

The comparative jurisprudence of catalysts preparation methods: II. Deposition-precipitation and adsorption methods.

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Abstract

The main purpose of using the comparative jurisprudence of methods of catalyst preparation is to look for similarities and differences between these methods as well as to clarify the same meaning in two different ways to reach different purposes, for example formation of material on another material and production of supported catalysts or composites.

The method of adsorption is used in various industrial purposes, including the preparation of catalysts and disposal of environmental pollutants. While deposition-precipitation (DP) is an important method used to prepare catalysts. We find that these two methods aim to form material on or within another material, but they differ in the mechanism of each process.

Keywords: Deposition-precipitation, Adsorption method, Supported catalyst

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Introduction

The comparison between the method of Deposition-precipitation and adsorption method shows the differences between them in terms of the technique and the purpose of their use in the preparation of catalysts. The scientific foundations of Deposition-precipitation method (DP) in catalyst preparation were discovered in the middle of 1980 [1,2]. This method combines all the requirements of the precipitation method related to the determined control of the precipitated particles involved size of these particles and their distribution. However, this method is based on the use of precipitation combined with deposition from a liquid medium [2,3]. On the other hand, the supporting of precursors is metal sols, poly nuclear hydroxo complexes (PHC) of metals, sols, or hydroxide precipitates [4-7]. Izaskun Barrio et al. reported to prepare of manganese oxide on alumina-coated monoliths by redox deposition-precipitation using acetone as solvent [8]. The deposition process was achieved by reduction of manganese permanganate with ethanol. The Lewis acid sites on the alumina catalyze this reaction. Thus, the precipitation is produced preferentially on the surface of the monolith and not in the bulk of the solution. Indeed, the monoliths prepared by this method are very active for the complete oxidation of oxygenated volatile organic compounds (VOCs). However, these monoliths consist of a mixture of complex phases including aluminum, sulfated alumina, potassium sulfate and manganese oxide.

The adsorption method can be used to prepare of supported catalyst and elimination of environmental pollutants [1]. The most important factors affecting adsorption are: (i) surface area and particle size of support or adsorbent, (ii) contact time or residence time, (iii) affinity of the solute towards the support or adsorbent and (iv) solubility of solute in solution. The adsorption method can be achieved with presence of the strong capacity of metal compounds for adsorption on support surfaces [9]. Liyun Zhang et al. studied preparation of palladium catalysts

supported on carbon nanotubes (CNTs) by an electrostatic adsorption method [1]. They found that CNTs functionalized with various surface oxygen functional groups (SFGs) were obtained by treating the raw CNTs with concentrated HNO_3 or $\text{HNO}_3/\text{H}_2\text{SO}_4$. The SFGs could decrease the point of zero charge (PZC) of the CNTs and promoted the adsorption of Pd cationic complexes on the CNTs. However, the SEA method was superior to the traditional incipient wetness impregnation method for the synthesis of highly dispersed Pd catalysts, which exhibited a high specific activity for the Suzuki coupling reaction. Generally, Pd nanoparticles are excellent catalysts in C-C coupling, hydrogenation, oxidation, and some other reactions [10]. In addition, Pd nanoparticles are immobilized on supports to hinder their aggregation during a reaction and also to ease separation and recovery from the reaction solution.

In fact, the jurisprudence of the comparison between the methods of catalysts preparation helps to improve and develop these methods through select the best methods or the integration of two methods together. This has been clearly demonstrated in DP method.

Adsorption Method

Adsorption allows the controlled anchorage of a precursor (in an aqueous solution) on the support [11-14]. The term adsorption is used to describe all processes where ionic species from aqueous solutions are attracted electrostatically by charged sites on a solid surface. Often consideration is not given to the difference between true ion exchange processes and electrostatic adsorption at the charged surface of oxides. Catalyst systems, which need charge compensating ions, are ideal materials for ion exchange (zeolites, cationic clays or layered double hydroxides). Instead most oxide supports, when placed in an aqueous solution, develop a pH-dependent surface charge. These oxides may show a tendency for adsorption of cations (SiO_2 - Al_2O_3 , SiO_2), or anions (ZnO , MgO) or both, cations in basic solutions and

anions in acid solutions (TiO_2 , Al_2O_3). The surface charge of an oxide depends on its isoelectric point as well as on the pH and ionic strength of the solution.

