

A Review on Studies and Research on Catalysts with Emphasis on Catalyst Deactivation

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ABSTRACT

Catalyst is a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change. In catalyzed reactions the catalyst lowers energy of activation. Catalyst increases rate of reaction. The deactivation of the catalyst can happen because of poisoning, coking or fouling and ageing. It is essential to know the mechanism of deactivation. The recovery of catalyst is widely investigated area of research because it has environmental and economical significance. The present paper summarizes research carried out on catalysts, their deactivation, regeneration and effect of various parameters on catalyzed reactions.

Key words: poisoning, regeneration, kinetics, mechanism.

INTRODUCTION

Reaction engineering is important and a key area of research and investigation as there is a lot of scope for improvement and optimization in the reaction pathways, mechanisms and reactor configurations. Many chemical reactions can be catalyzed by using different types of catalysts. Biocatalysts are also used for some specific reactions. [1-4] Reactive adsorption is also one of the important areas of research related to catalyzed reactions. [5-8] The catalyst form an unstable complex at active sites and then it is converted into product. The catalyst does not undergo chemical change during the reaction. Catalyst provides alternate route to the reaction with lower activation energy. The current review summarizes research and studies on various aspects of catalysts, catalyzed reactions and deactivation.

RESEARCH AND STUDIES ON CATALYST DEACTIVATION

Angeles-Wedler et.al. carried out research on palladium-catalyzed hydrodechlorination. [9] They investigated catalyst deactivation and regeneration. According to them, palladium-catalyzed hydrodechlorination is a promising alternative for the treatment of environmentally relevant water bodies. The sensitivity of the catalyst to poisoning and deactivation induced by reduced sulfur compounds (e.g. sulfides) is a limiting factor. They observed that under neutral pH condition, oxidative regeneration with permanganate delivered a slow recovery of catalyst activity. Also, they observed that changing the pH of the bulk solution to acidic resulted in the complete recovery of

catalyst activity within a regeneration time of about half an hour.

Bashiri and Rohani investigated the modeling of cobalt catalyst deactivation in the Fischer-Tropsch synthesis process. [10] They discussed the deactivating factors of cobalt catalyst. The factors like sintering, coke, poisoning and water were important from deactivation point of view. According to them, the water can be considered as one of the most important factors in deactivation of the catalyst. Markos et.al. investigated modelling of catalytic reactors with catalyst deactivation. [11] Their studies dealt with description of deactivation kinetics of heterogeneous catalysts caused by irreversible chemisorption of catalyst poison. Their studies were focused on catalyst deactivation caused by chemisorption of catalyst poison. Two limiting cases observed were, uniform mechanism of poisoning and shell progressive mechanism. The poison deposits preferentially in the pore mouth near the exterior surface of catalyst pellet in the shell progressive mechanism whereas in the uniform mechanism of deactivation free access of catalyst poison into the whole catalyst pellet is assumed. A review on kinetic modeling of deactivation of SAPO-34 catalyst during methanol to olefins (MTO) process was carried out by Ahmadi. [12] They described kinetic modeling for deactivation of SAPO-34 during MTO process. Also they presented relation between the coke content over SAPO-34 and cumulative amount of methanol fed to the catalysts to estimate the coke content on SAPO-34 at different reaction conditions.

Argyle and Bartholomew carried out review on heterogeneous catalyst deactivation and regeneration. [13] According to them, deactivation of heterogeneous catalysts is a problem that causes loss of catalytic rate with time. They carried out case studies on the deactivation

mechanisms of catalysts used for cobalt Fischer-Tropsch and selective catalytic reduction in order to provide additional depth in the topics of sintering, coking, poisoning, and fouling. They identified three main causes of catalytic deactivation namely chemical, mechanical, and thermal. Also they discussed five intrinsic mechanisms of catalyst deactivation (a) poisoning (b) fouling (c) thermal degradation (d) chemical degradation and (e) mechanical failure. Careful purification of reactants may prevent deactivation or mitigate it to some extent by adding traps or “getters” as components of the catalyst. Al-Adwani investigated the CO oxidation performance over a series of Pt-Pd/Al₂O₃ catalysts. [14] At conversions less than 50%, he noted significant differences when the temperature was ramped to just at the CO oxidation light-off point. It was also observed that the impact of different distributions was more apparent under conditions where a catalyst would be challenged.

