

# Improvement of Synergetic Effect In Heterogeneous Catalysis By Addition Of Metal Oxides

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## ABSTRACT

Over the past few years, synergetic effect has great importance in the heterogeneous catalysis structure. Synergetic effect provides the importance of the activity and stability of catalysis to produce desired product by improving the defects in the solid heterogeneous catalysis. These defects occur due to imperfection of the solid crystal lattices. And these defects can be improved by the addition of various metal oxides, which finally improve the synergetic effect or the defects in the heterogeneous catalysis. The metal oxide additives were found to influence the catalytic activity in the reaction, surface composition of the catalyst and the stability of catalysts during their operation. This paper reviews and assesses the effectiveness of different metal oxides additives in the heterogeneous catalysis activity and stability i.e. by improving synergetic effect in the heterogeneous catalysis.

**Keywords:** synergy effect, encapsulation, mimic enzyme, BET, coprecipitation, calcination.

## 1. Introduction

The development of environmentally started technologies, i.e. the heterogenization of active homogenous catalysts, has been given more importance in catalysis research fields [1]. In this, encapsulation/immobilization of metal complexes in porous materials is very attractive because the prepared materials could act as mimic enzymes. Upon physical entrapment in the supercages of zeolities, metal complexes can not only retain their activity and selectivity in homogeneous catalysis but also have high stability due to the reduced dimerization of complex molecules in cavities. These materials exhibit high activity in some industrially important reactions and possess the advantages of heterogeneous catalysis [2].

In the structure of particular solid, the unit cell is the building block of the structure. The repetitive units combine to forms lattice structure of the particular solid. This unit cells are of different types such as cube, cuboidal, rhombic, orthogonal, etc. The lattice structure provides the information of arrangement of cations and anions in the solid. Such that due to variation of ratio of these cations and anions some defects occurs in the lattice structure. Such that line defect, point defect, edge defect, etc. are cannot be explained together for the particular crystal or solid, therefore a new term is introduce as “Synergy effect” which means the interaction of multiple elements in a system to produce an effect different from or greater than the sum of their individual effects [3].

Since the synergy effects increases the activity and stability of the particular solid heterogeneous catalyst. This is because interactions of various elements in the particular substance, such that they lead to the vacancy and interstitial defects which effect the activity of the catalyst. The activity of heterogeneous catalyst is purely based on the adsorption by Langmuir theorem which is depends upon the surface area available for the adsorption. The surface area calculated by the BET method [4]. The varying surface area is due to the vacancy and interstitial defect in which the cations and anions are removed or may be fitted into the void spaces respectively in the system of multi elements.

Now this synergy effect can be improved in heterogeneous catalyst by adding metal oxide in it. We have chosen metal oxide because more diffusivity of the oxygen can increase activity and decrease synergy effect in the solid

heterogeneous catalyst [5]. By the addition of metal oxides many properties and selectivity of the catalyst increased and discuss in the overview of the catalyst.

## 2. Role of metal oxides in heterogeneous catalyst:

The heterogeneous catalysts are used in the many industrially chemically processes for producing most valuable and important products. In order to increase the activity and stability of the heterogeneous catalysts, the basic catalyst was often modified by different oxide additives. Besides  $ZrO_2$ , other irreducible oxides like  $Al_2O_3$ ,  $TiO_2$ ,  $Ga_2O_3$  have been investigated [6]. The effect of several additives such as boron, chromium, vanadium, tungsten and manganese, are also studied [7]. Several detailed papers were further devoted to the influence of small amounts of such additives as  $VO_x$  [8, 9],  $MnO_x$  [10, 11, 12], and  $MgO$  [13]. The metal oxides additives affect both the activation energy and pre-exponential factor in the synthesis processes. This means that both the number of the active centres and their energies are changed which leads to the compensation effect [13].

The changes in the catalytic activity under the influence of metal oxide additives are caused by control of adsorbent dispersion, increase in the concentration of metal oxide on the surface, and the related decrease of the capability of the surface to adsorb components which inhibits the reaction of formation of respective products [13]. The reaction conditions, including reaction time and temperature, greatly influenced the catalytic properties of the prepared catalysts [14].

## 3. Overview of addition of metal oxide in the heterogeneous catalysis:

An overview of the recent works undertaken for the field describing the preparation of catalysts and improvement in synergetic effect in the solid heterogeneous catalysis. Addition of metal oxide improves the many properties of the catalysts due to which their selectivity get increased for the particular process. The works for the improvement of synergetic effect till this year are discussed as follow:

### 3.1 Synergy effects between $\beta$ and $\gamma$ phases of bismuth molybdates in the selective catalytic oxidation of 1-butene (2003) :

The preparation of catalyst is done by coprecipitation in aqueous solution. Molybdenum solutions from ammonium heptamolybdate and bismuth solutions by solubilisation of bismuth sub nitrate with hot concentrated nitric acid were prepared. The bismuth solution was added into the molybdenum solution drop wise under vigorous stirring. For the phases preparation the pH conditions should be taken care. All the samples before filtration were kept in contact with mother liquors during 1 hr. at room temperature under vigorous stirring. After filtration the precipitates were dried overnight at 393K and then calcinated in a slow air flow for 5 hr. at 748K. By this process catalytic surface get increased and the active sites also which is tested by different instruments [5].

