The comparative jurisprudence of catalysts preparation methods: I. precipitation and impregnation methods.

Nasrallah M Deraz*

Physical Chemistry Department, Laboratory of Surface Chemistry and Catalysis, National Research Centre, Dokki, Cairo, Egypt

Abstract

The main objective of the comparison between both the method of precipitation or co-precipitation and impregnation method used in the preparation of catalysts is to clarify the advantages and disadvantages of each method and out of this comparison the most important recommendations for the superiority of one on the other or determine when to use one without the other.

Keywords: Precipitation or co-precipitation, Wet impregnation, Incipient wetness impregnation

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Introduction

As a result of the rapid development of everything, there has been a great development in the science and technology of preparing catalysts [1,2]. The existence of many modern techniques in the preparation of catalysts enabled us to make a scientific comparison between these methods to find out the most important features and avoid the full disadvantages of these methods, through the so-called jurisprudence of comparison between each or more methods according to the available in our hands.

Among the ways to prepare catalysts, method of precipitation or co-precipitation and impregnation method are the oldest ways to prepare catalysts. Despite the rapid development of the methods of preparing catalysts, these two methods are still and will continue to be used after the introduction of the development and control mechanisms. In this article will discuss the scientific idea, procedures and mechanisms of these methods.

Precipitation or Co-precipitation Method

Definition

It is one of the most widely employed catalysts preparation methods and may be used to prepare either single component catalysts or supported and mixed catalysts [3- 9]. In other words, this method can be used to prepare bulk and supported catalysts. This process is centered on the combination of aqueous phase metal salts and alkali solutions to produce an insoluble metal hydroxide and/or carbonate. The precipitation process can be induced by a change in conditions such as temperature, actual value and rate of pH, evaporation and concentration of salt. These parameters brought about progressive changes in the crystal growth and their aggregation. Indeed, an abrupt change and high concentration will result in small particles and large aggregate. Deraz et al. were studied the influence of precursor compounds on structural and catalytic properties of cobalt based catalysts [2]. They found that the use of different cobalt precursors influenced the physicochemical and catalytic properties of the catalysts prepared. The crystallite sizes of the cobalt metal and Co_3O_4 particles of the catalysts prepared via different cobalt precursors followed the order: Co-Cl>Co-S>Co-N. The catalysts based on cobalt chloride were found to have the highest catalytic activity the decomposition of H_2O_2 at 30-50°C.

Procedures of precipitation method

This method contains various steps as following: (i) Dissolution step in which the precursors of active components, often in their salt forms (nitrate is the preferred salt over chloride or sulfate) are first dissolved in water or suitable medium to form a homogeneous solution. (ii) Precipitation step in which the solution is subjected to pH adjustment or evaporation to force those salts to precipitate. During this precipitation, the salts may be hydrolyzed into hydroxide forms or oxides, so this step can be called hydrothermal process. (iii) Filtration and drying step in which the solid mass is then collected and dried gradually to about the boiling point of the medium. The dry mass obtained is in a loose state with irregular shape; therefore, this mass is first ground to powder form. A binder can be added to help bind together; the binder is chosen so that it is burned into volatile vapor of steam and carbon dioxide during calcination or activation. (iv) Calcination step is undertaken to convert the salt or hydroxide form of the active components into oxides by reacting with air at suitable temperature, for instance, acetate, carbonate or nitrate decomposes into oxide.

Precautions of precipitation method

There are many points to consider during the deposition process as follows:

a) Ammonia water is often used to increase pH value during precipitation step to avoid introduction of alkali metals in the final catalyst.

b) Care should be taken that temperature should not be raised too fast during the drying step, usually at 2 to 5°C per minute to allow the evaporation of water or solvent in the equilibrium state to help the component molecules redistribute to attain a more even distribution. However, slow evaporation of moisture allows development of tiny pore channel to avoid popcorn voids.

c) The catalysts also solidify into final form during the calcination step, i.e., amorphous into crystal; therefore, the surface and mechanical properties of the catalyst are decided mainly in this process. Consequently heating up should be slow, e.g., 2 to 5°C, to allow the component molecules to develop into a stable structure without strain. The final temperature of calcination should not be lower than the intended reaction temperature; usually about 50°C higher is used to ensure thermal stability of the catalyst during the reaction. The catalyst is then ready to be studied for its property.

d) If metal form of catalyst is desired, the catalyst is to be reduced to metallic form by reduction under a proper concentration of carbon monoxide or hydrogen prior to use. Sometime the fresh metallic catalyst is lightly partial oxidized to pacify its oxidation activity during transportation and storage. This reduction is often an exothermic process; here again temperature should not be over shot. Moreover, metal at high temperature tends to undergo sintering and salt formation with support such as aluminates, which is very difficult to be reduced into metallic form. High heating rate or too high a reduction temperature will cause the metal to aggregate together into a large crystal form; this reduce the degree of dispersion or the surface area of the active metal. Metal in this state is very active and will burn on contact with air; therefore, it should be protected under inner gas or liquid.

