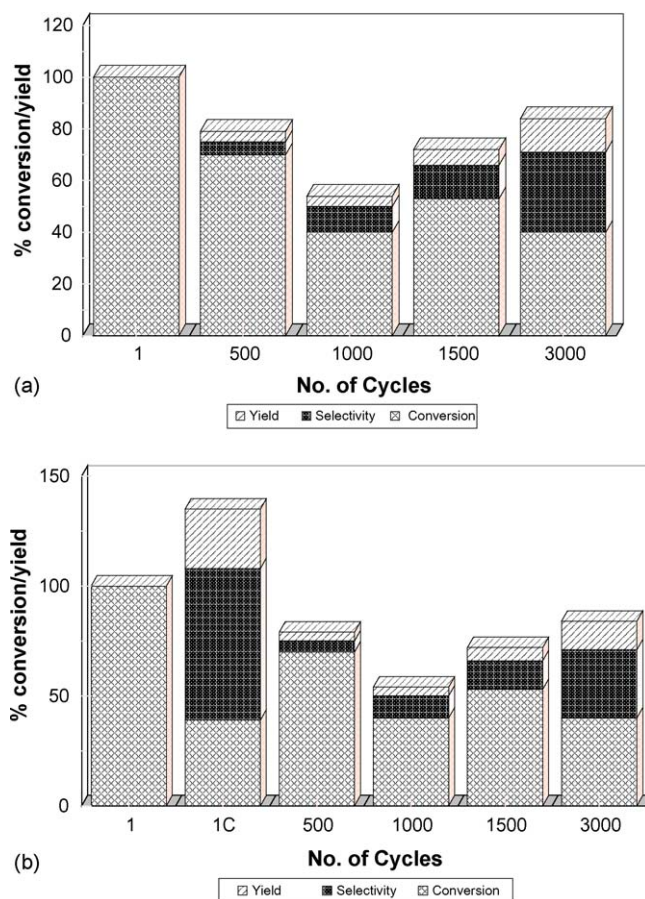


Fig. 11. (a) Conversion, selectivity, yield data as a function of cycle number for propane dehydrogenation over a Pt/alumina catalyst at 873 K. Each cycle of reduction/reaction/regeneration lasted ~15 min. (b) Conversion, selectivity, yield data as a function of cycle number for propane dehydrogenation over a Pt/alumina catalyst at 873 K. Each cycle of reduction/reaction/regeneration lasted ~15 min except cycle 1C which lasted 1 h.

librium yields are achieved on cycle one and maintained for over 3000 cycles (Fig. 12). If the cycle time for the platinum catalyst is extended to >1 h then the catalyst has a much improved yield (Fig. 11b). This behaviour reveals the linkage between

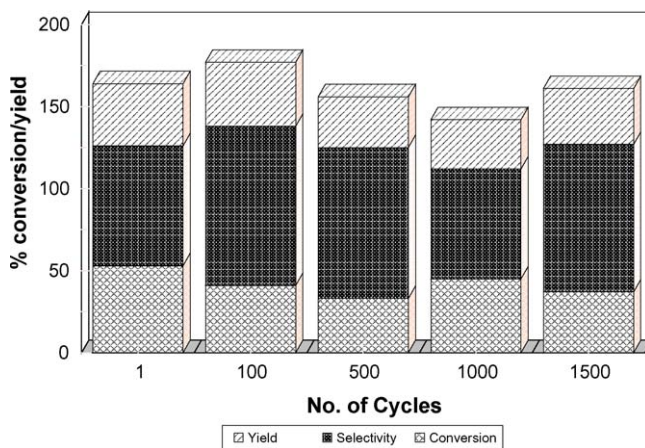


Fig. 12. Conversion, selectivity, yield data as a function of cycle number for propane dehydrogenation over a Cr₂O₃-K₂O/alumina catalyst at 873 K. Each cycle of reduction/reaction/regeneration lasted ~15 min.

