

## Review Article

# Zeolites: Promised Materials for the Sustainable Production of Hydrogen

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Zeolites have been shown to be useful catalysts in a large variety of reactions, from acid to base and redox catalysis. The particular properties of these materials (high surface area, uniform porosity, interconnected pore/channel system, accessible pore volume, high adsorption capacity, ion-exchange ability, and shape/size selectivity) provide crucial features as effective catalysts and catalyst supports. Currently, new applications are being developed from the considerable existing knowledge about these important and remarkable materials. Among them, those applications related to the development of processes with less impact on the environment (green processes) and with the production of alternative and cleaner energies are of paramount importance. Hydrogen is believed to be critical for the energy and environmental sustainability. It is a clean energy carrier which can be used for transportation and stationary power generation. In the production of hydrogen, the development of new catalysts is one of the most important and effective ways to address the problems related to the sustainable production of hydrogen. This paper explores the possibility to use zeolites as catalysts or supports of catalysts to produce hydrogen from renewable resources. Specifically, two approaches have been considered: reforming of biomass-derived compounds (reforming of bioethanol) and water splitting using solar energy. This paper examines the role of zeolites in the preparation of highly active and selective ethanol steam reforming catalysts and their main properties to be used as efficient water splitting photocatalysts.

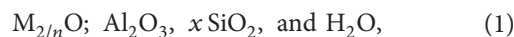
## 1. Zeolites: Composition, Structure, Properties, and Applications

Zeolites were first described in 1756 by the Swedish mineralogist Cronstedt [1]. However, the systematic research efforts on synthetic zeolites were initiated by Barrer in the late 1930s [2, 3]. Barret offered the first classification of zeolites based on molecular size [4]. Inspired by the work of Barrer, researchers at Union Carbide developed synthesis procedures for preparation of the first synthetic zeolites (i.e., zeolites A, X, and Y) that would find industrial applications [5–7].

Initially zeolites were applied as materials for drying and separation substances. Later, with the development of the concept of acid zeolite catalyst, in 1959, they were used as catalysts in the isomerization of hydrocarbons [8]. Previously, Houdry et al. [9] used them in catalytic cracking

of hydrocarbons. Since the development of the first concepts, to date many business processes based on zeolites as catalysts have been implemented. The specialization and knowledge of zeolites have grown so much that the International Zeolite Association (IZA) was founded [10] and currently there are numerous specialized scientific publications that collect not only the current knowledge about these materials but also their outstanding commercial application.

*1.1. Composition and Structure.* Zeolites are microporous crystalline aluminosilicates whose chemical composition is defined by the following general formula [11]:



where M is a metal cation of valence  $n$ ,  $x > 2$  and  $y > 1$ .

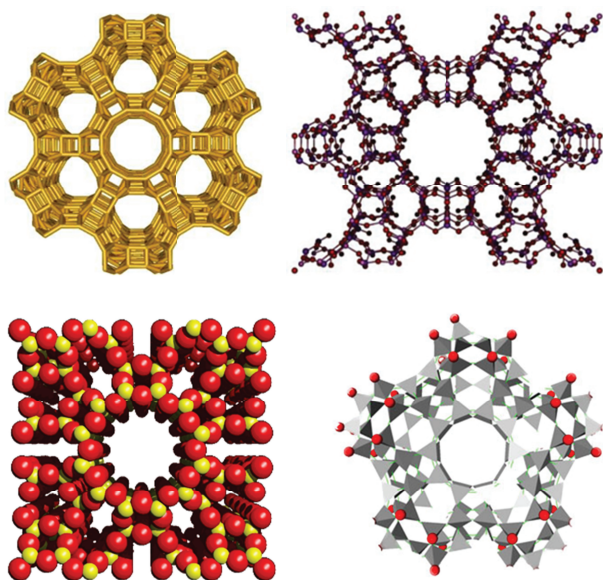


FIGURE 1: Representation of the projection of the framework structure of zeolites; (a) T-site connectivity only, (b) ball and stick, (c) space filling, and (d) (Si, Al)  $O_4$  tetrahedra.