Mechanisms of the precipitation method

The precipitation of a crystalline solid can be divided into three steps: super saturation, nucleation and growth. In the super saturation region the system is unstable and precipitation occurs as a result of any small perturbation. Super saturation is reached by means of physical transformations (change in temperature or solvent evaporation) or chemical processes (addition of bases or acids, use of complex forming agents). Formation of the solid phase occurs in two elementary steps:

(i) Nucleation, formation of the smallest elementary particles of the new phase which are stable under the precipitation conditions.

(ii) Growth or agglomeration of the particles. Under conditions of high super-saturation the rate of nucleation is much higher than the rate of crystal growth and leads to the formation of numerous but small particles. In this condition amorphous precipitates can be obtained [3,6].

Usually precipitates with specific properties are desired. These properties include the nature of the phase formed, chemical composition, purity, particle size, surface area, pore size, etc., as well as the requirements of downstream processes (drying, palletizing or calcination). Basically, all process parameters influence the quality of the final precipitates, and fine tuning of the parameters is necessary in order to produce the required material. Hydroxides and carbonates are the preferred precipitates because of their low solubility, easy decomposition and minimal toxicity and environmental problems [5].

Advantages and disadvantages of the precipitation method

Advantages of the precipitation method: (i) The homogeneity of component distribution, (ii) The relatively low reaction temperature, (iii) The fine and uniform particle size with weakly agglomerated particles, and (iv) The low cost.

Disadvantages of the precipitation method: Chemical precipitation is generally not a controlled process in terms of reaction kinetics and the solid phase nucleation and growth processes depending upon the precipitation reactions are highly susceptible to the reaction conditions. Therefore, the as synthesized solids have a wide particle size distribution, uncontrolled particle morphology with agglomeration and incomplete precipitation of the metal ions. However, the control over the stoichiometry of the precursors is rather difficult to achieve. Thus, this method is insensitive, semi-quantitative and long reaction time from 18 to 48h.

Impregnation Method

Impregnation

It is the procedure whereby a certain volume of solution containing the precursor of the active phase is contacted with the solid (support or another active solid phase), which, in a subsequent step, is dried to remove the imbibed solvent [3-5,10,11]. Thus, this method can be used to prepare supported and mixed catalysts.

Types of the impregnation method

There are two methods of contacting of the solid with solution may be distinguished, depending on the volume of solution: wet impregnation and incipient wetness impregnation. In *wet impregnation* an excess of solution is used. After a certain time the solid is separated and the excess solvent is removed by drying. The composition of the batch solution will change and the release of debris can form a mud which makes it difficult to completely use the solution. The heat of adsorption is released in a short time. In *incipient wetness impregnation* (also called capillary impregnation or dry impregnation) the volume of the solution of appropriate concentration is equal or slightly less than the pore volume of the support or another active solid phase. Once the catalyst is impregnated onto the support or another active solid phase, it is then dried and calcinated or reduced as described above.

Factors affect the impregnation method

There are some factors affect the as prepared catalysts by impregnation method such as temperature and the concentration of precursor. The operating variable is the temperature, which influences both the precursor solubility and the solution viscosity and as a consequence the wetting time. However, the maximum loading is limited by the solubility of the precursor in the solution. In addition, the concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying.

Advantages and disadvantages of the impregnation method

This method is faster, inexpensive, and allows the final property and configuration to be controllable in advance. It is, however, harder to prepare high concentration catalyst and to obtain even dispersion of catalyst components on the surface. But, wet impregnation method gains a great advantage when compared to other methods used in the preparation of catalysts, namely that it is easy to prepare a layer of active matter on the catalyst's surface. This could be attributed to change the solution transport from a capillary action process to a diffusion process, which is much slower [11].

Mechanisms of the impregnation method

There are two mechanisms according to type of the impregnation method. In the Incipient wetness impregnation method capillary action draws the solution into the pores. But, the solution transport changes from a capillary action process to a diffusion process in the wet impregnation method [11].

Conclusion

The author, after the previous presentation of each of the two methods of preparing the catalysts, believes that before selecting the method of catalyst preparation, we must define our goal of preparing the catalyst, taking into account the large difference between use at the laboratory level and half or full industrial level. The author believes that these two methods can not be dispensed with depending on the continuity of their presence in the scientific community and the continuous work on their development, as well as the least expensive ways. The method of impregnation is limited, especially at the preparation of catalysts with high concentrations. The precipitation method, although consuming large quantities of chemicals, is usable in all concentrations while attempting to overcome particles aggregation.

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***Correspondence to:**
Nasrallah M Deraz
Physical Chemistry Department
Laboratory of Surface Chemistry and Catalysis
National Research Centre
Cairo
Egypt
Tel: +201284425222, +201115996267
E-mail: nmderaz@yahoo.com