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Guiding questions for the synthesis of catalyst and its application in selective catalytic oxidation reactions

William G. Cortés-Ortiz[1,2*], Carlos A. Guerrero-Fajardo[2]

[1] Grupo de Investigación en Química Aplicada, Departamento de Química, Facultad de Ciencias, Universidad El Bosque, Colombia. E-mail: cortesgiovanni@unbosque.edu.co

[2] Grupo de Investigación Aprovechamiento Energético de Recursos Naturales, Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Colombia. E-mail: caguerrerofa@unal.edu.co

ABSTRACT

This paper presents a brief history of catalysis, as well as the processes of selective oxidation of hydrocarbons. On the other hand, the basic concepts involved in heterogeneous catalysis are mentioned, emphasizing the role of catalytic materials in chemical oxidation processes and posing a series of guiding questions to be followed when approaching a process catalyzed by solid materials. In the same way, the methods of synthesis of catalysts known in the literature as sol-gel and impregnation are shown, identifying the influence of each stage of preparation with the physical and chemical properties of the materials. Finally, a case study applied to the selective catalytic oxidation of methane and methanol using iron, molybdenum, and vanadium catalytic materials synthesized by the sol-gel method is presented.

Keywords: Heterogeneous Catalysis; Guiding Questions; Selective Oxidation; Methane; Methanol; Formaldehyde; Sol-Gel; Impregnation; Catalyst Synthesis; Calcination

1. Introduction

Catalysis is currently a discipline (or science) used for the production of many of the most demanded chemical products in the world. Thus, by using catalytic processes, petroleum derivatives and a large number of substances are obtained in order to enjoy life as we know it today. However, to reach the position where it is, many years have passed and perhaps an equal or greater number of researchers have directed the research. Thus, the following is a chronological presentation of the main advances in catalysis.

1.1 Advances in catalysis

Many authors agree in suggesting that the origin of the term catalysis is due to a series of investigations and events around 1800. Thus, before the introduction of the concept by Berzelius during the period of 1835 and 1836, catalysis was a subject of much debate[1]. Some authors suggest that the application of catalysis begins in the second decade of 1800 with the discovery of the hydrogen-oxygen reaction catalyzed by the platinum surface in 1823, work done by Döbereiner[2]. However, it can be said that the first application of catalysis was the production of ethanol by fermentation in antiquity, or, on the other hand, a little later in time, in the Middle Ages, around 1550 the use of sulfuric acid

as a catalyst for the synthesis of diethyl ether is reported[1]. Based on the above concerns about the specific timing of the use or definition of catalysis, the scientific community agrees that the concept of catalysis was well illustrated and its beginnings are attributed to the studies performed by Mitscherlich and Berzelius[1].

In 1834 Mitscherlich reported that using alcohol (ethanol) and dilute sulfuric acid at 140 °C the resulting products could be distilled by obtaining ether and water. Mitscherlich stated that the combinations and decompositions that occurred during this process were frequent and introduced the concept of "contact" to describe what was observed with alcohol and sulfuric acid. In the same way, Mitscherlich presented other reactions that he suggested were also caused by contact: ether formation, oxidation of ethanol to acetic acid, fermentation of sugar, production of sugar from starch by boiling with sulfuric acid, hydrolysis of ethyl acetate in a basic medium and the formation of ethene from ethanol by heating, also in an acid medium[1].

During this time, Berzelius, critically reviewed and summarized the scientific researches of the day and, in his report of 1835, listed a number of reactions taking place in the presence of a substance that remained unmodified and generated a number of cogent insights for the development of catalysis which are presented separately below:

"...This is a new power to produce chemical activity belonging to both inorganic and organic nature, which is undoubtedly more widespread than we have hitherto believed and the nature of which is still hidden from us..."

"...When I call it a new power, I do not mean that it is a capacity independent of the electrochemical properties of the substance. On the contrary, I cannot suppose this to be anything else than a kind of special manifestation of these, but so long as we cannot discover their mutual relation, it will simplify our investigations to regard it as a separate power..."

"It will also make it easier to refer to it if it possesses a proper name. I will therefore use a derivation known in chemistry, it will be called the catalytic power of substances, and the decomposition by means of it will be called the power of catalysis; just as the word analysis is used to denote the separation of the component parts of bodies by means of ordinary chemical forces..."

"Catalytic power actually means that substances are capable of awakening affinities which are dormant at a given temperature by their mere presence and not by their own affinity..."[1].

Berzelius' writing shows that the new finding was compelling for the academic society of the time and that it would bring a great number of benefits to the chemical processes being developed today. **Figure 1** summarizes the main processes evaluated during the 1800s that motivated Berzelius in his observations; it shows the use of acid as a catalyst for the hydrolysis of starch and the obtaining of sugars, as well as heterogeneous processes using metals as catalysts.
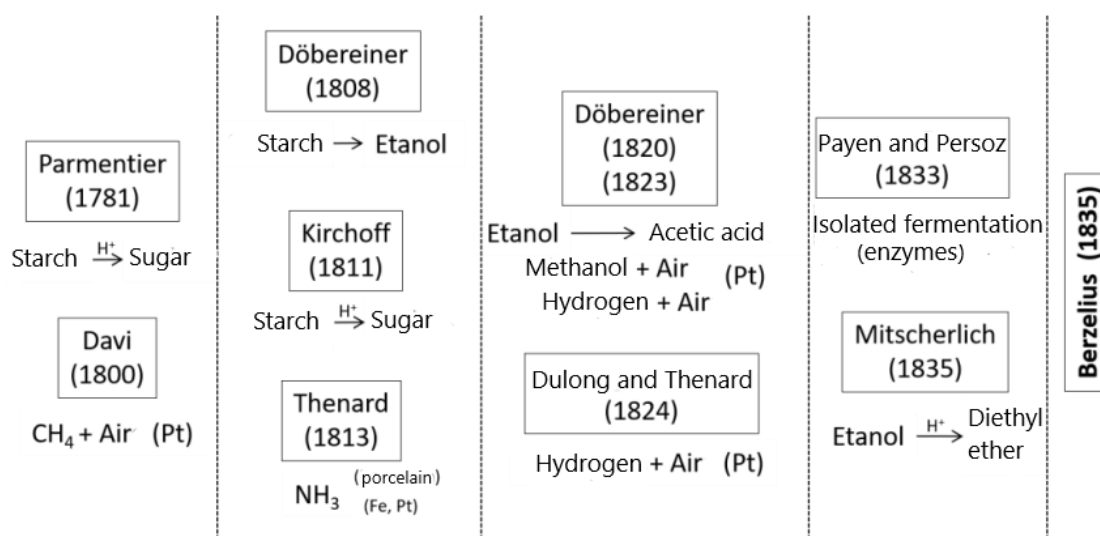

Figure 1. Early advances in catalysis. Source: own elaboration.

In this same period, around 1835, the discovery of heterogeneous catalysis was complemented by the studies of Kirchhoff, Davy, Henry, Philips, Faraday and Berzelius. It is important to mention that, in this same period, the Daguerre process was presented, considered as the first photographic procedure that used silver and copper plates for image fixation[2]. Likewise, the study of tribology and friction began coinciding with the industrial revolution.

The first chemical technologies based on surface catalyzed processes appeared in the period between 1869 and 1912, which generated a great impulse to the chemical industry that is still in use today. Thus, one of the first processes was the Deacon process, used for the production of chlorine gas from hydrochloric acid and oxygen, using copper as the first catalyst on a calcined clay ($HCl + O_2 \rightarrow H_2O + Cl_2$). Certain disadvantages were attributed to this process, such as corrosion of the reactor, low purity of the chlorine obtained and deactivation of the catalyst[3].

In the same way, the oxidation of sulfur dioxide ($SO_2 + O_2 \rightarrow SO_3$) was studied, the sulfur trioxide obtained is reacted with water to obtain sulfuric acid[4]. Likewise, during this period of time, the reaction of methane with water vapor was studied with great interest to produce synthesis gas, which is a mixture of carbon monoxide and hydrogen in different proportions ($CH_4 + H_2O \rightarrow CO + H_2$); carbon dioxide and sulfur compounds that are present as impurities are also formed[5].

Likewise, the oxidation of ammonia to produce nitric acid ($NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$) developed by Ostwald in 1901, which is considered to be one of the great large-scale processes of the chemical industry, was also studied. The process involves the catalytic oxidation of ammonia with air producing nitrogen oxide which is then oxidized to nitrogen dioxide and absorbed over water, thus forming dilute nitric acid, which is recovered by distillation[6]. In the first industrial process of nitric acid production, platinum was used as catalyst, then it was changed to platinum-rhodium alloys varying the rhodium content between 5% and 10% by mass. Despite the efforts to find another catalyst to reduce the production costs of nitric acid, platinum-rhodium alloys or platinum, palladium and rhodium are the catalysts used in this process[6].

Likewise, the study of hydrogenation began in the 1900s. A clear example is the hydrogenation of ethylene ($C_2H_4 + H_2 \rightarrow C_2H_6$) studied by Sabatier around 1902, considered the father of this process. Sabatier was the first to mention that, in a solid catalyzed process, a temporary and unstable intermediate was formed on the surface of the catalyst; he also predicted the reversibility of the hydrogenation reaction, suggesting that a catalyst used for hydrogenation would also catalyze dehydrogenation[7].