Zeolite framework is formed from corner sharing  $[SiO_4]^{4-}$  and  $[AlO_4]^{5-}$  tetrahedra which define the cavities and channels, in which the cations can be found coordinating to the framework oxygens and/or water molecules. Figure 1 shows the different representations, typical of those used in the literature, of the framework of one zeolite.

The ways to combine each tetrahedron are extremely wide. The structure of the zeolite is defined by its corner sharing tetrahedra of  $[SiO_4]^{4-}$  and  $[AlO_4]^{5-}$ , and these are called secondary building units (SBUs) [12] (see Figure 2).

The utility of these constructions is that the angles and distances of zeolites are contained in these SBUs, so the structural characterization of one zeolite could be carried out by examining the SBUs that it contains. There are 16 different SBUs, and the structure of each zeolite can be described using one or more of these SBUs.

In zeolites, the organization of  $TO_4$  tetrahedra can result in the formation of rings with different numbers of T atoms (Si, Al). The most common rings are 4-T, 6-T, 8-T, 10-T, and 12-T; however, zeolitic structures containing 14, 18, and 30 member rings have been also synthesized [13–20]. The size of the micropores of the zeolite varies depending on the number of members in the rings, between 4 and 12 Å. On rings, T-O-T angles vary mostly in the range  $130^\circ$ – $180^\circ$ . The flexibility of this angle is one of the most important factors determining the huge variety of existing zeolites.

**1.2. Properties.** Zeolites may act as molecular sieves, thus one of their main physical properties is the porosity. The microporous properties of zeolites make them present an extremely large internal surface area in relation to their external surface. Micropores are open to the outside allowing

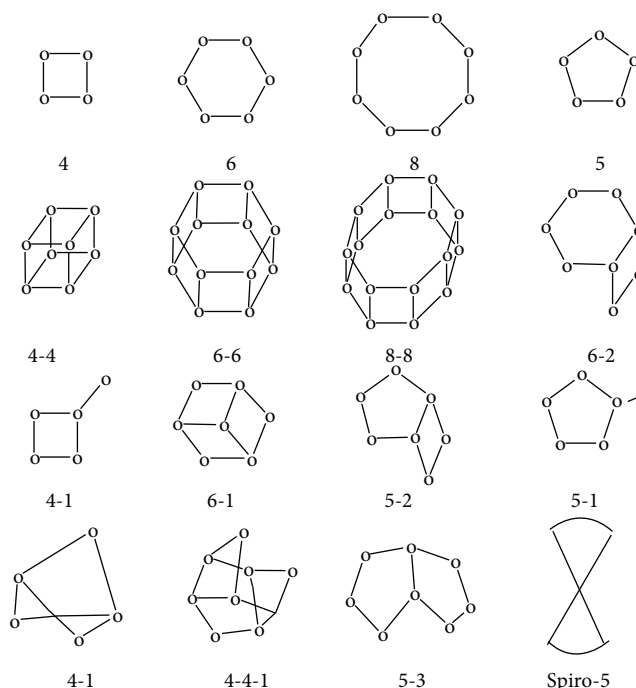


FIGURE 2: Basic secondary units (BSUs) to define the structure of zeolites.

the transference of matter between the intracrystalline space and the surrounding environment.

Tridimensional networks of well-defined micropores can act as reaction channels whose activity and selectivity will be enhanced by introducing active sites. The presence of strong electric fields and controllable adsorption properties within the pores will produce a unique type of catalyst, which by itself can be considered as a catalytic microreactor.

The size of the pores and channels of zeolites ranges between 4 and 12 Å [21] and the channel system may be mono-, bi-, or three-directional. Table 1 shows the classification of zeolites based on the number of tetrahedrals that form the pores and give access to the intracrystalline space [22–25].

Summarizing, the main properties of zeolites are as follows:

- (i) high surface area,
- (ii) molecular dimensions of the pores,
- (iii) high adsorption capacity,
- (iv) partitioning of reactant/products,
- (v) possibility of modulating the electronic properties of the active sites,
- (vi) possibility for preactivating the molecules when in the pores by strong electric fields and molecular confinement.

**1.3. Applications.** Zeolites have a variety of industrial applications, especially as ion exchangers, adsorbents, and chemicals catalysts.

