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Mini Review

Sintering process and catalysis

Abstract

Sintering process has strong effect on the active surface area and catalytically active sites involved the catalyst. This process has two mechanisms depending on the thermal diffusion of the constituents of catalysts. These mechanisms are atomic migration model and crystallite migration model. Sintering is strongly temperature-dependent. However, there are different parameters affect in catalyst sintering such as time and type of atmosphere. Sintering process is the main factor in the catalyst deactivation. The deactivation of catalyst is the dramatic loss in the active surface area. Sintering process resulted in enhancement in the metal – support interaction yielding a side effect on the activity of catalyst. The scientists of catalysis have different works to reduce the negative effect of sintering process. These scientists showed various attempts to control in the dispersion and redispersion of active constituents of catalysts.

Introduction

Catalysis is process containing change in the rate of a chemical reaction due to the use of catalyst [1-4]. A catalyst is a substance, or a mixture of substances, which increases the rate of chemical reaction by providing an alternative, quicker reaction path, without modifying the thermodynamic factors. The catalyst remains, in general, unaltered at the end of the catalytic process [1]. Catalytic technologies (catalyst and catalytic process) are critical to present and future energy, chemical process, and environmental industries.

According to the phase state of the reactants and catalyst, the catalytic processes are classified into two principle groups: homogeneous and heterogeneous processes. In homogeneous catalysis, the reactants, the products and the catalysts are in the same phase, usually the liquid phase. The catalysts are soluble acids, bases and salts. On the other hand, heterogeneous catalysis involved the catalyst, the reactants and the products in different phases. Usually the catalyst is a solid, and the reactants and products are in the liquid or gas phases.

The heterogeneous catalysis is the most widely used in industry depending upon several advantages as compared to homogeneous counterparts [5]. A heterogeneous catalyst is composed of several constituents such as support, promoter and active catalytic ingredients of metal or metal oxides....etc [1,6,7]. The deactivation of heterogeneous catalysts could be attributed to three major categories of mechanisms namely sintering, poisoning and coke formation (fouling) which may occur separately or in combination [8]. The catalyst sintering is the deriving force for catalyst deactivation, which yearly

causes billions of dollars of extra cost associated with catalyst regeneration and renewal. A detailed understanding of the sintering process will bring the required development for sintering-resistant catalysts. This goal is the major target for this study.

Sintering process

Sintering is the process of compacting and forming a solid mass of object by heat or pressure without melting it to the point of liquefaction [9,10]. Moreover, the sintering occurs naturally or artificially (manufacturing) processes. Sintering process is one of factors of the deactivation process in catalysis. Sintering is a complicated phenomenon because it appears in different applications such as catalysis, plastics and ceramics.... etc.

In the catalytic technologies, the loss of active surface area involved in both bulk or supported catalysts by the agglomeration or migration of small crystallites into larger ones is accompanied by the collapse of the pore structure and loss of internal surface area for these catalysts with subsequent deactivation process [11]. In other words, the catalyst sintering brought about loss in the dispersion of the active constituents for the catalysts.

From this point, sintering process was found to be sensitive to the factors that affect in the catalytic technologies such as temperature, metal loading, doping, metal – support interaction, nature of support, precursors, time and type of atmosphere, particle distribution and particle size [12,13]. In other words, the previous factors affect the rate of loss of dispersion (rate of sintering) for both bulk and supported

catalysts. For instance, the experiments have shown that the rate of loss of dispersion increases with increasing temperature even in absence of O₂. In the case of presence of O₂, some investigators have observed an increase in metal dispersion at certain temperatures [14,15]. In addition, the rate of loss of dispersion is larger in O₂ atmosphere than in H₂ atmosphere and so on [16,17].

Deraz suggested that both the calcination temperature and metal loading modify the concentration of active surface sites contributing in the chemisorption and catalysis of CO oxidation Cu- Zn mixed oxides with subsequent decrease in surface area of these catalysts [18].

Characteristics of sintering process

The nature of sintering process changes according to kind of heterogeneous catalyst and temperature as following [19-21]:

- Sintering on bulk catalysts is normally physical rather than chemical phenomena.
- Sintering on supported metal catalysts involves complex physical and chemical phenomenon.
- Sintering is strongly temperature-dependent
- The rate of sintering increases exponentially with temperature

Mechanisms of sintering process

Understanding sintering mechanisms may help us find routes to improve long term stability of catalysts. The mathematical models of sintering process based on postulated mechanisms for catalyst sintering have appeared in the literature [12,13]. The two major mechanisms of sintering of metal crystallite or particle growth appear to be: (i) atomic migration model (Ostwald ripening), the sintering occurs by migration of atomic or molecular over the catalyst surface upon collision with the stationary metal crystallites yielding particle growth due to van der Waals forces. In other words, this model involved short-distance and direction-selective migration of particles followed by collision and coalescence. On other hand, there are direct transfers of atoms between approaching particles. (ii) Crystallite migration model, the sintering to occur by migration of metal crystallites over the catalyst surface upon collision and fusion of metal particles yielding particle growth and/or formation of new compound via metal –support interaction. These processes depend on the mobility and diffusion of particles. The author speculated that the first model favors the grain growth or agglomeration in the bulk catalysts and both the first and second models were observed in case of supported catalysts.

Deraz reported that doping of CuO/Al₂O₃ catalyst with MgO brought about a measurable increase in both the specific surface areas and catalytic activities for the solids heated at 600°C. Opposite effect was observed for the doped solids calcined in air at 800°C. However, the heat treatment of MgO –

doped Cu–Al oxides at 600°C and 800°C resulted in change in the concentration of catalytically active constituents involved in chemisorption and catalysis of the CO oxidation reaction [22].

Overcome the catalyst sintering

In order to overcome the catalyst sintering, the particles sizes of catalysts must be low with subsequent increase in their surface areas via the following routes:

- The catalyst constituents have high thermal stability
- The preparation or reaction temperatures of the catalysts carries out at low temperature
- Avoid the metal – support interactions
- A good selection for time and type the atmosphere used in preparation and reactions of the catalysts.

These precautions may be lead to reduce the agglomeration or growth of the catalyst particles with subsequent overcome the sintering process.

Conclusions

The catalyst is the important component in catalysis. Catalysis has various industrial and environmental applications. From here, the preparation and characterization of the catalysts have a great importance. However, an importance of the factors that affect in the catalyst especially sintering process. The deriving force of the catalyst sintering is the thermal diffusion of active constituents. The speculated mechanisms of sintering indicate to an increase in the particle size by atomic or crystallite migration via ripening and coalescence. Sintering is a complicated phenomenon because it involves various mechanisms and the metal–support interaction which plays an important role in this process.

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