Finally, in this period of time, research was initiated for the synthesis of ammonia ($N_2 + 3H_2 \rightarrow 2NH_3$), an important process since then, since it has allowed obtaining a raw material required to obtain fertilizers which have increased the availability and possibility of access to food in the world. The catalyst used in the process contained iron with the highest oxidation state and potassium oxide working at high conditions (above 400 °C and 300atm) of temperature and pressure[8].

Continuing with the advance in time, at the beginning of 1900, the study of half-life times of light bulb filaments, as well as, gas absorption in masks and gas separation technologies; led to atomic and molecular adsorption researches, being one of the strongest researchers at this time Langmuir, around 1915. The properties of monolayers (physisorbed or chemisorbed), adsorption isotherms, dissociative adsorption, energy exchange and collisions between the gas phases and the surface were also studied in great detail[2].

On the other hand, electron diffraction on a surface was discovered by Davisson and Germer in 1927. At that time, the main academic and industrial laboratories focused their studies on the surface of catalytic materials. Thus, surface chemistry was placed at the center of the development of chemistry, due to two important aspects. The first was the intellectual challenge of understanding the diversity of surface phenomena and the second was the great importance it would have in energy conversion technologies[2].

Later, in the early fifties, research interest in chemistry focused its efforts on studies of molecular processes in the gas phase, due to the new techniques developed for this type of analysis. Likewise,

the development of technologies based on surface chemistry grew at a very high speed, especially in the areas of petroleum refining and the production of high value-added chemical products[2].

Subsequently, in the late 1950s the rise of the electronics industry based on solid-state devices and the availability of inexpensive ultra-high vacuum systems (developed for space science research) provided surface chemistry with new challenges and opportunities which resulted in an explosive growth of this discipline. In this respect, clean single crystal surfaces could be studied for the first time, and the preparation of surfaces and interfaces with known atomic structure and controlled composition was driving the development of microelectronics and computer technology[2].

New equipment and techniques were also developed that allowed the study of surface properties at atomic scale, as well as the identification of multiple phenomena that occur during the processes catalyzed by solids such as: adsorption, bond formation (chemisorption), fusion, diffusion, nucleation, growth, dispersion, desorption, among others, were evaluated at molecular scale, which generated a remarkable growth of surface chemistry that continues uninterrupted until the present[2].

According to the above, it is recognized the great efforts that have been made from the field of catalysis, with the ultimate goal of improving chemical processes looking for active, selective and stable materials, which allow high yields and thus low production costs. One such process that has advanced significantly over the years is selective catalytic oxidation, which will be discussed in the following section.

2. Selective catalytic oxidation

Based on the fact that catalysis is essential for the chemical industry since it participates in the production of about 90% of the chemical products that are commercialized, it is important to highlight that the selective oxidation reactions are considered as the most important group of reactions due to their role in the organic chemical industry and especially in the petrochemical industry[9]. Among the products obtained are acrolein, acrylic acid, acrylonitrile, methacrylic acid, maleic anhydride, phthalic anhy-

dride, ethylene oxide and propylene oxide[10].

In selective catalytic oxidation reactions, also called partial oxidation, the feedstocks are usually olefins, aromatic hydrocarbons, alkanes and, more recently, biomass derivatives. Accordingly, the use of olefins and aromatics is in an advanced state of development and the main current interest is focused on the functionalization of alkanes and biomass derivatives. The main advantages of the use of alkanes and biomass derivatives are based on their high availability and low price[9].

Heterogeneous catalytic processes aiming at selective oxidation must take into account at least seven fundamental principles, referred to in the literature as the seven pillars, which will influence the results of the catalytic process to be performed. These include: the importance of the oxygen of the catalyst lattice, strength of the metal-oxygen bond, the structure in which the active centers are incorporated, the oxidation-reduction properties of the catalyst, multifunctionality of the active sites, importance of having isolated centers, and the cooperation of crystalline phases[10]. These are discussed separately below.

2.1 Network oxygen

The importance of lattice oxygen in selective catalytic heterogeneous oxidation reactions was recognized in the 1950s. It was postulated that the lattice oxygen of a reducible metal oxide, O_2^- species, could serve as a versatile and more selective oxidizing agent than molecular oxygen, O_2[10]. In this aspect, a metal oxide lattice oxygen employed as a catalyst can remove hydrogens from the reactant to be oxidized generating a product with unsaturations and as a by-product water. In this process, the catalyst loses a surface oxygen atom from the lattice generating an anionic vacancy, while inside the crystal structure of the metal oxide there is a migration of oxygens to fill these vacancies. However, the catalyst will not be completely regenerated until the oxygen atoms used in the reaction are refilled and replaced by molecular oxygen from the feed. In this way, the catalyst will again be ready for another catalytic cycle. This series of steps is the basis of the reaction mechanism proposed by Mars van Krevelen[11–13].

2.2 Metal-oxygen bonding

The second pillar refers to the strength of the metal-oxygen (Me–O) bond. Thus, it is necessary to keep in mind that the bond strength must be intermediate under the reaction conditions. If the bond strength is too high, the reaction will not occur. On the contrary, if the bond strength is too weak, overoxidation will occur leading to the formation of undesired products[10]. The question that arises here is: what is strong and what is weak when referring to the Me–O bond strength. In this regard, Sabatier states that the interaction between a reactant and a catalyst to generate a product can't be too strong or too weak. It must be just what is necessary to maximize activity and selectivity towards a given product[14].

According to the above, it is necessary to be clear about the physical and chemical properties of the reagents to be used (and the reaction conditions), since depending on the type of substances in the feed, the choice of the catalytic material, i.e. the type of metal or metal oxide will be directed. Among the properties to keep in mind when facing a problem situation that requires the use of heterogeneous catalysts is to identify the electronegativity difference between the components of the catalyst, if it is a simple oxide the difference between the metal and the oxygen will indicate the type of bond. Ionic, covalent polar or non-polar and if it is a mixed oxide, it will be very interesting to recognize the values of electronegativity difference between the metals that compose it, as well as the relationship with the oxygen, which influences its catalytic properties.

2.3 Crystalline structure

The third pillar involves the need to have an appropriate crystal structure to accommodate the active centers. This involves the characteristics of the elements to be incorporated, the accommodation of the lattice oxygens, as well as the metal-oxygen bonds. Thus, the structure must: i) contain accessible lattice oxygens, ii) accommodate anionic vacancies without collapsing the structure, iii) allow rapid electron transfer and iv) allow diffusion of lattice oxygens[10].

2.4 Redox properties

In compliance with the third pillar, the fourth pillar, which refers to the reduction-oxidation properties, will be affected. In a catalytic oxidation process, oxygen is removed from the network favoring the solid to be reduced and the hydrocarbon to be oxidized. Subsequently, the removed oxygen must be replaced with oxygen from the feed, thus regenerating the catalyst for further reduction-oxidation cycles. In the most efficient catalysts, the center of molecular oxygen dissociation and the center where oxygen incorporation into the solid occurs is different from the catalytically active center. It is important to emphasize that the regeneration of the reduced metal oxide must be faster than the reduction of the catalytic system, otherwise, the reduction-oxidation cycle would be affected, the catalyst would be gradually reduced and therefore, the performance of the process decreases[10].

Put another way, in a catalytic reduction-oxidation process, initially the hydrocarbon is oxidized by the metal oxide, in this initial step the lattice oxygen (O_2^- species) of the metal oxide acts as the oxidizing agent and the metal oxide begins to reduce. In a separate step, the lattice oxygen vacancies, anionic vacancies of the reduced metal oxide, can be replaced by lattice oxygen from adjacent fully oxidized sites either surface or subsurface, which depends on the intrinsic nature of the metal oxide and the reaction conditions[10]. Concomitantly, the anionic vacancies migrate to the reoxidation site where molecular oxygen (O_2) is dissociated and incorporated into the solid, restoring the fully oxidized state of the metal oxide[10]. Finally, it should be kept in mind that a selective oxidation reaction involves one or more abstractions of hydrogen atoms from the hydrocarbon molecule, one or more insertions of oxygen atoms from the lattice, and several electron transfers[12].

2.5 Multifunctionality of active sites

The fifth pillar concerns the multifunctionality of the active sites. It is necessary to keep in mind that the active centers of a selective metal oxide are generally multifunctional and, in most cases, multimetallic, but, at least, they must be bifunctional and bimetallic[10]. Such active centers serve several functions in the catalytic cycle, such as: i) substrate chemisorption, ii) hydrogen abstraction, iii) oxygen

insertion, iv) substrate activation, and v) facilitate product desorption[10]. It is considered that only a small fraction of the catalyst surface is active, which can be caused by dislocations, crystal steps, corners, among others, which in turn influences the catalytic performance. On the other hand, different process variables such as temperature, pressure and contact times between feed reagents and catalyst are key factors in the optimization of a catalytic process[15].