TABLE 1: Zeolite classification according to the pore size.

| Zeolite classification | Number of the oxygen atoms in the opening ring | Pore diameter (Å) | Example of zeolites                             |
|------------------------|--|-------------------|---|
| Small pore             | 8  | $3 < \theta < 5$  | Erionite, A, ITQ-3                              |
| Medium pore            | 10   | $5 < \theta < 6$  | ZSM-5, ZSM-11, ITQ-1                            |
| Large pore             | 12   | $6 < \theta < 9$  | X, Y, Beta, $\Omega$ , mordenite, ITQ-7, ITQ-21 |
| Extralarge pore        | 18   | $9 < \theta$      | MCM-9, VIP-5, ITQ-33                            |

Zeolites as adsorbents are used in processes of separation and purification of gases and liquids due to their ability to adsorb selectively molecules of different size or polarity. They are used in the separation of oxygen from air to remove the water and CO<sub>2</sub> from gas streams, separation of the linear branched hydrocarbons, and in the elimination of volatile organic compounds from automobile and industrial exhausted gasses [6, 26–35].

The most important application of zeolites as ion exchangers is the extraction of cations Ca<sup>2+</sup> and Mg<sup>2+</sup> of domestic and industrial waste water [34]. Sodium zeolite A is used in the formulation of detergents to replace polyphosphates and others highly polluting compounds. They are also used in extraction of NH<sub>4</sub><sup>+</sup> from waste water [33] and they have been also used extensively in nuclear waste cleanup (i.e., after the Three Mile Island and Chernobyl nuclear accidents).

Regarding to the use of zeolites as catalysts or catalyst supports, their use is very common in industrial processes of refining, petrochemicals, and fine chemicals. The replacement of conventional catalysts in many processes by zeolites is due to improvements that these materials introduce in the catalytic activity and selectivity.

For the commercial application of zeolites as catalysts together with a good texture-related properties (area, porosity) and a high number of active sites, zeolites must have good thermal stability, since a large part of catalytic processes are conducted at elevated temperatures. Moreover, it is very frequent that the catalysts used in reactions involving hydrocarbons are deactivated by coke deposits formed during the reaction. Thus, they need to be regenerated. The regeneration is conducted by burning the coke at temperatures above 500°C [36–38]. The thermal stability of a zeolite depends on the aluminum content. Al–O bonds are weaker than the Si–O one (Al–O distance is larger than Si–O), therefore the stability depends on aluminum content [39]. Thus, in order to carry out a sufficient number of reaction-regeneration cycles, zeolites with high thermal stability are required, that is, zeolites with Si/Al  $\geq$  5 [40]. These compositions in some cases can be achieved by direct synthesis (i.e., Beta and ZSM-5 zeolites), and in other cases in which it is not possible by direct synthesis it can be achieved by chemical or hydrothermal treatments of synthesized zeolite (i.e., zeolite Y) [41–43].

The substitution of Si by Al together with the corresponding compensation cations has another additional effect on the properties of the zeolites, hydrophilicity/hydrophobicity [30]. The hydrophilic-hydrophobic character has focused on applications of great practical interest. Thus, the hydrophobic zeolites are able to carry out reactions that require absence of

water, without the necessity to remove it from the medium, because the reaction takes place almost entirely inside the zeolite, which being hydrophobic will be water free [44]. For example, silicalite (ZSM-5 structure with Si/Al > 1000) [45] has very low amount of aluminum, in such a way that its crystals ( $d = 1.7$  g/cc) can float in the water [46]. By contrast, zeolite X, with high Al content, has a pronounced hydrophilic character, which permits separating a mixture of oxygen and nitrogen [47] due to the higher quadrupole moment of the nitrogen.

