



A Review on the Applications of Self Regenerating Catalysts

Ronak Upadhyay^{*}, Shaaz Khatib^{*}, Atmin Parekh^{*}

Department of Chemical Engineering, Institute of Chemical Technology, Mumbai-400019, India

*- All authors have contributed equally in the manuscript.

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Abstract

Metallic catalysts have a tendency to lose their activity over time due to various reasons such as change in oxidation state of the metal, deposition of material on the catalyst or structural rearrangement of the catalysts. Metallic catalysts (such as Pt based catalysts) are often rare and expensive. Therefore, there is currently an interest in developing self-regenerating catalysts which independently recover their activity after deactivation without human intervention and which thus have a high turnover number. Our aim is to review the applications of these catalysts and study their mechanism of regeneration in various systems. Perovskites based catalyst systems have shown indication that they can be used instead of the conventional catalyst used in the automobiles to treat exhaust gases, in a cost effective manner. A modification of the crystallographic structure has enhanced the regenerative ability of cobalt nanoparticles, have found application in the Fischer Tropsch Synthesis. Self-healing non precious metal-based catalyst provides an economic alternative in hydrogen production by water splitting with sunlight as the main energy source. Palladium based self-healing catalysts are used in CO detection devices. 'Kearby' Catalyst, a self-regenerating catalyst used in the preparation of the vinyl monomers via catalytic dehydrogenation.

Keywords: self-regenerating, Perovskites, Kearby catalyst, Fischer Tropsch Synthesis, CO detection, vinyl monomers.

1. INTRODUCTION:

Self-regenerating catalysts are essentially those catalysts which heal themselves once their structure or stability is disturbed and in some cases those catalysts which regenerate their active sites using external agents without an additional regeneration step. These catalysts are involved in making a process economical by ensuring there is no need for catalyst regeneration or make up. Also it helps in retention of catalytic activity over a long time. It is seen that the processes of wear and tear are

thermodynamically favoured due to the expected entropy production making self-healing look as impossible, but actually the structural disarrangements require a thermodynamically stable structure, favouring self-healing processes. The processes differ in the way they may be triggered, as the self-healing may be internally triggered like biological systems or may need an external trigger like some polymer matrix which triggers repair by using heat. In case of metallic systems there are three methods to carry out self-

healing that are by forming precipitates at fractured sites for repair, or using an alloy matrix with microfibers to repair and finally using a healing agent like an alloy embedded in the metal. Self-regeneration of a catalyst can also be attained if processes that cause catalyst deactivation such as coking are prevented by a component of the catalyst or if it is possible for the catalyst to attain its original oxidation state. The cost of self-regenerating catalyst would economize with the introduction of non-precious metal nanoparticles in perovskites. To support this idea, Yanagisawa et al, proposed a stability analysis using Ab initio thermodynamics [12]. We hereby provide the applications of self-regenerating catalysts in various processes.

2. SELF-REGENERATING CATALYST IN CARBON MONOXIDE DETECTORS:

Carbon monoxide is a colourless, odourless and toxic gas. Therefore, build-up of carbon monoxide in an enclosed space can't be detected by a person and can be fatal. Build-up of carbon monoxide can be a major hazard in homes that use a heating system such as gas central heating boiler or in the workplace where people use engines, furnaces, forges, or any other equipment that uses oxygen to produce energy through combustion. Carbon monoxide detectors, therefore, become essential in warning a person that carbon monoxide levels have exceeded the safe limit.

2.1. Type of carbon monoxide detectors

Carbon monoxide detectors come in two types: inexpensive detector strips and more

expensive electronic alarms [1].

Inexpensive detector strips, also known as chemical "blob" detectors, are pieces of plastic with a small beige-coloured "blob" in the middle. If there's a high-level of carbon monoxide in the room, the blob changes colour from beige to a darker blue. The disadvantage with these detectors is that they require continuous monitoring. Electronic detectors come in 3 types. First is colorimetric detectors that have a chemical blob inside similar to the ones chemical "blob" detectors use. A light beam shines onto the blob and a photoelectric cell measures the light reflected back. If the blob turns dark then, less amount of light will be reflected back and the alarm will sound. The second type are metal oxide detectors that measure the heat generated in the oxidation of carbon monoxide and the third type are electrolytic detectors that measure the change in thermal conductivity of the sensing system.