The strong electrostatic adsorption method is a simple approach to synthesize supported metal catalysts. This method is based on an electrostatic mechanism. This mechanism speculated that the oxygen surface functional groups on the support can be protonated and deprotonated to be positively or negatively charged as a function of pH relative to the point of zero charge [15]. The basic condition for obtaining desired results from the adsorption method is high capacity of metal compounds on support surfaces.

Deposition- Precipitation Method

In this method, [12-14,16] two processes are involved: (i) precipitation process, it is the creation of a solid from bulk solutions or from pore fluids depending upon sufficient force of gravity (settling) to bring the solid particles together; (ii) Deposition process, it is interaction of the precipitate particles with the support surface.

Indeed, the slurries are formed using powders or particles of the required salt in amounts sufficient to give the desired loading, and then enough alkali solution is added to cause precipitation. However, precipitation in the bulk solution must be avoided, since it gives rise to deposition outside the pores of the support. A well-dispersed and homogeneous active phase is reached when the -OH groups of the support (for example, the silanols of silica) interact directly with the ions present in the solution, thereby also determining the nature of the phase formed [12,16,17]. The nucleation rate must be higher at the surface than in the bulk solution and the homogeneity of the solution must be preserved. A method to obtain uniform precipitation is to use the hydrolysis of urea as a source of -OH instead of conventional alkali. Urea dissolves in water and decomposes slowly at ca. 90°C, giving a uniform concentration of -OH in both the bulk and pore solutions. Thus the precipitation occurs evenly over the support surface, making the use of urea the preferred method for amounts higher than 10-20%.

Reasons to use of DP method

The reasons for using DP method are to avoid or overcome some problems that arise from the adsorption method during preparation of certain catalysts. Therefore, the reasons cited by some scientists as follows [1,18,19]: (i) Weak capacity of some metal compounds for adsorption on support surfaces such as the deposition of inorganic Fe(III) salts on SiO_2 or Al_2O_3 , (ii) The adsorption of some chloro complexes of noble metals results in the contamination of the surface of dispersed metallic particles with chloride ions, which are catalytic poisons in many reactions such as poisoning of supported gold particles by chlorine atoms when gold chloride adsorbed on the surface of various oxide supports [8]. The poisoning effect of the chlorine atoms is much weaker, when a gold precursor is deposited as hydroxide particles [18,19].

Ways of DP method

DP method can be carried out by the following three ways [20]: (i) A precipitating agent is added to a support suspended in a

solution of a precursor of an active component. (ii) A solution of a precursor is added to a suspension of a support in an alkali solution. (ii) A solution of a precursor is mixed with an alkaline agent to obtain colloidal compounds of the precursor as PHC or sols, and then this solution is brought into contact with a support.

Mechanisms of the Deposition-Precipitation and Adsorption Methods

Adsorption method is based on electrostatic mechanism [13]. Deposition-precipitation technique is depended upon super saturation, nucleation, growth and settling [21,22]. Rodolfo Zanella et al. [22] reported to Mechanism of deposition of gold precursors onto TiO_2 during the preparation by cation adsorption and deposition - precipitation with NaOH and urea. In case of the DP urea method, the authors reported that all the gold present in solution is deposited on the TiO_2 surface as a gold(III) precipitate, which is not gold(III) hydroxide as occurred in case of cation adsorption.

Conclusion

The author assumes that the use of the adsorption method in the preparation of catalysts compared to DP method is limited and depends on the capacity of the substance absorbed on the support surface. The DP method is therefore more prevalent for the absorption method. It was also found that the mechanism of occurrence of each method is different from the other in the sense that the mechanism of DP method is complex issue. Both DP and adsorption methods can be used for preparation of supported catalyst.

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