The negative charge associated with the tetracoordinated aluminum is compensated by cations that can be easily exchanged for other cations by ion exchange processes [48]. The exchange of cations is favored by the fact that the cations are not covalently bonded to the structure; they are placed inside the zeolite cavities compensating the defect of charge. The size and charge of the exchanged cations are important variables in the zeolite reactivity. Cations of large size will leave small free spaces in the cavities difficulting the entrance of reactants. This effect is very useful in those reactions where the selective control is based on geometric effects [49, 50]. Among the exchangeable cations that can be introduced into the zeolite, the proton occupies a special place. The protons are bonded to an oxygen bridge between one silicon and one aluminum [51, 52]. Due to the presence of channels and cavities of different sizes within the same structure, as well as the existence of nonequivalent positions, there is a paramount importance to predict minimum energy positions, and therefore the location of the exchangeable cations [53], and especially the localization of the protons that will determine the activity in acid catalyzed reactions.

New scientific applications were considered in the 1980s and 1990s for exploring zeolites as advanced solid state materials. Ozin et al. [54] considered that zeolites could represent a “new frontier” of solid state chemistry with interesting properties (nanometer dimension window, channel and cavity architecture) for innovative research and development. Among others they consider applications such as: molecular electronics, quantum dots/chains, zeolite electrodes, batteries, nonlinear optical materials, and chemical sensors. Other applications recently reported are related to the use of zeolites as low  $k$  dielectric materials for microprocessors [55].

Future trends in zeolites include (i) discovery of new zeolitic materials, (ii) continuous use in petroleum refining (high octane and reformulated gasoline, processing of heavy crudes, production of diesel, and so forth), (iii) use in the preparation of organic chemical intermediates or end-products, and (iv) use in sustainable processes to produce biocompounds and green fuels.

Considering the future trends, it is quite evident that zeolites are of great interest for the industry, especially due to the potential they present in fields that are of paramount importance for the future of our industrialized society, such as raw material transformation, environmental pollution control, and energy production and storage.

This paper focuses on the application of zeolites for energy production. Specifically, the use of zeolites in the production of hydrogen from renewable energy sources is collected: biomass (ethanol reforming) and solar (water splitting).

## 2. Zeolites for Hydrogen Production

The future energy economy will have an important role for hydrogen ( $H_2$ ) as a clean and  $CO_2$ -neutral energy source [56]. Thus, it has been projected as one of the few long-term sustainable clean energy carriers. Currently the synthesis of molecular hydrogen occurs mostly by nonsustainable methods such as steam reforming (SR) of natural gas or gasification of coal, which is associated with the emission of large quantities of greenhouse gases (GHG), especially carbon dioxide ( $CO_2$ ) [57–60]. Thus, to realize the full benefits of a hydrogen economy, increased energy security, diverse energy supply, and reduced air pollution, hydrogen must be produced cleanly and efficiently from available renewable resources. Hydrogen can be produced from renewable resources (e.g., biomass and water) using renewable energy sources (e.g., sunlight, wind, wave, or hydropower) [61–66].

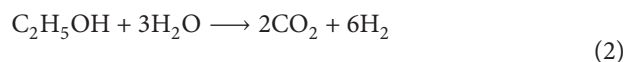
Two important approaches are considered in this paper to produce hydrogen from renewable sources and reduce the  $CO_2$  emissions. One approach is to apply reforming methods to biomass-derived compounds, for example, bioethanol. Because biomass consumes atmospheric carbon dioxide ( $CO_2$ ) during growth, it can have a small net  $CO_2$  impact compared with fossil fuels. The second approach considers the production of hydrogen by water splitting using solar energy. Hydrogen production by water splitting corresponds to those methods including outside the C-cycle. This process is very attractive due to the potential to use the solar energy which is very abundant.

The use of catalysts to improve the production of hydrogen by reforming of bioethanol and water splitting has been reported. Among them, zeolites seem to have a promised future as catalysts and catalyst supports. Here we will review first the use of different zeolites in the production of hydrogen by ethanol (or bioethanol) steam reforming. We will show the influence that the zeolites have as supports to prepare ethanol reforming catalysts with high activity, selectivity, and stability. Second, we will show the last advances in the use of the zeolites to produce hydrogen by water splitting process and the promised future that these materials have by taking advantage of solar energy.