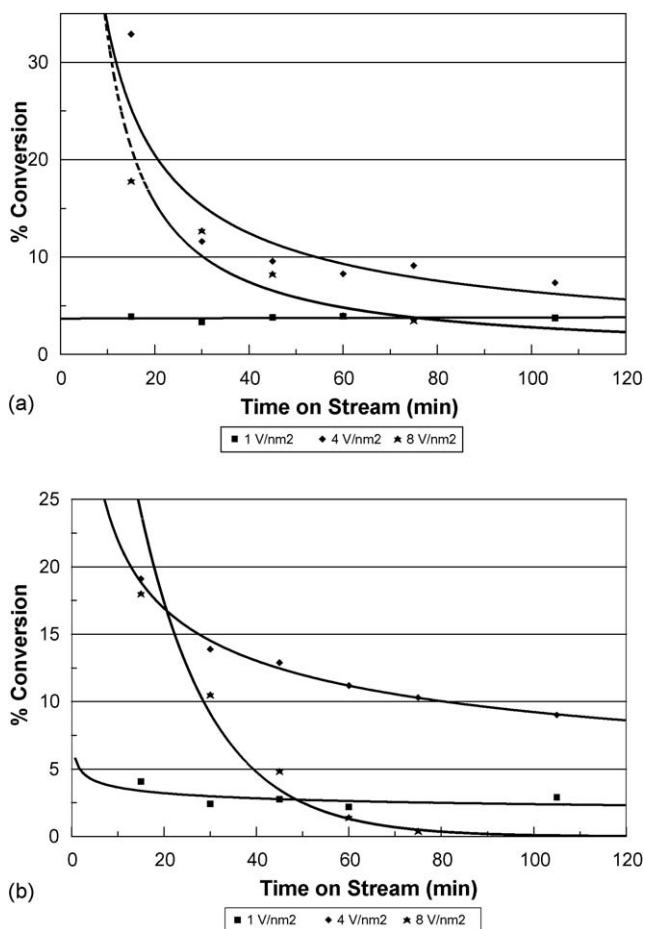


Fig. 13. (a) Deactivation profiles of three vanadia/alumina catalysts, with vanadia loadings of 1, 4 and 8 V/nm, during butane dehydrogenation at 873 K. (b) Deactivation profiles of the three vanadia/alumina catalysts during butane dehydrogenation at 873 K after regeneration in oxygen at 873 K.

deactivation, regeneration, catalyst and process. The catalyst and process are intrinsically linked to maximise the effectiveness. Even where theoretically it should be possible to switch catalysts, as in the above case, subtleties of the catalysis can result in immiscibility.

Finally let us revisit the concept that the initial state of a catalyst is unique. In hydrogenation catalysis examples shown above, regeneration could not bring the catalyst back to its original state. The same is true in high temperature dehydrogenation. Fig. 13a shows the initial decay for three vanadia/alumina catalysts during butane dehydrogenation at 873 K. Fig. 13b shows the decay profiles for the same catalysts after regeneration in oxygen at 873 K. If the process is repeated the profiles match those of Fig. 13b, not Fig. 13a. This change is also apparent in the TPO profiles. In Fig. 14a the TPO from a fresh catalyst that has been run for 1 h at 873 K under butane. Fig. 14b is the TPO from the same catalyst after a second run of 1 h butane at 873 K. There has been a significant change in the TPO profile as has there been in the deactivation profile.

This change between the first and subsequent runs raises questions in the study of deactivation and regeneration. It is important that the first run and regeneration are not studied in

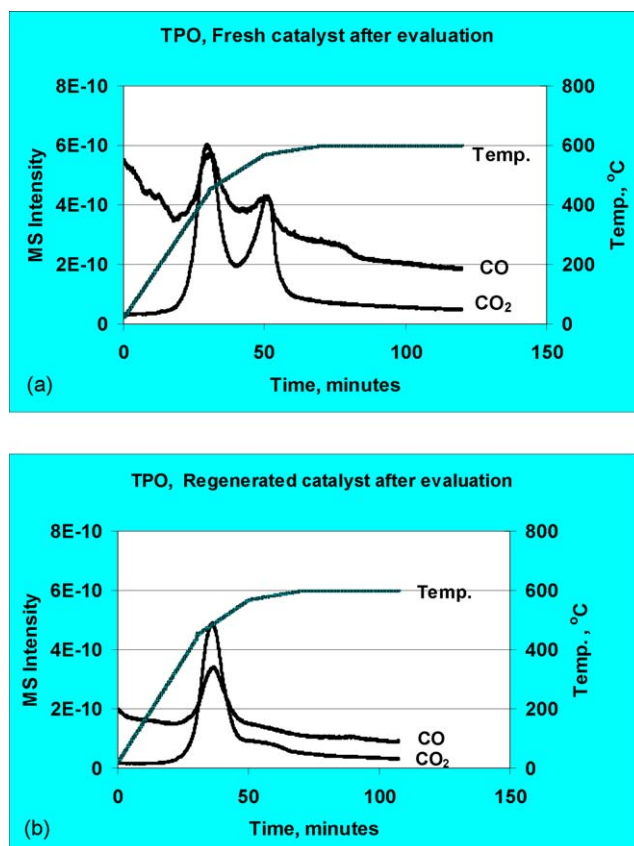


Fig. 14. (a) Temperature programmed oxidation (TPO) of 4 V/nm vanadia/alumina catalyst after initial butane dehydrogenation run. (b) TPO of 4 V/nm vanadia/alumina catalyst after second butane dehydrogenation run following regeneration.

isolation but the second and, if necessary, the third cycle must be considered if a meaningful interpretation of the processes are to be developed.

3. Conclusions

In this paper the effect of deactivation and regeneration has been exemplified with a range of catalysts and reactions. Overall trends are hard to come by and considerable work still has to be done. Catalyst deactivation and regeneration is a multi-faceted issue that is often poorly understood yet is a fundamental part of catalyst design. Too often the question “where is the catalyst in deactivation terms when we probe the catalytic reaction?” is not considered. Similarly if the catalyst is to be regenerated are we studying the correct surface? Studying catalyst deactivation may not be fashionable but it is pivotal in delivering a generation of catalysts with 100% selectivity that is needed for a green and sustainable chemical industry.

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