2.6 Isolated site

The sixth pillar to consider in the design of selective oxidation catalysts is the so-called isolated site or center. The isolated site hypothesis in its original version states that the reactive surface lattice oxygens must be spatially isolated from each other, in defined groups, on the catalyst surface to achieve selectivity[10]. A clear example of the importance of isolated sites is presented in the partial oxidation of propylene to acrolein. For this process, it has been established that the presence of groups containing between two and five adjacent oxygen atoms is sufficient to obtain the desired partial oxidation product, acrolein. If the lattice groups contain more than five adjacent oxygens on the catalyst surface, consecutive reaction and the formation of total oxidation products is favored[10].

2.7 Phase cooperation

The last pillar, called phase cooperation, refers to catalytic systems in which the required catalytic functions can't be incorporated into a single host crystal structure. In this case, the best approach is to find two or more crystalline phases that separately contain all the necessary functions for a catalytic reaction, locating them in a proximate manner, and thus forming coherent layers or interfaces that can communicate with each other and thus generate phase cooperation. For phase cooperation to be effective, it is necessary that the two phases have contact with each other in order to facilitate their cooperation at the atomic scale[10].

Based on the above, the seven principles presented are an excellent guide for decision making when facing the challenge of performing selective catalytic oxidation processes. Now, another concern would arise and that is how to prepare the catalyst? For this, some aspects and methods of preparation of catalytic materials will be discussed below.

3. Catalyst preparation methods

Initially it is key to keep in mind that solid catalysts are highly sophisticated materials derived from chemicals obtained after various processes. The catalytic properties of heterogeneous catalysts are strongly affected by each step of the preparation as well as by the quality of the starting chemicals. The choice of a laboratory method for the preparation of a catalyst will depend on the desired physical and chemical characteristics of the final composition[16]. Likewise, it should be considered that the preparation of a catalyst with suitable physical and chemical characteristics that will lead to having the required properties for a practical application will always be a real challenge.

Indeed, many characteristics related to the active metal particles, including high dispersion, adequate composition when forming alloys, low mobility, as well as characteristics of the support, among which are: high and good pore distribution, adequate acidity or basicity and thermal stability, are necessary to obtain high activity and selectivity, chemical, thermal and mechanical stability, as well as fast mass and heat transfer.

In this way, the ideal catalyst for a specific process should fulfill everything in the same material. In addition, it is necessary to avoid creating a structure that is only a laboratory curiosity and that for technical or economic reasons cannot be manufactured on an industrial scale[17].

Despite the variety of possibilities for the preparation of catalysts, within the research group it has been considered that before the preparation it is necessary to answer six key questions (Figure 2), which will allow making the best decision regarding the preparation method, type of active species required, definition of the appropriate support, (if necessary) calcination temperature, calcination medium (oxidizing, reducing or inert) which will guarantee obtaining materials with known properties to be applied in a defined process. **Figure 2** shows what the group called guiding questions for the preparation of catalytic materials: active, selective and stable.

The scheme presented in **Figure 2** allows following a sequence of questions that every research-
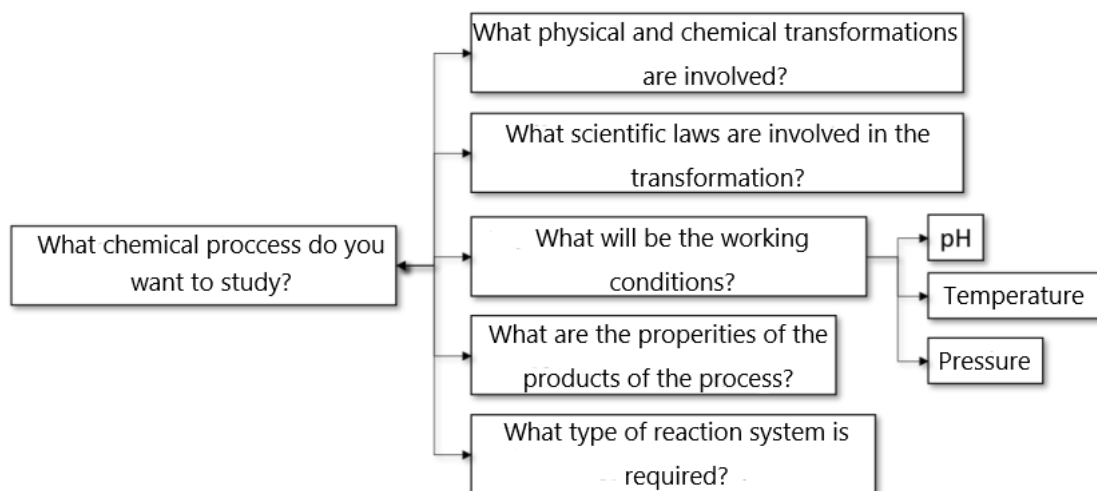
Figure 2. Guiding questions for the preparation of catalysts. Source: own elaboration.

er in the field of catalysis implicitly asks himself at the moment of facing a specific challenge. Firstly, it is necessary to be clear about the chemical process to be studied, to identify that it is thermodynamically feasible (to recognize the free energy change), otherwise, regardless of whether the most complete catalyst is prepared, the results will not be favorable. Secondly, it is necessary to be clear about the physical and chemical transformations that will occur, in this aspect it is important to identify the possible reaction mechanisms that will allow to propose what will occur during the process and how it will be affected by one or another operating variable. Subsequently and based on the second question, it is necessary to recognize the laws and theories of chemistry and physics that play a relevant role during the transformation, thus allowing the process to be classified into one of the two major types of chemical reactions that use catalysts, such as acid-base reactions or reduction-oxidation reactions.

The next question is directly related to the reaction itself, at what conditions will the process be carried out; the answer to this question, and in general to all of them, is interrelated with the others. Thus, in order to propose a specific temperature or a particular pH, the physical and chemical properties of the reactants, as well as those of the reaction products, must be known, avoiding at all costs secondary reactions that influence the performance of the catalytic process.

As mentioned above, the physical and chemical properties of the product of interest must be known,

which answers the fifth question. This is perhaps one of the issues that receives little attention despite being very important, since by knowing these properties it is possible to work under conditions that enhance the production of the product of interest, reducing secondary substances that can, among other things, poison the catalytic material.

Finally, although not directly related to the synthesis of catalytic materials, the types of reactor that can be used should be evaluated, recognizing the materials of manufacture and the possible role during the catalytic process, as reports can be found in which a particularly high activity is attributed to reactor walls made of glass, Teflon, copper or other metals.

As an example of the latter, there are reports of the effect of the reactor wall composition on the homogeneous oxidation of natural gas evaluated at a pressure of 30atm and a temperature between 350–400 °C, surprisingly, the methanol selectivity values were higher than 89.5% when the reactor used was made of glass, with a methane conversion of 10.0% at 50 atm pressure and 350 °C[18]. When Teflon was used, 8.0% methane conversion and 93.0% selectivity to methanol were obtained at 30atm and 361 °C. In addition, when similar conditions were used, but with other materials such as stainless steel, 94.5% methanol selectivity and 2.0% methane conversion were obtained; while when silver and copper were used, 20.0% and 22.0% methanol selectivity and 1.5% and 1.0% methane conversion were obtained, respectively[18]. According to the results, it can be

noted that the type of reactor material affects both methanol selectivity and methane conversion. This is due to the different adsorption heats of each molecule on each type of material, which will be the critical step of the reaction.

Based on the above, it is evident that, like any scientific activity, the preparation and evaluation of catalysts must follow a series of steps ordered on the basis of specific questions and that, depending on the decision taken, very favorable results will be obtained in the desired reaction.

Once the above questions have been answered, it is necessary to choose one of the three main methods for the preparation of catalytic materials, which are: i) mass and supported catalysts, ii) impregnated catalysts and iii) mixed agglomerated catalysts. The difference between supported and impregnated materials is mainly based on the fact that impregnated catalysts are obtained by wetting (impregnation) of a previously formed support with solutions of the active phase. Once the impregnation has been carried out, the other unitary operations of drying and calcination are performed. On the other hand, supported catalysts include the formation of the support and the active phase in the same process. On the other hand, mixed agglomerated catalysts refer to the mixture of active phases with a previously formed support or with a support precursor. In this type of materials, depending on the agitation (time and speed) and thermal processes (drying and calcination), agglomerates of the active phases will be generated[16]. Once the type of method to be used has been chosen, the unitary operations required for its synthesis are carried out. **Figure 3** shows the main unit operations usually applied in the preparation of catalysts[16].

Figure 3 shows the different unit operations used for the synthesis of catalytic materials, depending on the selected preparation method, a specific group of unit operations must be applied. In the same way, a direct relationship with the previously mentioned guiding questions is observed, since the choice of one or another unitary operation is affected by each of the answers to the guiding questions for the preparation of catalysts. For the particular case, the present paper will focus on two methods of preparation of catalytic materials; supported materi-
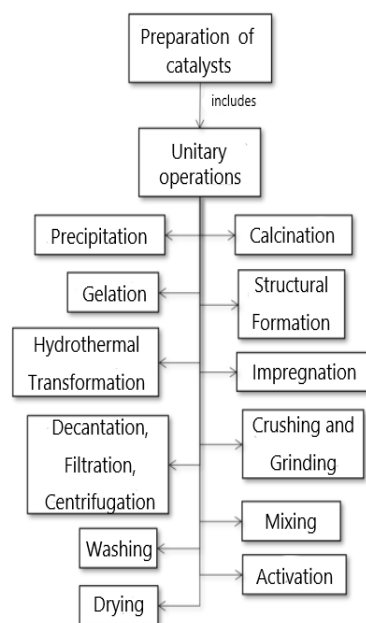

Figure 3. Unit operations for the preparation of catalysts. Source: own elaboration.

als prepared by the sol-gel method and impregnated materials.