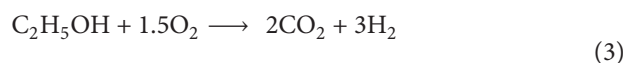
*2.1. Zeolites as Constituents of Catalysts for the Sustainable Production of Hydrogen via Ethanol/Bioethanol Reforming.* Among the liquid biomass-derived molecules that can be

used as hydrogen source, primary alcohols are interesting compounds because they can be converted to hydrogen by steam reforming using moderate reaction conditions. The most part of the reforming studies related to alcohols from biomass is focused on ethanol. Ethanol is considered an interesting alternative for the sustainable hydrogen production because of (i) its low toxicity; (ii) its low production costs; (iii) the fact that it is a relative clean fuel in terms of composition; (iv) its relatively high hydrogen content; (v) its availability and easiness of handling.

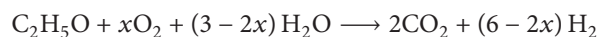
Catalytic hydrogen production from ethanol can be performed by (i) steam reforming (SR), represented by the reaction (2), (ii) partial oxidation (PO), represented by the reaction (3), and (iii) autothermal reforming (ATR), represented by the reaction (4) as follows:



$$\Delta H_0 = +173.3 \text{ kJ/mol,}$$



$$\Delta H_0 = -552.0 \text{ kJ/mol,}$$



$$\Delta H_0 = 173.3 - x^* 552 \text{ kJ/mol.} \quad (4)$$

The SR of ethanol, reaction (2), is an endothermic reaction which takes place at temperatures between 673 and 1073 K and with a kinetic slower than the PO reaction. SR operates at lower temperature and produces a higher number of molecules of  $H_2$  per molecule of converted ethanol ( $H_2/C_2H_5OH = 6$ ), thus the overall efficiency of this reaction is higher than that obtained by PO processes.

The PO of ethanol, reaction (3), occurs between 973 and 1273 K. It is an exothermic reaction. It has several advantages: allows working with adiabatic reactors without the necessity to supply external heat and the kinetics is rapid. Obtaining hydrogen from bioethanol by reaction PO is an option that has been rarely investigated, because it would involve the separation of water included in raw bioethanol, which would mean a high energy cost.

The third option combines the advantages of both approaches, SR and PO. This option includes the simultaneous reaction of ethanol with water vapor and oxygen in an oxidative reforming process (autothermal reforming, ATR), reaction (4). The input of the external heat is not necessary since it is generated by introducing small amounts of oxygen. The moles of  $H_2$  obtained per mole of ethanol are higher than that in the case of the PO reaction but lower than that in the case of SR.

The choice of the reforming route is based on the type of fuel cell, the demands and volume of the system, and management strategy. Nevertheless, the SR of ethanol has been the most studied route. The amount of published studies on the SR of ethanol is lower than that on hydrocarbons or methanol. Several reviews about the development of catalysts applied to ethanol SR have been published lately [67–70]. Catalytic materials such as



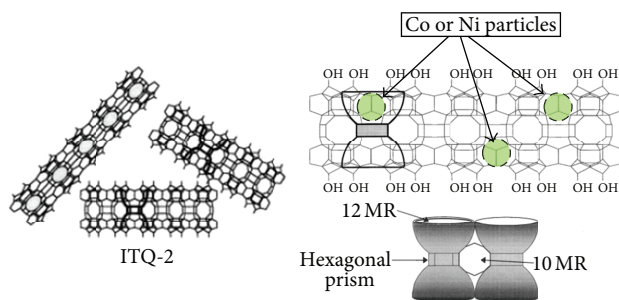


FIGURE 3: Structure of delaminated zeolite ITQ-2 [103].

