STUDIES ON THE DEACTIVATION OF Pd/Al_2O_3 CATALYST FOR SELECTIVE HYDROGENATION OF ACETYLENE

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ABSTRACT

Studies on deactivation of a selective acetylene hydrogenation catalyst, Pd/Al_2O_3 have been undertaken. The mechanisms of acetylene hydrogenation have been discussed. Analysis of various parameters indicate three possible causes for deactivation, viz., i)inferior attrition strength of the catalyst pellet leading to Pd metal loss, ii)presence of Ni in the non-reducible form and iii)presence of Fe on the surface of the catalyst physically blocking the active catalyst Pd sites.

INTRODUCTION

Cracking of hydrocarbons is used commercially to produce ethylene, a basic petrochemical feed stock and is always contaminated with small amounts of acetylene. Selective hydrogenation of acetylene fraction in presence of large amounts of ethylene is usually carried out over an alumina supported Pd catalyst(1). This serves a dual purpose (i.e) i)depletion of acetylene from as high as 2% to trace ppm levels ($<$ 3 ppm) - a requirement if ethylene is to be used for making polyethylene and ethylene oxide(2) and ii)to help in economy of operation.

The quality of a catalyst good enough to achieve both these ends is crucial and classification of catalysts based on formation of ethylene and ethane from acetylene is lucidly brought out in figure 1.(1).

The reactions involved here are:

$$HC \equiv CH + H_2 \longrightarrow H_2C{=}CH_2 \quad ....1$$
$$HC \equiv CH + 2H_2 \longrightarrow H_3C{-}CH_3 \quad ....2$$
$$H_2C = CH_2 + H_2 \longrightarrow H_3C{-}CH_3 \quad ....3$$

In reaction 1, i.e. the selective hydrogenation, there is a net ethylene gain whereas reactions 2 and 3 result in a net loss by formation of ethane.

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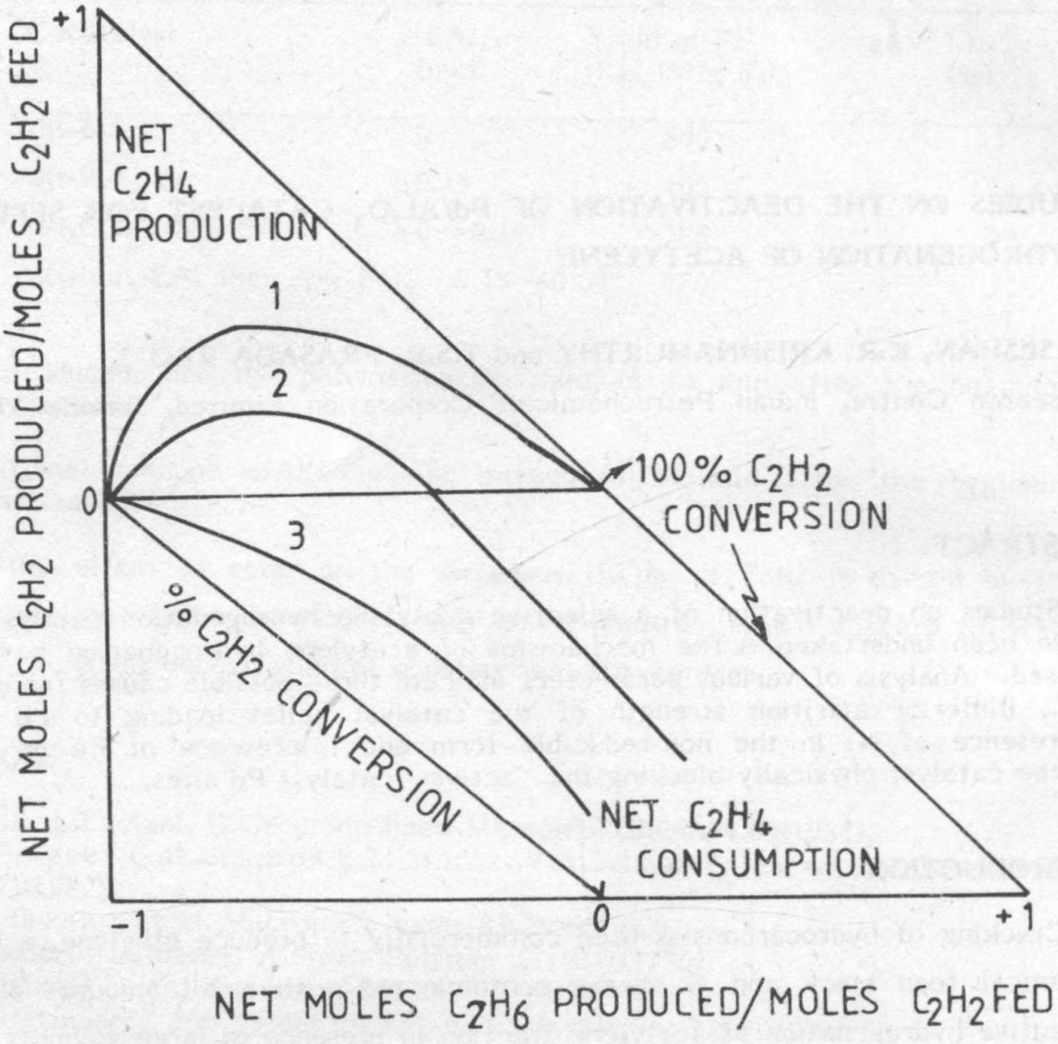