3.1 Sol-gel synthesis

In the 1970s, a one-step sol-gel method was developed to synthesize metals in inorganic gels. This method consisted of dissolving a suitable metal precursor in an alcoholic solution containing the support precursor[19,20]. In order to maintain the high porosity of the wet gel, in the final dry material, supercritical drying was employed imagined as a way to remove the solvent from the gel without causing gel collapse and avoiding the destructive effects of capillary pressure[21].

In the following decades of the 1980s and 1990s, the use of functionalized ligands was proposed to anchor metal complexes to the silica gel in a one-step process[22]. In addition to obtaining uniform, nanometer-sized and homogeneously distributed metal particles in a silica matrix, several studies showed that the use of such functionalized ligands brought significant improvements in the morphology of the final material and a considerable simplification in fabrication, since the advantageous aerogel-like morphology can be obtained after a facile evaporative drying process allowing to avoid technical difficulties inherent to supercritical drying[23].

The use of mono or bimetallic catalysts, prepared in this way (and called cogelated catalysts), in some reactions of industrial interest demonstrated that the catalysts showed high activities and selectivities, excellent mass transfer, reasonable stability and easy regeneration, in comparison with many conventional catalysts[24].

Based on the above and bearing in mind that during the synthesis process by the sol-gel method different phases are evidenced, the following are the specific definitions related to the process.

Firstly, a sol is a colloidal suspension of solid particles in a liquid; on the other hand, a colloid is a suspension in which the dispersed phase is so small ($\approx$1 nm–1 μm) that gravitational forces are negligible and interactions are dominated by short-range effects, such as Van Der Waals attractions and electrostatic forces resulting from surface charges[17]. Finally, a gel can be interpreted as continuous solid and liquid phases of colloidal dimensions.

Thus, continuity (continuous phases) means that one could travel through the solid phase from one side of the sample to the other without having to enter the liquid; and conversely, one could make the same journey entirely within the liquid phase. Since both phases are colloidal in dimension, a line segment originating in one pore and running perpendicular to the nearest solid surface must reemerge in another pore less than 1 μm away. Similarly, a segment originating within the solid phase and running perpendicularly through the pore wall must re-enter the solid phase at a distance of 1 μm[17].

Thus, in principle the process in which a gel is formed from the particles of a sol, when attractive forces cause them to stick together as if forming a network, was designated sol-gel process. In other words, the sol-gel process must involve the formation of a gel by the aggregation of particles in a sol. However, the sol-gel process is often used in the literature to designate a process leading to a gel (or sometimes a suspension) from a homogeneous solution of soluble monomer precursors, whatever the underlying physical or chemical mechanisms. Indeed, other aggregation mechanisms have been suggested in several cases[17]. Based on the above, almost all metal oxides can be synthesized by the sol-gel process. Abundant literature can be found on

SiO_2, Al_2O_3, TiO_2, ZrO_2, as well as, the corresponding mixed oxides[25–27]. In fact, all porous oxide-type materials used in heterogeneous catalysis as support or precursors of catalytic supports, can be prepared by the solgel method[17]. Thus, the best starting material for the sol-gel preparation of metal oxides are the class of metal-organic compounds known as metal alkoxides[27]. All metals form alkoxides having the following general formula:

$$M(OR)_x \tag{1}$$

Where M is a metal (Si, Zr, Al, Ti...), R is an alkyl group (most frequently $-CH_3$, $-C_2H_5$, $-C_3H_7$, or $-C_4H_9$) and x is the valence state of the metal (for example: $x = 4$ with Si, Zr and Ti and $x = 3$ with Al).
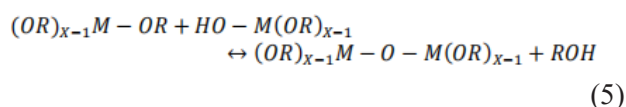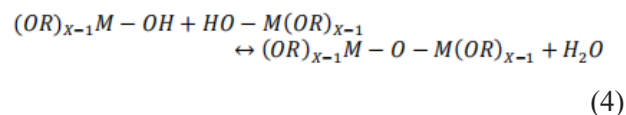
Metal alkoxides, which are soluble in ethanol, are popular precursors because they are rapidly hydrolyzed to the corresponding hydroxide, except the most studied among them, tetraethyl orthosilicate (silicon tetraethoxide, tetraethoxysilane) TEOS, $Si(OC_2H_5)_4$, which requires an acidic or basic catalyst for hydrolysis[17]. The reaction is called hydrolysis because a hydroxyl ion binds to the metal atom as presented in the following reaction:

$$M(OR)_X + H_2O \leftrightarrow HO - M(OR)_{X-1} + ROH \tag{2}$$
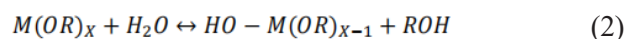
Where, again, R is an alkyl group and therefore ROH is an alcohol. Depending on the amount of water and catalyst present, hydrolysis can be completed until all OR groups are replaced by OH.

$$M(OR)_X + XH_2O \leftrightarrow M(OH)_X + XROH \tag{3}$$
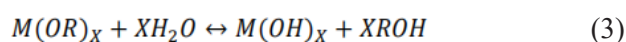
The other option during synthesis is to stop the reaction while the metal is only partially hydrolyzed $M(OR)x\text{-}n(OH)n$. Thus, two partially or fully hydrolyzed molecules can be joined in a condensation reaction as presented in the following equations.

$$(OR)_{X-1}M - OH + HO - M(OR)_{X-1}$$
$$\leftrightarrow (OR)_{X-1}M - O - M(OR)_{X-1} + H_2O \tag{4}$$

$$(OR)_{X-1}M - OR + HO - M(OR)_{X-1}$$
$$\leftrightarrow (OR)_{X-1}M - O - M(OR)_{X-1} + ROH \tag{5}$$

By definition, condensation releases a small molecule such as water or alcohol. This type of reaction can continue to build large and long chains of silicon, aluminum, titanium or zirconium by a polymerization process in alcoholic medium[17]. The
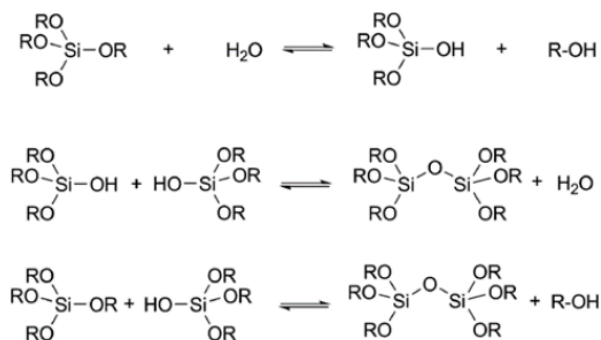
Figure 4. Chemistry associated with the formation of a sol–gel material[17].

basic chemistry associated with the formation of a typical sol-gel material is presented in **Figure 4**.

In the case of silicon alkoxides, hydrolysis occurs by a nucleophilic attack of the oxygen contained in water on the silicon atom and is more rapid and complete when an acidic (HCl, CH_3COOH, HF) or basic (NH_3, KOH, amines) catalyst is used. Under acidic conditions, an alkoxide group is likely to be protonated in a fast first step. The electron density is removed from silicon making it more electrophilic and thus more susceptible to attack by water[17].

Under basic conditions, water is most likely to dissociate to produce nucleophilic hydroxyl anions in a rapid first step. The hydroxyl anion then attacks the silicon atom; polymerization to form siloxane bonds occurs either by a condensation reaction producing water or producing alcohol[17].

Depending on the conditions, a wide spectrum of structures ranging from molecular networks to colloidal particles can result. Although condensation of silanol groups can proceed thermally without involving a catalyst, the use of acidic or basic catalysts similar to those used for hydrolysis is often useful and several mechanisms have been suggested to explain the role of the catalyst[25,28].

An important advantage of sol-gel chemistry over conventional techniques of oxide preparation is the possibility of preparing mixed oxides, such as SiO_2–ZrO_2, SiO_2–Al_2O_3, SiO_2–TiO_2, among others, with excellent control of the mixture due to its ability to adjust the relative reactivity of the precursor[27,29,30]. On the other hand, a possible disadvantage that may occur is attributed to the dispersion of the active phase of the catalytic material, in this aspect, it may occur that this is not available on the

surface of the catalyst, on the contrary, remaining immersed in the network of the oxide used as support thus influencing the catalytic activity of the material[31].

According to the above, there is evidence of extensive work done in sol-gel synthesis, as well as great contributions to understand each of the stages involved in the process. Thus, in the following section, another of the methods used for the preparation of catalysts will be addressed, which, although by itself would not be a method, but rather a unitary operation in the synthesis of supported catalysts, is interesting and widely used in the catalytic industry.