metallic oxides ( $\text{ZnO}$ ,  $\text{MgO}$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{SmO}_3$ ) [71–73], supported metals ( $\text{Co}/\text{Al}_2\text{O}_3$ ,  $\text{Co}/\text{La}_2\text{O}_3$ ,  $\text{Co}/\text{SiO}_2$ ,  $\text{Co}/\text{MgO}$ ,  $\text{Co}/\text{ZrO}_2$ ,  $\text{Co-ZnO}$ ,  $\text{Co}/\text{TiO}_2$ ,  $\text{Co}/\text{V}_2\text{O}_5$ ,  $\text{Co}/\text{CeO}_2$ ,  $\text{Co}/\text{Sm}_2\text{O}_3$ ,  $\text{Co}/\text{CeO}_2\text{-ZrO}_2$ ,  $\text{Co}/\text{C}$ ,  $\text{Ni}/\text{La}_2\text{O}_3$ ,  $\text{Ni}/(\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3)$ ,  $\text{Ni}/\text{Al}_2\text{O}_3$ ,  $\text{Ni}/\text{MgO}$ ,  $\text{Ni-Cu}/\text{SiO}_2$ ,  $\text{Ni-Cu}/\text{Al}_2\text{O}_3$ ,  $\text{Ni-Cu-K}/\text{Al}_2\text{O}_3$ ) [74–85], and precious metals supported on oxides ( $\text{Rh}/\text{TiO}_2$ ,  $\text{Rh}/\text{SiO}_2$ ,  $\text{Rh}/\text{CeO}_2$ ,  $\text{Rh}/\text{ZrO}_2$ ,  $\text{Rh}/\text{Al}_2\text{O}_3$ ,  $\text{Rh}/\text{MgO}$ ,  $\text{Rh}/\text{Al}_2\text{O}_3$ ,  $\text{Rh}/\text{CeO}_2\text{-ZrO}_2$ ,  $\text{Rh-Au}/\text{CeO}_2$ ,  $\text{Rh-Pt}/\text{CeO}_2$ ,  $\text{Pd}/\text{CeO}_2$ ,  $\text{Pt}/\text{CeO}_2$ ,  $\text{Au}/\text{CeO}_2$ ,  $\text{Pd}/\text{Al}_2\text{O}_3$ ,  $\text{Pt-Pd}/\text{CeO}_2$ ) [86–99] are reported in these reviews.

Thermodynamic analyses have shown that a high conversion of ethanol to hydrogen is possible above 523 K and also that the high water/ethanol molar ratio of raw bioethanol is beneficial to increase hydrogen yield and to decrease the formation of byproducts such as methane, carbon monoxide, and carbon deposition. Table 1 shows a summary of the possible reaction pathways followed by the ethanol during its catalytic SR. The extension in which each reaction takes place over the catalyst will depend on the nature of metal, type of precursor, preparation method, type of support, presence of additives, and operating conditions.

Among them, it is found that support plays an important role in the preparation of highly active and selective ethanol steam reforming catalysts since it helps in the dispersion of metal catalyst and enhances its activity via metal-support interactions. Specifically, it has been found that high surface areas of the support improve the catalytic activity [73, 100], and the particular topology or crystalline structure of one support can affect the metal dispersion of the metallic particles improving their stability against sinterization [101, 102]. Taking this into account, the singular structure of zeolites would make these materials attractive to be used as supports for dispersing active metal phases [102–105].

Campos-Skrobot et al. [103] reported the first work in the steam reforming of ethanol using zeolites as support. Specifically, they studied the Y-zeolite exchanged with Na. According to the results reported by these authors, the NaY zeolite had the prime function of increasing the surface area, aiming higher reforming reaction efficiency. Potassium and rhodium were added to NaY zeolite in order to improve reforming performance. They found that the addition of Rh and K allowed to prepare an ethanol steam reforming catalyst with high activity and  $\text{H}_2$  selectivity. Best conversion

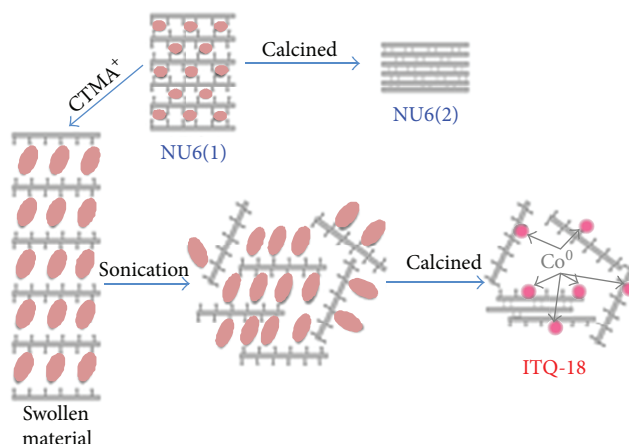


FIGURE 4: Synthesis of delaminated zeolite ITQ-18 (adapted from [105]).

values were achieved for higher  $\text{H}_2\text{O}/\text{ethanol}$  ratio and higher reagent flow. They also verified that reagent flow has greater influence on hydrogen yield than K addition. They concluded that NaY zeolite-supported Rh can be considered promising catalyst for ethanol steam reforming, when compared with other existing studies.