Fig.1 Reaction coordinates for acetylene hydrogenation.

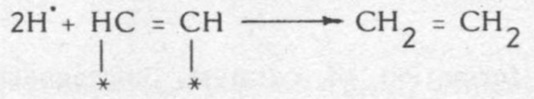
From figure 1, the following points can be noted. Along y-axis, represents ideal situation i.e., there is no ethane formation. Catalyst 1 and 2 represent good systems which result in net ethylene production. Trend along x-axis is fair in that there is acetylene removal whereas catalyst 3 is poor, showing net ethylene loss.

Mechanism of acetylene hydrogenation over supported Pd/Al_2O_3 catalyst

Three major routes are known to be operative during the reaction (3-5).

1) the selective and required reaction proceeds via an associative adsorption of acetylene as

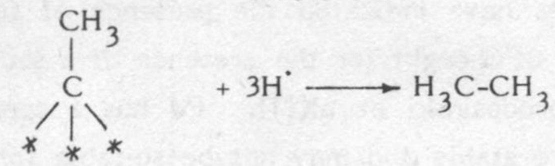
Route 1



$$2H^{\cdot} + \underset{*}{\underset{|}{HC}} = \underset{*}{\underset{|}{CH}} \longrightarrow CH_2 = CH_2$$

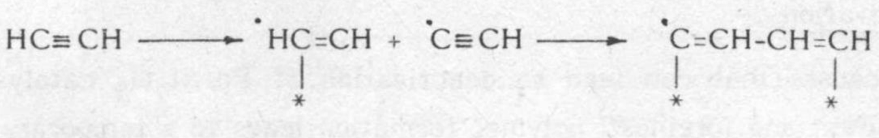
2) reactive adsorption of acetylene with adsorbed hydrogen atoms to form ethylidyne species which are responsible for direct ethane formation and resultant reduction in selectivity

Route 2



3) dissociative adsorption of acetylene which results in polymer species (C_4^+). Commercially this is known as green oil formation and deactivates the catalyst by migration of polymer to the surface and covering the active catalytic Pd sites.