3.2 Impregnation synthesis

The impregnation synthesis of catalytic materials is included in the group of supported materials. Supported catalysts are usually employed because they combine relatively high dispersion (amount of active surface area) with a high degree of thermostability. Usually, the preparation of supported catalysts aligns all the unitary operations aiming to disperse the active agent on a support, which can be inert or catalytically active; the wetting of the support with a solution or a "slurry" of precursors of the active phase is the operation that characterizes this type of preparations[16].

Most solid catalysts contain two components: the active component and the support. The support provides the shape and size of the catalyst and also determines the external surface area, mechanical strength and porous structure of the catalyst. Generally the catalytically active component is applied finely divided on the external surface of the support, however, the desired distribution depends on the conditions under which the catalyst is to be employed[32].

To guarantee the accessibility of the reactants to the active sites, the particle size of the catalyst plays an important role, likewise, it is considered that the length of the catalyst pores affects the reaction rate much more than their diameter. Likewise, it is necessary to keep in mind that the particle size of the catalyst influences the pressure of the system, especially in the catalytic bed, which makes the small particle size of the catalyst a limiting factor, since it is usually sought that the catalytic systems work at

the lowest possible pressures[32].

Based on the above, a uniform distribution of the active component across the support is more advantageous and attractive, without having to reach particle sizes smaller than 5 mm. On the other hand, it should also be kept in mind that the reaction rate is determined by the rate of transport of the reactants to the active sites, in this case, the most favorable option is to deposit catalytically active particles on the external part of the materials, thus seeking to improve the adsorption and diffusion of the reactants and products on the catalyst[32].

In the same way, when consecutive catalytic reactions can lead to undesired products and thus decrease the selectivity, it is useful to place the active component on the external surface of the catalyst, this location of the active centers on the surface of the support is called eggshell. On the other hand, catalysts containing catalytically active sites on the surface (eggshell) can lose activity by attrition, therefore, it is much more favorable to deposit the active component in a subsurface layer leading to an egg white type distribution. In this way, when the reactants or reaction products may generate some components that poison the active sites, an egg white type distribution is very favorable, since these poisons will remain on the outer layer of catalytic material[32].

Based on the above it is important to keep in mind that industrially employed catalysts can be easily developed by the application of active components by impregnation. Commercially a wide range of supports are available in different shapes and sizes, of specific surface areas, different pore structures and perhaps most importantly with the required mechanical strength[32]. Thus, the question that arises is how is adsorption on the support surface? That is, what kind of interactions are generated? The answers to the above questions will allow to understand a little more about the supported catalytic materials prepared by impregnation; as well as, to recognize the unit operations that are followed during the synthesis.

To answer the questions, the adsorption of a precursor of an active component of an impregnating solution on the surface of a support can determine the final distribution of the active component

through the support after drying. The first reports on diffusion and adsorption in heterogeneous systems were made in the late 1960s, suggesting a relationship between the adsorption of the precursor and the distribution of the active component[33-35]. In the same way, the effect of the impregnation of adsorbed components on the distribution on the support was extensively studied, presenting useful mathematical expressions related to experimental results[36].

When the precursor of the active component is applied for adsorption on the surface of the support, the loading that can be achieved is small. Therefore, adsorption of active precursors is often employed with precious metals. The most effective application for the impregnation of catalytic supports is by adding a volume of impregnating solution equal to the pore volume of the support; this procedure is called incipient wet impregnation or dry impregnation[37]. During this process, impregnation occurs promptly since the solution-substrate interaction occurs rapidly. The dissolved active precursor is transported by convection into the pores of the support, an analogous procedure is immersion impregnation[37]. It is important to emphasize that diffusion through liquids is a slow process, a calculation based on the Fourier number indicates that to assume the same concentration in both the liquid phase and the pore system can easily take 10 hours[32].

According to the above, although the solution-support interaction can occur rapidly, one of the variables to guarantee a good distribution of the active phase will be the time that the system remains in impregnation. By extending the period of contact time between the support and the solution containing the active precursor, an increase in the layer thickness of the active component will be achieved[32]. Reviewing in the literature, so far it is not distinguished if in the process of impregnation of a support occurs an adsorption or a chemical interaction, different systems have been studied seeking to clearly identify what occurs, as well as, to verify the influence of the addition of inorganic acids such as nitric or organic acids such as oxalic acid or tartaric acid[38]. The results obtained suggest the formation of an egg white distribution when used in the preparation of platinum catalytic materi-

als supported on alumina, this is due to the fact that the acid reacts more easily with the surface of the alumina than with the platinum hexachloride, which leads to the immobilization of the metal in the inner part of the support[32].

Thus, it is observed, as previously mentioned, that the method of preparation of catalysts by impregnation allows obtaining catalytic materials with different distributions. Within these we distinguish the so-called egg yolk, if the active centers are in the interior of the support; egg white if the active component is located in a subsurface area and finally the so-called egg shell, in which the active sites are on the surface of the support. On the other hand, the variable that influences the distribution of the active components, morphology and properties of this type of catalytic materials is mainly the impregnation time, without leaving aside the physical and chemical properties of both the support and the active component to be used.

So far, the initial part of the preparation process of this type of materials has been mentioned; next, the following stages of drying and calcination will be discussed, which also influence the final properties of the catalyst to be obtained.

To begin with, it is necessary to keep in mind that after impregnation the distribution of a dissolved, non-adsorbed precursor on the surface of the support is uniform. The next step during preparation corresponds to drying; to understand whether drying can affect the distribution of the precursor, it is necessary to consider some aspects related to this operation using porous materials.

Moisture transport in porous materials can proceed by a movement of the liquid to the external surface due to a vapor flow (water or solvent used) through the pores of the material or by movement of the adsorbed liquid within the material layers. Based on this, the movement of the liquid within the support or within the material layers can affect the distribution of the active precursor[32].

The drying rate is a function of time. Initially the rate is constant, the vapor transport from the external surface of the catalyst together with the heat flow determines the drying rate. Likewise, within the porous material capillary forces are responsible for the rapid transport of liquid to the external surface. When the transport of liquid to the external surface of the catalytic material can no longer be maintained, areas of the surface begin to dry. At this point, the drying rate is determined by the evaporation of liquid from the external surface and also by the vapor flow through the empty pores in the dry areas[32].

Based on the above, capillary forces play a very important role during the drying process. Depending on the strength of the dipole-dipole or ion-dipole interactions generated between the solution containing the active site precursor and the walls of the porous material the liquid will flow to the external surface and then pass to the gaseous state. In this process of liquid transport, the active component migrates from the interior of the support to the exterior, which will influence the type of location it takes, usually external, but by modifying the synthesis conditions (mainly pH) it can be located in subsurface or internal locations of the support.

Subsequently, the materials are calcined. This can be carried out in an inert, reducing atmosphere or in air. It is typically carried out at temperatures higher than those at which the catalytic material will be used in the reaction and its regeneration. Several processes occur during calcination, among them: i) loss of chemically bound water (the water that presented Van der Waals interactions is removed in the drying process), ii) loss of carbon dioxide, iii) modification of the texture through sintering (small crystals or particles that increase in size), iv) modification of the structure, v) generation of the active phase and vi) stabilization of the mechanical properties of the material[16].

It should be noted that depending on the decalcination temperature, one or another phase of the active component will be obtained, in the same way, controlling the temperature can influence the morphology of the catalyst; by increasing the temperature, the micropores collapse and therefore the average pore size increases. Based on the above, calcination, like all unitary operations during the synthesis of materials, will influence the catalytic activity of the material. In this specific case, calcination will depend on two specific variables: temperature and time, which will lead to specific chemical species.

4. Synthesis of iron, molybdenum and vanadium materials by the sol-gel method for methanol oxidation: Case study

In this section, a series of ordered steps to be followed for the synthesis and evaluation of catalytic materials is presented. In this way and based on the guiding questions, the results obtained during the evaluation of iron, molybdenum and vanadium catalysts in the catalytic oxidation process of methane and methanol will be presented.

Thus, in response to the first guiding question that suggests recognizing the chemical process to be studied, it is identified that the process of interest is the selective catalytic oxidation of methane and methanol in order to obtain formaldehyde. Continuing with the second guiding question, the physical and chemical transformations involved are related to the abstraction of hydrogen in an initial step to form methyl radicals from methane and methoxy radicals from methanol, by means of their dissociative adsorption[39,40].

Subsequently, the third question suggests identifying the scientific laws involved. For this case and based on the intermediates formed, the different reaction products will be affected by the type of reaction that occurs. Thus, depending on the active centers, acid-base type reactions or oxidation-reduction reactions may occur[41]. Regarding the reaction conditions (fourth guiding question) for gas-phase reactions, the aspects that directly influence the activation of the reactants are temperature and pressure.