2.2. Need for self-regenerating catalysts in carbon monoxide detectors

During World War II, the U.S. National Bureau of Standards developed a CO detection device for military use [2]. It included a battery of glass tubes containing a silica gel impregnated with palladium and molybdenum salts. The catalyst could only be used once, which presented a serious disadvantage for continuous or quasi-continuous monitoring for CO. Palladium catalyst used is expensive and catalyst regeneration involved an expensive procedure of employing a battery of reagent columns in succession. Thus there was a need of developing self-

regenerating catalysts in CO detection devices.

2.3. The self-regenerating catalyst used

The ‘blob’ of the CO detector consists of silica gel (which act as an inert carrier) impregnated with a mixture of a palladium salt, a molybdenum compound, and a salt of a transition metal, namely, copper, iron or nickel [2].

2.4. Mechanism

The silica gel is "aquated", i.e., moist, from the moisture it adsorbs from the atmosphere, which normally has a relative humidity greater than about 20% or it may be inherently water containing [2]. The adsorbed moisture provides the necessary water to ionize the catalyst. The oxidized state of the catalyst is yellow in colour, changing to blue on being reduced by CO or other reducing gas, as illustrated in figure 1. In the oxidized state, both the copper and palladium are bivalent. Palladium is used as a catalyst since it has very low activation energy for getting transformed from its +2 oxidation state to its neutral oxidation state and vice versa. Exposure of the catalyst to CO reduces the copper and the palladium to lower valence states. CO takes up oxygen from the catalyst and is oxidized to carbon dioxide. As, the palladium is reduced, it donates electrons to the yellow hexavalent molybdenum, reducing it to the blue form wherein molybdenum exists both in the +5 and +6 oxidation states. On exposure to air, the univalent copper catalyses the oxidation of both the palladium and the blue form of the molybdenum thus

regenerating the catalyst in its yellow form.

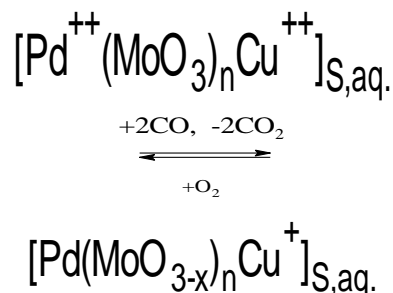


Fig 1 Conversion of catalyst from its yellow form to its blue form in the presence of CO and regeneration of the yellow form in the absence of CO and presence of O₂ [2].

2.5. Other applications of the catalyst

The catalyst used in CO detectors can also be used for other reducing gases. It can be used to convert unsaturated hydrocarbons to oxygenated petrochemicals [2]. It is used in CO removal devices for use in automobiles, airplanes, industrial plants, mines, homes. It also provides a superior filter for gas masks designed to remove CO.

3. SELF-REGENERATIVE KEARBY CATALYST IN THE PREPARATION OF VINYL MONOMERS:

Preparation of vinyl monomers by the catalytic dehydrogenation of hydrocarbons is widely practiced. Of the many catalysts examined for this reaction, the self-regenerative Kearby catalysts (described in US patent 2395875) are particularly suitable for the preparation of vinyl aromatics such as styrene, vinyl toluene and divinylbenzene and also C₄—C₅ alkenes including 1,3-butadiene and isoprene.

3.1. Need for self-regenerating catalyst

Coking of the catalyst is a major problem in preparation of vinyl monomers by the catalytic dehydrogenation. Coke deposits may amount to 15% or even 20% (w/w) of the catalyst and accordingly they may deactivate the catalyst either by covering of the active sites, and by pore blocking [4]. The carbonium ion intermediates undergo side reactions which involve combination, rearrangement and dehydrogenation into coke-type structures that are deposited on to the catalyst surface [4]. Therefore, developing a self-regenerating catalyst with a greater lifetime can be advantageous in large scale continuous production of these monomers.