Route 3



$$HC{\equiv}CH \longrightarrow \overset{\bullet}{H}C{=}\underset{*}{\underset{|}{CH}} + \overset{\bullet}{C}{\equiv}CH \longrightarrow \overset{\bullet}{\underset{*}{\underset{|}{C}}}{=}CH{-}CH{=}\underset{*}{\underset{|}{CH}}$$

The design of a successful catalyst should be made by keeping in mind, among other things, modifications required to orient the reaction towards selective acetylene hydrogenation.

Catalyst recipie

Supported Pd/Al_2O_3 catalyst is generally used for partial hydrogenation reaction. The catalyst is usually a shell type low metal loading ($<$ 0.04%) over an alumina support which does not actively involve in catalytic action. Why is Pd unique in that it hydrogenates C_2H_2 preferentially? In fact, independently, rates for hydrogenation of acetylene and ethylene over Pd is nearly same, but in a mixture, the specificity for acetylene hydrogenation is attributed to the preference of Pd metal for C_2H_2 chemisorption compared to C_2H_4. Investigations have shown(6) that, separate sites do exist for ethylene and acetylene adsorption on supported palladium. Ethane is known to form(7) directly from both acetylene and ethylene.

One way of improving selectivity of the catalyst is by dosing it with trace ppm levels of CO(7). They occupy sites of hydrogen and result in its depletion thereby bringing down the reaction probability of route 2. In addition, CO by occupying metal sites reduces the dissociative adsorption of acetylene, bringing down polymer formation (route 3).

Alternatively, during formation of catalyst, impregnation of elements like Ni, Cu, Pt etc., have also been tried out (7,8). Impregnation of the support with an element like Ni helps in preparation of a shell type catalyst where the small amount of Pd can be coated later at the surface. Ni can play a supporting role in hydrogenation activity and it has been reported that NiS is a selective hydrogenation catalyst(9). EDAX results have indicated the presence of sulphur in such catalyst systems(10). Another line of thought for the presence of a second metal on supported Pd catalyst is due to Borodosinski et al(11). Pd has a tendency to form hydride phases (α & β) which are stable and may not be suitable for hydrogenation, though the chances of formation of Pd-H phases at such small concentration of Pd is remote. However, alloying with a metal like Cu takes care of the breaking of Pd-H bonds and non-formation of the phase. Further, it is claimed that Cu provides sites for desorption of hydrogen (spill over?), thereby helping the catalyst efficiency.

Catalyst deactivation

The major causes that can lead to deactivation of Pd/Al_2O_3 catalyst have been well defined. First and foremost, polymer formation leads to a temporary deactivation from which the catalyst life can be restored by regeneration. Secondly, being a shell type catalyst, depletion of the active Pd component by attrition is plausible and therefore mechanical properties of the catalyst pellet is very important. Additionally deposition of permanent positions like Fe, Hg, P etc have been observed by Auger studies (12). It was shown that these sit over the active sites like an umbrella, physically blocking the site from catalysing the reaction.

AIM OF THE INVESTIGATION

Basically the deactivation of a Pd/Al_2O_3 catalyst results from the polymer (C_4^+) coating that occurs over the catalyst. The cycle life of a catalyst is determined among other things, by catalyst selectivity. But for optimum operation, life of the catalyst assumes significance. What are the factors that contribute and lead to deactivation of catalyst? Efforts have been made to identify these factors by a systematic analysis of the catalyst system. For this purpose, two samples of Pd/Al_2O_3 catalyst designated as catalyst A and catalyst B were chosen. Catalyst A exhibited very high and sustained activity and selectivity, while the performance of catalyst B was relatively poor and unsteady. The possible reasons for such a difference in activity of the two catalysts have been analysed in terms of the factors that govern the cause of deactivation. Such studies help in understanding the behaviour of the catalyst in relation to its preparation as well as maintenance.

EXPERIMENTAL

The catalysts were characterised for their structural, compositional and mechanical properties. Methods included XRD, ESCA, EDAX, temperature programmed reduction (TPR) studies, surface area measurement, pore size distribution methods, attrition loss measurements, AAS etc. Standard procedures have been adapted in all methods, except in case of attrition losses of catalysts were measured under identical conditions(10).