For the case of methane, activation is a difficult task and requires high temperatures (above 500 °C) since the molecule consists of one C atom surrounded by four H atoms (CH_4) and the sp3 hybridization of the carbon atomic orbitals makes the carbon-hydrogen bond very strong[42]. On the other hand, the activation of methanol (on the hydroxyl group) does not require such high temperatures, from 200 °C onwards products (dimethyl ether) attributed to reactions on acid centers of the catalyst can already be observed[43,44]. At higher temperatures the redox centers of the catalyst are activated and formaldehyde is obtained as an oxidation product of methanol[45,46].

The next question, related to the properties of the reaction products of the process is key, since it allows establishing variables such as the feed ratio of the reactants to the reactor and the contact time, in order to optimize the yield towards the products of interest. Thus, for the selective oxidation of methane, a methane/oxygen ratio must be found that guarantees that the redox cycle of the catalyst remains favored towards the reoxidation of the catalytic material and low contact times in order to avoid over-oxidation of the products leading to the formation of carbon oxides. Something similar happens in the methanol oxidation process, only that for this reaction the activation process occurs at lower temperatures.

Thus, the formaldehyde formed from methane oxidation must desorb quickly since the high temperature (between 500 °C and 700 °C) rapidly oxidizes it to carbon oxides[42]. To achieve this, the contact time between the reagents and the catalyst must be short maximizing the yield to formaldehyde. On the other hand, in the oxidation of methanol, reaction products are observed as early as 200 °C, the first of which is dimethyl ether, attributed to acid centers of the catalyst[43]. As the temperature increases, the redox cycle is activated and the formation of formaldehyde increases[47]. The formaldehyde formed, can follow two routes; i) continue oxidation to formic acid and this to carbon oxides or react with methanol from the feed to produce dimethoxymethane and water[41].

Finally, in response to the last question, the reaction system, specifically the catalytic reactor, must be inert and withstand temperatures up to 700 °C; thus, an excellent option is a quartz reactor.

Taking into account the answers to the previous questions, the most important aspects of the process to be evaluated were identified, then the question focuses on the synthesis method. For this particular case, the sol-gel method was selected for the following reasons: i) it allows having high surface areas, values above 500; ii) high dispersion of the active centers. In this aspect, it should be considered that although the sol-gel method allows high dispersion of the active species, it can also generate their occlusion; iii) versatility during the synthesis; iv) possibility of formation of bimetallic materials and v) good thermal stability[27,31].

Considering the above, the results of the cat-
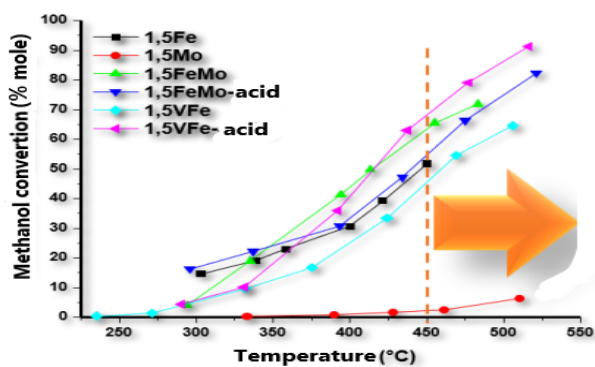
(a)
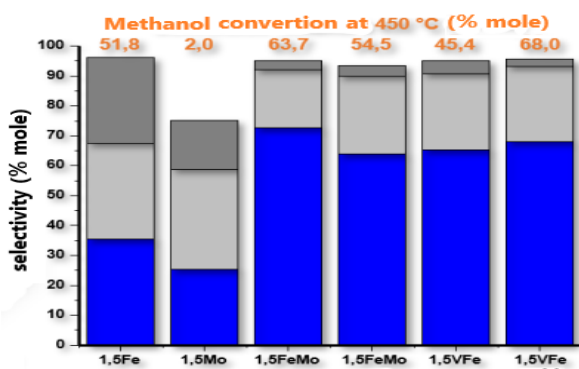
(b)

Figure 5. (a) Methanol conversion as a function of temperature and (b) Selectivity to formaldehyde (■), carbon monoxide (▨) and carbon dioxide (▨).

alytic activity of monometallic iron-molybdenum catalysts and bimetallic iron-molybdenum and iron-vanadium materials in the selective oxidation reaction of methane and methanol are presented below. All materials were prepared by sol-gel method and calcined at 750 °C, the detailed description of the synthesis process can be found in previous publications[31,48].

Catalytic experiments for the partial oxidation of methane and methanol were performed in a fixed-bed quartz tubular reactor at atmospheric pressure. The reaction temperature range was between 200 and 550 °C for methanol oxidation and between 500 and 750 °C for methane oxidation. 100mg of catalyst diluted with silicon carbide at a catalyst/silicon carbide mass ratio (1:0.5) was used. The feed consisted of a molar ratio of 6.0/13.0/81.0 (methanol/oxygen/nitrogen) and 32.0/4.3/63.7 (methane/oxygen/helium). Analysis of the reactants and products was carried out by gas chromatography using a thermal conductivity detector (TCD)[48].

In **Figure 5a**, the results of the catalytic activity of the materials in the selective oxidation of methanol are presented. The materials are named xMetal, where x refers to the metal loading expressed in mass percentage. In the same way, in order to identify the influence of the acid medium during the synthesis of the catalysts, the results of materials named xMetal-acid, which were synthesized using nitric acid, prior to gel formation, are presented.

The influence of temperature on the catalytic activity of the materials is observed, thus, as the temperature increases, the methanol conversion also increases (**Figure 5a**). In the same way, it is highlighted that bimetallic materials perform better than monometallic materials, which is related to one of the pillars mentioned, called phase cooperation. It can be observed that the most active material includes iron and vanadium synthesized in acid medium. The low pH during the synthesis influences the hydrolysis of the silicon precursor and thus the dispersion of the metallic iron and vanadium species. As previously mentioned, the materials were calcined at 750 °C in oxidizing atmosphere which allowed obtaining iron and vanadium oxides with the highest oxidation state. Thus, iron oxides are based on a network of O_2^- packed anions in which small Fe cations are located between octahedral and tetrahedral coordinated interstices[49].

Under reducing calcination conditions, wustite ($Fe_{1-x}O$) is formed, which is classified in the group of cubic crystallizing minerals, which contain Fe^{2+} in octahedral sites and is often non-stoichiometric with cation deficiency. Under oxidizing conditions hematite (α–Fe_2O_3) is formed which crystallizes according to the corundum structure (trigonal system, hexagonal scalenohedral class). Hematite contains Fe^{3+} in the octahedral sites. Between wustite (reducing conditions) and hematite (oxidizing conditions) is magnetite (Fe_3O_4) a spinel with Fe^{3+} in tetrahedral sites and a 50:50 mixture of Fe^{2+} and Fe^{3+} in octahedral sites[49].

As for vanadium and due to the calcination temperature, vanadium oxides with oxidation state +5 were obtained. V_2O_5 is an orange colored acid oxide in which vanadium ions are present in distorted octahedra. The structure of V_2O_5 often approximates to have zigzag ribbons of square pyramids of

45

V_2O_5[50].

In this way, iron and vanadium oxides generate a synergistic process that allows the activation of the methanol molecule. Thus, the mechanism of catalytic oxidation of methanol has been extensively investigated and suggests, in a first step, the formation of methoxy groups[45,46]. The formation of these intermediate groups is due to the dissociative adsorption of methanol on an acid-base dual site, formed by an accessible cation and an oxygen ion from the surface[39,40]. The subsequent transformation of the adsorbed methoxy groups is mainly due to two aspects: i) acidic strength of the active center on which they are adsorbed (influence towards dehydration reactions) and ii) the nature of the nearby active centers (will influence towards redox reactions). In other words, the desorption of the reaction products may be more favored on weak acid sites with respect to strong acid sites[46].

Based on the above, the order of the materials with respect to methanol catalytic activity at 450 °C was 1.5VFe-acid > 1.5FeMo > 1.5FeMo-acid > 1.5Fe > 1.5VFe > 1.5Mo (**Figure 5a**). Now, as for the selectivity at the same temperature, formaldehyde is observed as the major formation product except for monometallic molybdenum catalytic material.

Again, the bimetallic materials have a better performance in terms of selectivity towards formaldehyde with values close to 70mole%. The difference is small among the bimetallic catalysts with respect to the selectivity to formaldehyde, however, the best of them is 1.5FeMo. Punctually, one of the industrial methods for the production of formaldehyde from methanol employs iron molybdate catalytic materials[51]. Thus, studies of the surface of iron molybdate catalysts have led to the conclusion that it is extremely important that the surface is dominated by molybdenum species and that molybdenum tends to segregate on the surface, even if the loading levels are very low[52]. Thus, the catalyst performance depends critically on the molybdenum levels on the surface.

Finally, for methanol oxidation it can be concluded that bimetallic materials present better activity and selectivity with respect to monometallic catalysts. There is a synergistic effect between iron and molybdenum in both activity and selectivity towards formaldehyde, attributed to phase cooperation and multifunctionality of the active sites. On the other hand, no influence of the acidic medium in the synthesis on the selectivity to formaldehyde is observed.

Comparing the catalytic activity of the bimetallic catalysts, now in the selective oxidation of methane (**Figure 6a**), it is observed that as the temperature increases, the conversion of the hydrocarbon increases.