Chica et al. [102, 105] also studied zeolitic materials as support of catalyst for the SR of bioethanol. They used two delaminated zeolites (ITQ-2 and ITQ-18) with high external surface area ( $835$  and  $611\text{ m}^2/\text{g}$ , resp.) to support Ni and Co.

ITQ-2 delaminated zeolite consists of thin sheets of  $2.5\text{ nm}$  in height presenting a hexagonal array of “cups” ( $0.7\text{ nm} \times 0.7\text{ nm}$ ) that penetrate into the sheet from both sides connected by a double 6-member ring (MR) window (Figure 3) [102]. ITQ-18 is another delaminated zeolite which has been obtained by expanding and exfoliating a laminar precursor of NU-6 zeolite [106] (Figure 4). The singular structure of these delaminated zeolites, and particularly the very high and well-defined external surface area, makes these materials very attractive to be used as supports for dispersing active metal phases.

Ni and Co were supported on pure silica ITQ-2 and Co on ITQ-18 with low aluminum content ( $\text{Si}/\text{Al} = 100$ ). For comparison reasons, catalysts based on amorphous silica containing the same amount of Co and Ni (20 wt.%) were also prepared. High catalytic activity, selectivity, and stability (again coke deposition) were reported for the delaminated zeolite-based catalysts. The excellent catalytic performance exhibited was attributed to the combination of three effects. It was attributed first to the absence or very low concentrations of acid sites in the delaminated ITQ-2 and ITQ-18 zeolites, respectively. The absence of acid sites would help to decrease the dehydration reaction that leads to the formation of ethylene and subsequent formation of coke, the main causative of the catalyst deactivation. It was attributed second to its high external surface, which can provide a large surface for coke deposition and help to slow down the deactivation effects, and third to the especial structure

of these delaminated zeolites formed by array of “cups” distributed along of sheets (see Figures 3 and 4), which can provide an excellent position for the stabilization of the Ni and Co metal particles improving their dispersion and preventing their agglomeration during the reduction and reaction stages. An important conclusion was that while an amorphous support such as SiO<sub>2</sub> leads to Co and Ni-based catalysts with low stability, the use of delaminated zeolites, with a crystalline structure, allowed to prepare a much more stable bioethanol steam reforming catalyst.

In the before reported studies, zeolites are acting as simple supports for metals for ethanol steam reforming [102–105]. However, since zeolites exhibit functional properties such as ion exchange, the charge state of the metal could affect the SR of ethanol. In this line, Inokawa et al. [104] compared the ethanol reforming properties of zeolite Y supporting transition metals and encapsulating transition metal cations.

They studied the catalytic activity of conventional zeolite Y with a Si/Al ratio of 2.75, loaded with Ni and Co and their cations. The results obtained suggest that transition metals selectively enhanced the dehydrogenation of ethanol. In addition, the incorporated transition metal cations by ion exchange led to the production of mainly C<sub>2</sub>H<sub>4</sub> during ethanol steam reforming, indicating that the presence of the cations accelerates the dehydration of ethanol. Thus, the presence of transition metal cations in zeolite Y seems to have a significant influence on the ethanol reforming reaction. These authors suggest that conventional zeolites supporting transition metals are more attractive for industrial applications than zeolites with a high Si/Al ratio supporting noble metals, due to advantages of cost and availability, although the H<sub>2</sub> yields produced by Y zeolite containing Co and Ni cations were inferior to that for zeolite Y supporting Rh [103]. In addition, they think that H<sub>2</sub> production from ethanol using zeolites with low or medium Si/Al ratios supporting transition metals such as Co and Ni could be improved by the removal of the metal cations within the zeolites.