### 3.2 Addition of metal oxide additives in $Cu/ZnO/ZrO_2$ catalysts for the production of methanol from $CO_2$ and $H_2$ (2006) :

These types of catalysts are prepared by two methods: (A): Co-precipitation and calcination of the precipitate of mixed basic carbonates. The solution of  $ZrOCl_2$ , nitrates of Cu and Zn, component M (= Ga, B, In, Gd, Y, Mg, Mn), and 0.25 mol/L solution of  $Na_2CO_3$  are added to a vessel containing demineralised water under vigorous stirring. Only boron was introduced as borax. The process of precipitation was carried out at temperature of 338K and a constant pH 7. The precipitation is added to the mother liquor and kept for 24hr at the same temperature under stirring and then washed away many times by demineralized water, dried for 3hr at 383K and calcined for 3hr for 623K for air. (B): Firstly, the citrate complexes of metals are decomposed and then required amounts of nitrates of Cu, Zn, Zr, and M added under intense stirring to the 2 M solution of citric acid. The amount of citric acid is calculated as 1/3 mol citric acid per gram equivalent to each metal plus 2%. The solution is then evaporated in vacuum overnight at 363K, then dried at 403K for 8hr, then calcined on air for 1hr at 373, 473, 523 and 573K temperature respectively. The reagent grade chemicals were used in both methods [13].

The oxide additives lead to drastic difference in the activity of the  $Cu/ZnO/ZrO_2$  catalysts in the reaction of the methanol synthesis from  $CO_2$  and  $H_2$  as well as in the RWGS reaction. The highest yield obtained with the  $Ga_2O_3$  additive and lowest yield obtained by  $In_2O_3$ . In the catalysts produced by complexing with citric acid, the growth of copper crystallites during the calcination, reduction and operation of in the reactor is restricted such that small crystallites are consumed by the growing big crystallites [13].

### 3.3 Oxidation of cyclohexane over iron and copper salen complexes simultaneously encapsulated in zeolite Y (2008):

This type of catalyst is prepared by three steps such as preparation of salen ligands, preparation of salen, and lastly mixing of first two. Preparation of salen ligands are carried out by 0.1 mol aliquot of ethylenediamine which dissolved in 25ml of ethanol then this mixture added to solution of 0.2 mol of salicylaldehyde in 150ml of ethanol under stirring conditions. The obtained solution was refluxed for 1hr, cooled down and then kept at ambient temperature for 3hr. the formed yellow solid was filtered and recrystallized from ethanol [2].

Cu (salen) and Fe (salen) complexes prepared by 0.01 mol of salen ligand which is dissolved in 50ml of ethanol, and then the mixture was heated to boiling temperature. The solution of 0.01 mol of metal salt added drop wise to the 125ml of ethanol. The resultant solution was stirred and refluxed for 1hr. after the solution was cooled to room temperature; the product was separated from  $\text{CHCl}_3$ /petroleum ether by the process of filtration and recrystallization. This salen can be obtained by the process of ion-exchange method [2].

Thirdly, the metal complex was encapsulated in zeolite by using the flexible ligand method. In this method salen complex and salen ligands are mixed together and sealed into a round flask. The complexation was carried out at  $150^\circ\text{C}$  for 24hr under high vacuum conditions. Uncomplexed ligands and complex molecules adsorbed on the surface were removed by Soxhlet extraction with acetone. The extracted sample was further ion-exchanged with 0.1 M NaCl aqueous solution to remove uncomplexed metal ions, and then washing with deionized water until no  $\text{Cl}^-$  anions could be detected with  $\text{AgNO}_3$  aqueous solution [2].

In this process the synergetic effect attributed to the interaction of Fe(salen) and Cu(salen) via the lattice oxygen of zeolite host and the formation of a binuclear (Cu,Fe)(salen)/Y complex through the phenolate bridge of salen ligands. The reaction conditions including reaction time and temperature mostly influenced the catalytic properties of the prepared catalysts [2].

### 3.4 Influence of solid acids as co-catalysts on glycerol hydrogenolysis to propylene glycol over Ru/C catalysts (2008):

This type of catalyst can be obtained by three different processes which are described as follows:

#### 3.4.1 Preparation of TPA/ $\text{ZrO}_2$ :

This method is known as impregnation method in which zirconium hydroxide was prepared by hydrolysis of zirconium oxychloride by the drop wise addition of aqueous  $\text{NH}_3$  solution until the solution reaches a pH of 10. The precipitate then filtered and washed with deionized water until it was free from chloride ions as determined by the silver nitrate test. The obtained zirconium hydroxide then dried at  $120^\circ\text{C}$  for 12hr, grinded well and dried for another 12hr. This is the support on which the solution of the TPA and methanol is added while stirring. The extra methanol is removed on rota evaporator. The resulting solid then dried at  $120^\circ\text{C}$  overnight and then calcined in air at  $300^\circ\text{C}$  for 2hr [14].

#### 3.4.2 Preparation of CsTPA:

This is prepared by adding the  $\text{CsNO}_3$  drop wise to TPA solution at room temperature, which leads to the white precipitate. This solution kept for ageing overnight. After this excess water gets removed slowly on a water bath. The resulting sample dried further in an oven at  $120^\circ\text{C}$  for 12hr and calcined at  $300^\circ\text{C}$  for 2hr [14].

#### 3.4.3 Preparation of Cs/TPA $\text{ZrO}_2$ :

This is prepared by exchanging protons of TPA of TPA/ $\text{ZrO}_2$  catalyst. The actual catalyst was produced after calcinations at  $300^\circ\text{C}$  for 2hr. The activity of glycerol hydrogenolysis depends on the amount of acidity of the solid acids. This combine catalysts increases active sites and hence the activity of catalysts [14].

## 4. Conclusion:

From the data many observations can be made regarding the process of addition of the oxides to the respective heterogeneous catalyst. Regarding pH maintenance of the catalyst at the time of metal oxide addition. Due to the high oxygen mobility in the lattice catalyst can regenerate active sites. We reported simple methods to prepare the catalysts with the addition of oxygen such that their synergetic or defects in the catalyst will improve by increasing active sites at the surface area of the catalyst.

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