The most active material at 650 °C included iron and vanadium synthesized in acidic medium. Thus, the order of the materials in terms of methane activity at 650 °C was: 1.5VFe-acid > 1.5FeMo-acid > 1.5VFe > 1.5FeMo.

It's important to note that, for selective methane oxidation, the acidic medium during synthesis does markedly influence the catalytic activity (**Figure**
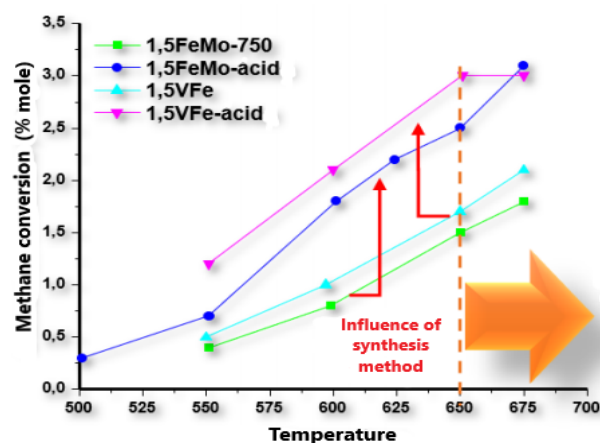
(a)
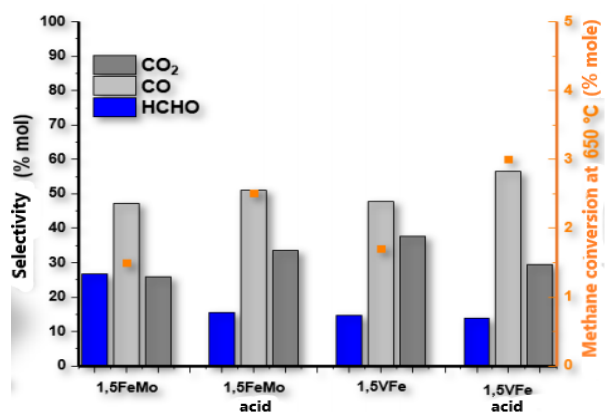
(b)

Figure 6. (a) Methane conversion as a function of temperature and (b) Selectivity to formaldehyde, carbon monoxide and carbon dioxide.

6a). The higher activity of the materials in which nitric acid was included during the synthesis, with respect to the materials that did not include acid can be attributed to the physical and chemical properties of the catalyst to the extent that: i) the acid medium influences the hydrolysis of the silica precursor, ii) the condensation reactions in acid medium lead to the formation of more linear structures, which favors the availability of the active centers of the catalyst and iii) the dispersion of the metallic species on the silica is greater[48].

Thus, the higher activity is related to the dispersion of metal oxide species, suggesting the presence of isolated sites (another pillar mentioned previously) that increase catalytic activity. Thus, the isolated site hypothesis states that the reactive surface lattice oxygens must be spatially isolated from each other in defined clusters on the catalyst surface to achieve higher selectivity[10]. Based on the above, the metal-oxygen bond oxygens are isolated favoring methane activation.

Regarding the selectivity to formaldehyde at 650 °C the material that presents the best behavior is 1.5FeMo (**Figure 6b**). This behavior is explained from the phase cooperation and the host structure in the catalytic material, in view that iron (Fe_2O_3) and molybdenum (MoO_3) species with the highest oxidation state (Lewis acid sites) influence the activation of the methane molecule and selective reactions to formaldehyde through the initial formation of the methyl peroxide radical. Another option for obtaining formaldehyde is based on the prior formation of methanol by the reaction between the adsorbed methyl group (CH_3^*-adsorbed) and oxygen (network or feed), the methanol is then oxidized to formaldehyde generating hydrogen as a by-product[53].

Figure 6b shows the formation of carbon oxides due to their greater stability at the reaction temperature with respect to formaldehyde. This behavior is largely due to the total oxidation of the intermediate reaction products. It is important to note that the production of carbon monoxide is higher than that of carbon dioxide, confirming the formation of intermediate products such as methanol and formaldehyde itself, which continue the oxidation process to carbon monoxide and carbon dioxide.

On the other hand, it has been established for methane oxidation the different types of products and the yield as a function of the reaction temperature. It is highlighted that in the temperature range between 400 °C and 600 °C the formation of oxygenated products occurs with yields lower than 5% in mol; between 600 °C and 900 °C the oxidative coupling of methane is favored for the formation of ethane and ethene. Likewise, the obtaining of synthesis gas ($CO + H_2$ mixture) is observed in temperature ranges between 500 °C and 1200 °C[54]. Finally, at temperatures above 1200 °C, combustion is favored, producing carbon dioxide and water ($CO_2 + H_2O$)[54]. In this order of ideas, the values obtained for formaldehyde from the direct oxidation of methane are in the reported range.

5. Conclusions

Over the years, great efforts have been made in the field of catalysis, with the ultimate goal of improving chemical processes by searching for active, selective and stable materials that allow high yields and thus low production costs.

Heterogeneous catalytic processes aiming at selective oxidation must take into account at least seven fundamental principles that will influence the results of the catalytic activity to be performed.

The application of the guiding questions for the synthesis of catalytic materials will allow to approach the diverse and complex processes of selective oxidation in a systematic way and with an overview of the possible results, leaving in the background the trial and error that, so far, although it has provided important results, should not be the way to work in science.

Based on the guiding questions, it is identified that for the selective oxidation of methane and methanol it is necessary to synthesize materials with active centers capable of activating methane or methanol molecules without enhancing sequential reactions that lead to obtaining undesired products such as carbon oxides.

The best activity in the catalytic oxidation of methanol is observed when bimetallic catalysts were used, which is related to the phase cooperation between the metallic species. By including iron and molybdenum, layers or interfaces are formed that can communicate with each other and therefore

generate a cooperation that influences the activation of the methanol molecule.

In the catalytic oxidation of methane the activation of the C–H bond is the first crucial step in the formation of partial oxidation products or combustion products; once the first C–H bond is broken, the resulting CH_3 fragment is highly reactive and depending on the availability and types of active centers, partial oxidation reactions towards methanol and formaldehyde or combustion reactions producing CO_2 and H_2O take place.

Acknowledgements

References

1. Burtron D. Development of the science of catalysis. In: Ertl G, Knözinger H, Schüth F, *et al.* (editors). Handbook of heterogeneous catalysis. Weinheim: Wiley VCH Verlag GmbH; 2008. p. 17–38. doi: 10.1002/9783527610044. hetcat0002.

2. Somorjai G. Surfaces—An introduction. In: Introduction to surface chemistry and catalysis. Wiley; 1994. p. 1–36.

3. Nieken U, Watzenberger O. Periodic operation of the deacon process. Chemical Engineering Science 1999; 54(13–14): 2619–2626. doi: 10.1016/S0009–2509(98)00490-4

4. Gómez–García MÁ, Dobrosz–Gómez I, Gil-Pavas E, *et al.* Simulation of an industrial adiabatic multi–bed catalytic reactor for sulfur dioxide oxidation using the Maxwell–Stefan model. Chemical Engineering Journal 2015; 282: 101–107. doi: 10.1016/J.CEJ.2015.02.013

5. Hu YH, Ruckenstein E. Catalytic conversion of methane to synthesis gas by partial oxidation and CO_2 reforming. Advances in Catalysis 2004; 48: 297–345. doi: 10.1016/S0360-0564(04)48004-3

6. Sadykov V. Oxide catalysts for ammonia oxidation in nitric acid production: Properties and perspectives. Applied Catalysis A: General 2000; 204(1): 59–87. doi: 10.1016/S0926-860X(00)00506-8

7. Lattes A. From catalytic hydrogenation to the chemical theory of catalysis: Paul Sabatier, genius chemist, apostle of decentralization (in Spanish). Comptes Rendus de l'Académie des Sciences-Series IIC-Chemistry 2000; 3(9): 705–709. doi: 10.1016/S1387-1609(00)01184-1

8. Zimdahl R. Nitrogen. In: Six chemicals that changed agriculture. Colorado, CO, USA: Elsevier; 2015. p. 55–72.

9. López Nieto JM, Solsona B. Gas phase heterogeneous partial oxidation reactions. In: Jacques C, Védrine JC (editors). Metal oxides in heterogeneous catalysis. Amsterdam, Netherlands: Elsevier; 2018. p. 211–286.

10. Grasselli RK. Fundamental principles of selective heterogeneous oxidation catalysis. Topics in Catalysis 2002; 21(1–3): 79–88. doi: 10.1023/A:1020556131984.

11. Mars P, Van Krevelen DW. Oxidations carried out by means of vanadium oxide catalysts. Chemical Engineering Science 1954; 3: 41–59. doi: 10.1016/S0009-2509(54)80005-4.

12. Reddy BM. Redox properties of metal oxides. In: Metal oxides: Chemistry and applications. USA, Boca Raton: CRC Press Taylor & Francis; 2005. p. 215–246.

13. Hodnett BK. Heterogeneous catalytic oxidation. London, United Kingdom: John Wiley & Sons Inc.; 2000.

14. Medford AJ. From the Sabatier principle to a predictive theory of transition-metal heterogeneous catalysis. Journal of Catalysis. 2015; 328: 36–42. doi: 10.1016/j.jcat.2014.12.033.