Chen et. al. investigated steam reforming of higher hydrocarbons in a novel membrane reformer. [15] Their investigation was focused on catalyst deactivation and engineering control. They investigated the catalyst deactivation and reformer performance in a novel circulating fluidized bed membrane reformer (CFBMR) for steam reforming of higher hydrocarbons. They observed that the reformer has a strong tendency for carbon formation and catalyst deactivation at low steam to carbon feed ratios (≤ 1.4 mol/mol) for high reaction temperatures (700 K) and high pressures (≥ 506.5 kPa). Liu et. al. carried out deactivation mechanistic studies of copper chromite catalyst for selective hydrogenation of 2-furfuraldehyde. [16] They investigated deactivation mechanisms of copper chromite (CuCr₂O₄-CuO) catalyst for vapor-phase selective hydrogenation for furfuryl alcohol using ex situ and in situ X-

ray absorption fine structure (XAFS), X-ray photon spectroscopy (XPS), and Auger Electron Spectroscopy (AES). According to their investigations, catalyst poisoning due to the adsorption of species derived from furfural and furfuryl alcohol are one of the dominant causes for deactivation when operated at 200°C. Larsson carried out studies on catalyst deactivation in three different industrial processes. [17] The investigation was carried out for three industrial processes namely: 1) selective catalytic reduction (SCR) for abatement of NO_x from biomass combustion using V₂O₅-WO₃/TiO₂ catalysts; 2) Catalytic oxidation of volatile organic compounds (VOC) from printing industries using a Pt/γ-Al₂O₃ catalyst; and 3) Ni and Pt/Rh catalysts used in steam reforming reaction of bio-syngas obtained from biomass gasification. According to him, key to further optimize catalyst structures with respect to catalyst performance and apparent lifetime lies in understanding the poisoning mechanisms and the impact on catalyst performance. Rashidzadeh et.al. studied catalyst deactivation in a commercial hydrocracking process. [18] They discussed the causes of deactivation in a commercial hydrocracking unit called Isomax. They proposed a 5 lump kinetic model including catalyst decay function for hydrocracking of vacuum gas oil (VGO) in a commercial plant. They observed that the tendency of the catalyst to crack VGO and diesel to gas and naphtha was negligible and compatible with the nature of amorphous catalysts. The kinetics of propane dehydrogenation and catalyst deactivation over Pt-Sn/Al₂O₃ catalyst was studied by Zangeneh et.al. [19] They carried out performance tests in a fixed-bed integral reactor. They analysed the experimental data by integral and a novel differential method of analysis. They observed that the reaction was not limited by external and internal mass transfer

limitations, implying that the employed kinetics could be considered as intrinsic ones. Diez et.al. carried out investigation on the effect of chemical composition of Mg-Al mixed oxides on both the acid-base properties and the deactivation process during the gas phase self-condensation of acetone. [20] They observed that the initial deactivation rate, increased linearly with the density of surface basic sites. Also The Mg_yAlO_x activity declines in the acetone oligomerization reaction. This may be because of the fact that a blockage was developed on both base and acid active sites by a carbonaceous residue formed by secondary reactions.

CONCLUSION

The factors like sintering, coke, poisoning and water were important from deactivation point of view. Understanding the poisoning mechanisms and the impact on catalyst performance is important aspect of the research on catalyzed reactions. The causes for catalyst deactivation can be chemical, mechanical and thermal. The current review provides summary of research carried out on catalyst deactivation with respect to mechanism, affecting parameters and modeling of deactivation process.

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