RESULTS AND DISCUSSION

Typical characteristics of fresh and used catalysts A & B are given in table 1 for comparison.

TABLE 1

Characteristics of different Pd/Al_2O_3 catalysts

	Catalyst A		Catalyst B	
	Fresh	Used	Fresh	Used
Phases identified	α-Al_2O_3,NiO & $NiAl_2O_4$	Same	α-Al_2O_3,NiO & $NiAl_2O_4$	Same
Surface area, m^2/g	34	30	42	35
Pore volume ml(NTP)/g	0.15	-	0.14	-
Pd content, %	0.030	0.025	0.03	0.025
Attrition loss[a]	3.2	4.1	9.2	9.5
Reducible Ni, %	0.623	-	0.055	-
Coke deposition, %	nil	24.02	nil	23.2

time on stream of Catalyst B is one sixth of that of Catalyst A

[a] relative units

Uniformaly all the catalysts have similar compositions showing phases like α-Al_2O_3, NiO and $NiAl_2O_4$ from XRD data. The concentration of Pd is below the detection limits of XRD, to show up. Surface area and pore volume of the catalysts are similar. The difference in performance of catalysts A and B may however, be attributed to the following. Firstly, the attrition loss of catalyst B is nearly 3 times than that of catalyst B. The immediate consequence of this is loss of material from the surface of catalyst and this being a shell type catalyst leads to loss of active component from the surface. This is reflected on the Pd concentration of the catalysts. Inferior attrition strength of catalyst B results in a loss of ~ 16% of Pd within a shorter period of time on stream.

The temperature programmed reduction curves for the catalysts are given in figure 2.

It may be observed that catalyst A undergoes facile reduction. TPR peaks are observed at 403 K for palladium and at 523 K corresponding to NiO. However,