15. Andrew SPS. Theory and practice of the formulation of heterogeneous catalysts. Chemical Engineering Science 1981; 36(9): 1431–1445. doi: 10.1016/0009-2509(81)85106-8.

16. Perego C, Villa P. Catalyst preparation methods. Catalysis Today 1997; 34: 281–305. doi: 10.1016/S0920-5861(96)00055-7.

17. Heinrichs B, Lambert S, Job N, *et al.* Sol-Gel synthesis of supported metals. In: Regalbuto J (editors). Catalyst Preparation Science and Engineering. Boca Raton, USA: CRC Press, Taylor& Francis Group; 2007. p. 163–208.

18. Hunter NR, Gesser HD, Morton LA, *et al.* Methanol formation at high pressure by the catalyzed oxidation of natural gas and by the sensitized oxidation of methane. Applied Catalysis 1990; 57: 45–54. doi: 10.1016/S0166-9834(00)80722-8.

19. Teichner S, Gardes G. Methods for the manufacture of composite catalysts containing a composition of a transition metal on a support. US3963646A.

20. Astier M. Preparation and catalytic properties of supported metal or metal-oxide on inorganic oxide aerogels. Studies in Surface Science and Catalysis 1976; 1(3): 315–330. doi: 10.1016/S0167-2991(08)63961-0.

21. Kistler S. Coherent expanded-aerogels. Journal of Physical Chemistry 1931; 36(1): 52–64. doi: 10.1021/j150331a003.

22. Kaiser A, Gorsmann C, Schubert C. Influence of the metal complexation on size and composition of Cu/Ni nano-particles prepared by sol-gel processing. Journal of Sol-Gel Science and Technology 1997; 8(1–3): 795–799. doi: 10.1007/BF02436940.

23. Heinrichs B, Noville F, Pirard JP. Pd/SiO$_2$-Co-gelled aerogel catalysts and impregnated aerogel and xerogel catalysts: Synthesis and characterization. Journal of Catalysis 1997; 170(2): 366–376. doi: 10.1006/jcat.1997.1772.

24. Lambert S, Cellier C, Grange P, *et al.* Synthesis of Pd/SiO$_2$, Ag/SiO$_2$, and Cu/SiO₂ cogelled xerogel catalysts: Study of metal dispersion and catalytic activity. Journal of Catalysis 2004; 221(2): 335–346. doi: 10.1016/j.jcat.2003.07.014.

25. Brinker CJ, Scherer G. Sol-gel science the physics and chemistry of sol-gel processing. San Diego, USA: Academy Press. Inc; 1990.

26. Ward D, Ko E. Preparing catalytic materials by the sol-gel method. Industrial & Engineering Chemistry Research 1995; 34(2): 421–433. doi: 10.1021/ie00041a001.

27. Schneider M, Baiker A. Titania-based aerogels. Catalysis Today 1997; 35: 339–365. doi: 10.1016/S0920-5861(96)00164-2.

28. Brinker CJ. Hydrolysis and condensation of silicates: Effects on structure. Journal of Non-Crystalline Solids 1988; 100(1–3): 31–50. doi: 10.1016/0022-3093(88)90005-1.

29. Lecloux AJ, Pirard JP. High-temperature catalysts through sol-gel synthesis. Journal of Non-Crystalline Solids 1998; 225: 146–152. doi: 10.1016/S0022-3093(98)00034-9.

30. Dutoit D, Scheneider M, Baiker A. Titania-Silica mixed oxides: I. influence of sol-gel and drying conditions on structural properties. Journal of Catalysis 1995; 153(1): 165–176. doi: 10.1006/jcat.1995.1118.

31. Cortés Ortiz WG, Baena Novoa A, Guerrero Fajardo CA. Structuring-agent role in physical and chemical properties of Mo/SiO$_2$ catalysts by sol–gel method. Journal of Sol-Gel Science and Technology 2019; 89(2): 416–425. doi: 10.1007/s10971-018-4892-7.

32. Geus J. Production of supported catalysts by impregnation and (viscous) drying. Catalyst Preparation Science and Engineering 2007: 341–370. doi: 10.1201/9781420006506.

33. Weisz PB. Sorption-diffusion in heterogeneous systems part 1. Transactions of the Faraday Society 1967; 63: 1801–1806. doi: 10.1016/j.leukres.2014.12.005.

34. Weisz PB. Sorption-diffusion in heterogeneous systems part 2. Transactions of the Faraday Society 1967; 63: 1807–1814. doi: 10.1039/TF9676301807.

35. Weisz PB. Sorption-diffusion in heterogeneous systems part 3. Transactions of the Faraday Society 1967; 63: 1815–1823. doi: 10.1039/TF9676301815.

36. Lee S, Aris R. The distribution of active ingredients in supported catalysts prepared by impregnation. Catalysis Reviews - Science and Engineering 1985; 27(2): 207–340. doi: 10.1080/01614948508064737.

37. Gaigneaux E, Vos DE, Jacobs P, *et al.* Scientific bases for the preparation of heterogeneous catalysts. Belgica: Elsevier Science; 2002.

38. Richardson J, Harker J. Crystallisation. In:

Coulson and Richardson's chemical engineering. 5th ed. Reino Unido: Elsevier Science; 2002. p. 827–897.

39. Ai M. Catalytic activity for the oxidation of methanol and the acid-base properties of metal oxides. Journal of Catalysis 1978; 54(3): 426–435. doi: 10.1016/0021-9517(78)90090-8.

40. Pernicone N, Lazzerin F, Liberti G, *et al.* On the mechanism of CH_3OH oxidation to CH_2O over MoO_3–$Fe_2(MoO_4)_3$ catalyst. Journal of Catalysis 1969; 14(4): 293–302. doi: 10.1016/0021-9517(69)90319-4.

41. Delgado D. Influence of phase composition of bulk tungsten vanadium oxides on the aerobic transformation of methanol and glycerol. European Journal of Inorganic Chemistry 2018; 10: 1204–1211. doi: 10.1002/ejic.201800059.

42. Navarro RM, Peña MA, Fierro JLG. Methane oxidation on metal oxides. In: Fierro JLG (editors). Metal oxides chemistry and applications. New York, USA: Taylor & Francis Group; 2006. p. 463–482.

43. Tatibouët JM. Methanol oxidation as a catalytic surface probe. Applied Catalysis A: General 1997; 148(2): 213–252. doi: 10.1016/S0926-860X(96)00236-0.

44. Hu H, Wachs IE. Catalytic properties of supported molybdenum oxide catalysts: In situ Raman and methanol oxidation studies. Journal of Physical Chemistry 1995; 99(27): 10911–10922. doi: 10.1021/j100027a035.

45. Liu YC, Griffin GL, Chan SS, *et al.* Photo–oxidation of methanol using MoO_3TiO_2: Catalyst structure and reaction selectivity. Journal of Catalysis 1985; 94(1): 108–119. doi: 10.1016/0021-9517(85)90086-7.

46. Chung JS, Miranda R, Bennett CO. Mechanism of partial oxidation of methanol over MoO_3. Journal of Catalysis 1988; 114(2): 398–410.

doi: 10.1016/0021-9517(88)90043-7.

47. Wachs IE, Deo G, Juskelis MV, *et al.* Methanol oxidation over supported vanadium oxide catalysts: New fundamental insights about oxidation reactions over metal oxide catalysts from transient and steady state kinetics. Studies in Surface Science and Catalysis 1997; 109: 305–314. doi: 10.1016/S0167-2991(97)80417-X.

48. Cortés Ortiz WG. Partial oxidation of methane and methanol on $FeOx^-$, $MoOx^-$ and $FeMoOx$–SiO_2 catalysts prepared by sol-gel method: A comparative study. Molecular Catalysis 2020; 491: 110982. doi: 10.1016/j.mcat.2020.110982.

49. Parkinson GS. Iron oxide surfaces. Surface Science Reports 2016; 71(1): 272–365. doi: 10.1016/j.surfrep.2016.02.001.

50. Weckhuysen BM, Keller DE. Chemistry, spectroscopy and the role of supported vanadium oxides in heterogeneous catalysis. Catalysis Today 2003; 78: 25–46. doi: 10.1016/S0920-5861(02)00323-1.

51. Kong L. Green and rapid synthesis of iron molybdate catalyst by mechanochemistry and their catalytic performance for the oxidation of methanol to formaldehyde. Chemical Engineering Journal 2019; 364: 390–400. doi. 10.1016/J.CEJ.2019.01.164.

52. Yeo BR. The surface of iron molybdate catalysts used for the selective oxidation of methanol. Surface Science 2016; 648: 163–169. doi: 10.1016/j.susc.2015.11.010.

53. Brown M, Parkyns N. Progress in the partial oxidation of methane to methanol and formaldehyde. Catalysis Today 1991; 8: 305–335. doi: 10.1016/0920-5861(91)80056-F.

54. Arutyunov V. Direct methane to methanol: Historical and kinetics aspects. In: Methanol: Science and engineering. Reino Unido: Elsevier; 2018. p. 129–172.