3.2. The self-regenerating catalyst used

The catalyst comprises magnesium oxide (50%-95% by weight) as the base material, iron(III) oxide (3%-49% by weight) as the active ingredient, potassium oxide (0.5%-10% by weight) as the promoter and copper(II) oxide (0.5%-20%) as the stabilizer which prevents the promoter from volatilizing or becoming inactive [5].

3.3. Mechanism

Steam is a major constituent of the gaseous reactant stream. Its function is to dilute and thus reduce the partial pressure thereof in the reaction zone [5]. Steam performs another important function wherein, it undergoes water gas reaction with the coke deposited on the catalyst to form carbon oxides and hydrogen [5]. The potassium oxide promoter minimizes the content of carbon by enhancing the rate of gasification of the deposited carbon with steam. This may be because of the increase

in the adsorption of steam in the presence of the potassium oxide promoter [6]. Potassium oxide also neutralizes acid sites which would catalyze coke deposition via the carbonium ion mechanism previously mentioned thus inhibiting coke deposition [4].

4. SELF-REGENERATING CATALYST FOR FISCHER-TROPSCH SYNTHESIS:

Fischer-Tropsch synthesis involves the conversion of syn gas to liquid fuels and chemicals after syn gas is produced by coal gasification or steam methane reforming. Indirect coal liquefaction involves generation of syn gas via coal gasification followed by syn gas cleaning and water gas shift reaction (to control the ratio of CO and H₂O). The clean syn gas is then converted to liquid fuels and products by Fischer-Tropsch Synthesis. This technology has been commercialized at Secunda in South Africa where Sasol Chemical Ltd. has two production units which together generate 160000 barrels of liquid per year [7]. In Fischer-Tropsch synthesis (FTS), the primary reaction involves the hydrogenation of CO and polymerization of hydrocarbons [8].

4.1. Need for self-regenerating catalyst

One of the main deactivation mechanisms of catalysts is the change of the catalyst oxidation state by oxidation or reduction. Metallic Co is the preferred catalyst for Fischer Tropsch Synthesis; however, the presence of water has made it difficult to implement Co due to oxidation [8]. The oxidized Co is usually removed from the reaction stream and regenerated by hydrogen reduction. A self-healing catalyst

would be one that actively reduces the oxide as it grows. This approach would preserve the metallic state of the catalyst without separate steps for regeneration.

4.2. Mechanism

The catalysts which are the Co_3O_4 nano rods in this given process are self-healing [9]. The rods have a spinel structure which expose the (110) facet of the crystal exposing both Co^{+2} and Co^{+3} on the surface. Now whenever the reaction is carried out the water which is a reagent tends to oxidize the Co^{+2} and thereby results in reduction of catalyst activity. In this case however since Co^{+3} is also present, it reduces the oxidized part of the catalyst thereby restoring the catalyst activity. It is seen that there is no change in selectivity or conversion in the process. In contrary if nanoparticles were used this would not be the case since there is no Co^{+3} on the surface.

5. SELF-REGENERATING CATALYSTS IN AUTOMOTIVE-EMISSIONS CONTROL:

Catalysts are used in the automobiles in order to bring down the emissions of various gases due to the incomplete combustion to acceptable limits as well as maintain the fuel economy without affecting the overall performance.

5.1. Need for the self-regenerating catalysts

It is seen that the catalyst performance starts decreasing as the distance travelled by the automobile increases. This happens mainly due to the decrease in the surface area of the precious metals in the catalyst due to a process called grain growth. This

generally occurs due to the redox environment present in the exhaust and high temperature. Because of this problem we require a higher supply of precious metals which is a problem and also higher maintenance problems. This problem is quite evident in the conventional catalysts and reduced to quite an extent in these “intelligent catalysts” as they are called, since they prevent grain growth [10].