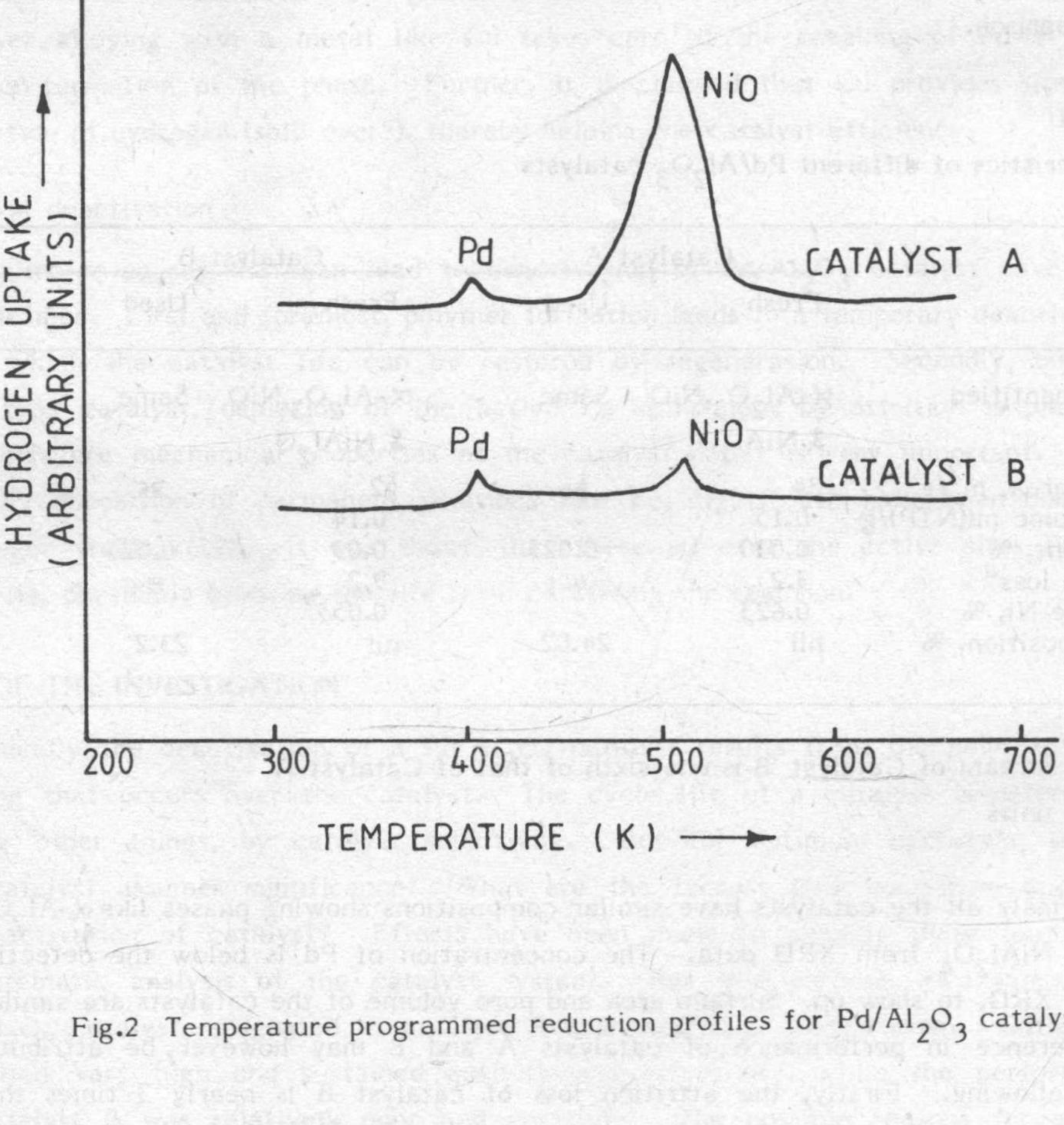


Fig.2 Temperature programmed reduction profiles for Pd/Al_2O_3 catalysts.

in catalyst B, the reduction peak at 523 K is nearly absent. The reason for this may be found in the XRD data. Nickel is present in catalyst B mostly as $NiAl_2O_4$ which does not undergo reduction upto 973 K. Though both catalysts contain NiO and $NiAl_2O_4$, it is possible that catalyst B predominantly contains $NiAl_2O_4$ resulting from reaction of NiO with Al_2O_3 caused probably by a higher temperature of catalyst preparation. Percentage of reducible nickel in catalyst A is nearly 10 times (0.623%) than that of catalyst B (0.055%). This results in a situation almost as if Ni is not available and present as an inert support. Coupled with the loss of Pd due to poor attrition strength, the catalyst B shows up to be inferior.

Dispersion measurements for Pd could not be carried out owing to experimental difficulties. Firstly, the concentration of Pd is low for doing a H_2/O_2 titration and use of CO is restricted due to the fact that presence of both linear and bridge carbonyls may yield erroneous dispersion values. Efforts are however being made for CO chemisorption with the assumption that the bridge carbonyls may be absent due to the small amount of Pd present. XPS analysis of the spent catalyst B has shown presence of, in addition to Al, Si, Ni and Pd, weak peaks corresponding to Fe. As mentioned earlier, this again is a potential poison, deactivating the active sites by physically blocking them. Presence of Fe was not however noted in the case of either in fresh catalyst B or in fresh or spent catalyst A.

CONCLUSIONS

A combination of factors seem to account for the relatively faster deactivation of catalyst B. These include poor attrition strength resulting in loss of palladium from the surface, presence of nickel in the non-reducible form, thereby not contributing to activity and presence of iron on the surface of the catalyst poisoning the active palladium sites. The study therefore, gives an insight into the factors that cause the deactivation of the catalyst both at preparation and utilization stage.

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