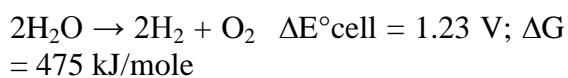
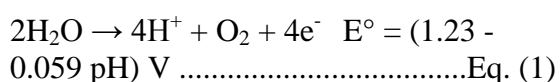
5.2. Mechanism

The temperatures in the exhaust are around 1000°C and the exhaust gases are in a continuous phase of state changes. The precious metal in the “intelligent catalyst” is coordinated with the perovskite oxide precipitate from the crystals and form Nano sized precious metal particles under oxygen deficient condition. The precious metal is prevented of grain growth through movement in and out of the crystal. Under a reducing environment (at high temperature) the precious metal moves out of the crystal whereas under the oxidizing atmosphere it moves in the crystal thereby acting as a self-regenerating catalyst [10]. In conventional catalysts due to high temperature and such fluctuating atmospheres, sintering and grain growth occur eventually deactivating the catalyst [10]. An investigation on the usage of copper nanoparticles as catalyst in layered perovskites has potential for the economical usage of self-regenerating catalyst. Copper is essentially used in the matrix of a perovskite, which is of the K_2NiF_4 - type layered perovskites. This study also hints at additional materials which may serve to be catalyst materials, for example, La_2NiO_4 , Sr_2CrO_4 and Sr_2VO_4 . The usage of a non-precious

metal would make the application more economically viable [12].

6. SELF REGENERATING CATALYST FOR HYDROGEN PRODUCTION BY WATER SPLITTING:

Current energy resources largely rely on fossil fuels that are expected to be depleted in 50-200 years. On a global scale, the intensive use of this energy source has resulted in highly detrimental effects to the environment. Therefore, there has been a move towards generating hydrogen as a fuel which is a clean fuel since water is generated as a by-product. Hydrogen production by water splitting, with sunlight as the main energy source, is a promising way to produce hydrogen. This method is inspired by plants, which utilize solar energy to generate chemical energy by the process of photosynthesis [11]. The equations below illustrate the oxidation and reduction reactions that together represent the overall reaction i.e. splitting of water to hydrogen and water:



6.1. Need for self-regenerating catalyst

As seen in the above equation, water electrolysis is an endothermic reaction which requires external energy input to proceed. The thermodynamic and kinetic limitations of the water oxidation reaction, involving multi-electron transfer, are

especially challenging to overcome, and depend significantly on pH. Hence, to evolve hydrogen in a sustainable manner, it is necessary first to synthesize a highly active catalyst for water oxidation that is capable of lowering the activation energy of the anode reaction close to the thermodynamic minimum. Rare and expensive metals, such as platinum and iridium are widely used for water oxidation in modern technology. Catalysts used in such multi-electron reactions (such as water oxidation) are prone to structural rearrangement and instability during turnover. Inspired by plants and algae, which manage to use abundant, non-toxic transition metals for the same purpose, these expensive catalysts stand to be replaced by cheaper catalysts such as cobalt oxide, nickel oxide and manganese oxide based catalysts. The transition metal atom in the catalyst is reduced during the water splitting reaction. The transition metal in its new oxidation state may be inactive and may dissolve into the electrolyte. Nevertheless, research on the long-term mechanical and chemical stability of these catalysts is also necessary for its commercial application.

6.2. Mechanism

To illustrate the mechanism of self regeneration, the cobalt oxide catalyst is electrodeposited from a solution containing cobalt and phosphate ions at neutral pH. The electrolyte used contained a phosphate buffer. Co (II), Co (III), and most probably Co (IV) oxidation states are involved during water oxidation. When the film is held at open circuit potential, the film was observed to gradually dissolve. When a potential bias of 1.3 V versus a

standard hydrogen electrode was applied (also sufficient for water oxidation to occur) no film dissolution was observed until the potential bias was removed thus indicating the re-deposition of the catalyst as the reaction proceeds. This phenomenon was observed only when the electrolyte contained a proton accepting buffer. This is because the protons generated in vicinity of the catalyst surface, when not transported into the bulk of the electrolyte by proton acceptors, accumulate and cause a local decrease in pH, leading to the dissolution of the catalyst film. Figure 2 illustrates the catalytic mechanism which involves two steps: Firstly, is the equilibrium step which involves proton coupled electron transfer (PCET) between Co (III)-OH and Co (IV)-O species, resulting in the release of hydrogen. This is followed by a rate limiting step which involves reaction of the catalyst with water resulting in the formation of an O-O bond after which the resulting O₂ molecule is released [9]. Under buffered, neutral to alkaline conditions, aqueous Co⁺⁺ ions in the solution are oxidized upon the application of a sufficiently positive potential and deposit as a Co (O) OH species. This material is further oxidized to the mixed Co (III)-OH and Co (IV)-O oxide thus completing the cycle.

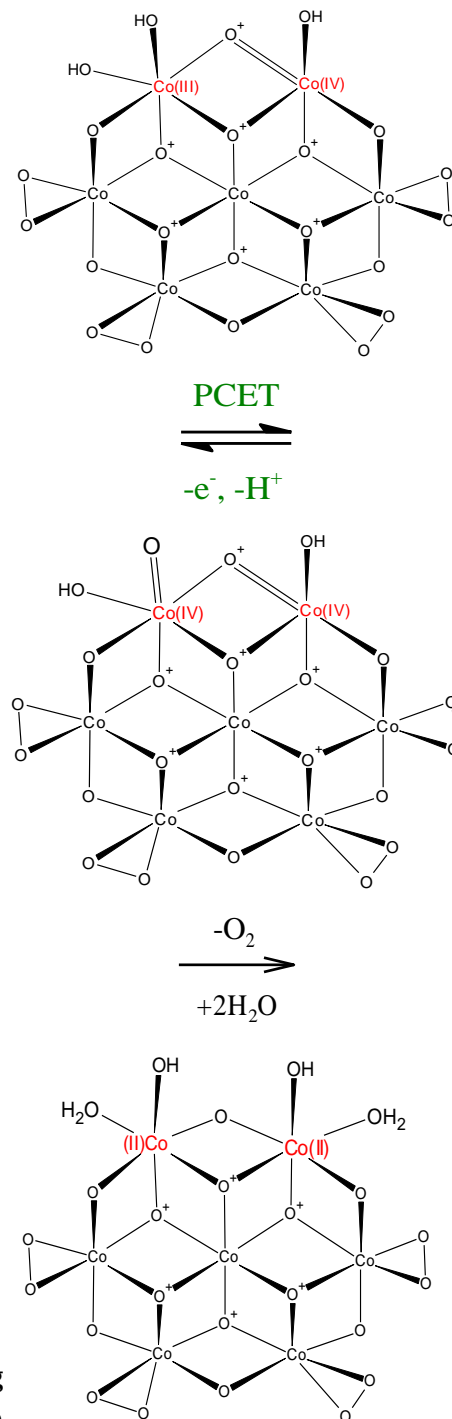


Fig of
the :
[Co (III)-OH] ↔ [Co (IV)-O] + H+ + e⁻.
Rate limiting step: O-O bond formation
[11]

Application	Cause of Catalyst Deactivation	Self-Regenerating Catalyst Used
CO detector	Change in oxidation	Silica gel, palladium

	state of metal atom	salt, molybdate, salt of a transition metal (like Cu)
Manufacture of Vinyl monomers	Deposition of coke on catalyst	MgO, Fe ₂ O ₃ , K ₂ O, CuO
Fischer Tropsch Synthesis	Change in oxidation state of metal atom	Cobalt based
Automotive -emissions control	Grain growth and sintering at high temperatures and alternating reduction-oxidation atmospheres	Pd doped into LaFeO ₃ , Rh or Pt doped into CaTiO ₃ , La ₂ NiO ₄ , Sr ₂ CrO ₄ and Sr ₂ VO ₄
H ₂ production by water splitting	Change in oxidation state of metal atom	Cobalt oxide based

Table 1: Comparison between the various applications in which self-regenerating catalysts are used

7. Conclusion

The use of self-regenerating catalysts in applications such as in CO detectors and for catalytic dehydrogenation of vinyl monomers has been well established. There has been research recently in developing self-regenerating catalysts for Fischer Tropsch synthesis, in automotive emission control and for hydrogen generation via water splitting. These catalysts have been able to deal with problems associated with catalyst deactivation as a result of coking of the

catalyst, change in catalyst oxidation number or any other structural change in the catalyst thereby increasing catalyst life times. The catalyst self-regeneration mechanisms can be useful in developing self-regenerating catalysts for a variety of other applications.

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