One important factor affecting the stability of steam reforming catalysts is the formation of carbonaceous deposits. These deposits can block the active sites and finally encapsulate the metallic particles deactivating the catalyst completely. Therefore, the stability of the catalysts is directly related to their tendency to form carbon. The coke formation on the catalysts during reforming of ethanol is due to the imbalance between their formation and consumption reactions (Table 2). This balance formation/consumption is determined by the reaction conditions and especially by the selected catalyst composition: active phase and support.

In order to reduce the coke formation over zeolite-based catalysts and increase the ethanol SR activity at low temperature, Kwak et al. [107] prepared MgO/zeolite Y catalysts loaded with bimetallic Ni-Ga. The impregnation of Ga between the Ni and Mg components led to significantly higher reforming activity compared to the conventional Ni/Mg/zeolite Y catalyst. The main products from steam reforming over the Ni/Ga/Mg/zeolite Y catalyst were only H<sub>2</sub> and CH<sub>4</sub> at above 550°C, and the catalytic performances depended on the amount of Ga. H<sub>2</sub>

production and ethanol conversion were maximized over Ni(10)/Ga(30)/Mg(30)/zeolite Y at 973 K, ethanol:H<sub>2</sub>O = 1:3, and a gas hourly space velocity (GHSV) of 6740 h<sup>-1</sup>. This high performance was maintained for up to 59 h.

These authors also studied the deactivation of these catalysts. They found that deactivation was largely retarded in the zeolite-based catalyst containing Ga compared to that of the catalyst without Ga. The authors reported that after 60 h the XRD peaks of the carbon and Ni metal were too enlarged while the other peaks assigned to metal or metal oxides species were very small (Figure 5). The improved stability at the slower deactivation rate achieved with the Ni/Ga sample could not be unequivocally attributed to carbon formation. The simultaneous addition of Ni/Ga could also have depressed the sintering between the Ni and the support, contributing to retard of the catalytic deactivation.

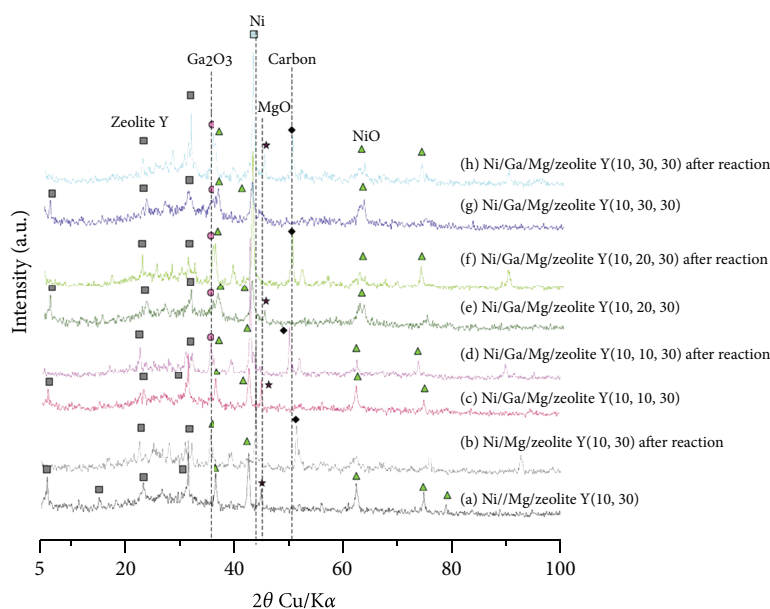
It is clear that basicity decreases significantly the formation of coke since it contributes to the inhibition of side reactions that would lead to the formation of coke precursors (Table 2). In this sense, Inokawa et al. [108] studied the ethanol steam reforming over Ni supported on zeolite Y with basicity controlled by the exchange of alkali cations. As a result, it was found that the exchange of Na<sup>+</sup> for K<sup>+</sup> and Cs<sup>+</sup> affected not only characteristics of the zeolites such as adsorption and basicity but also those of Ni, such as reducibility and catalytic activity. Ion exchange mainly brought an increase of basic sites, which were slightly strengthened. It was found that Ni species on the Cs-Y zeolite were reduced at a lower temperature than Na-Y zeolite. H<sub>2</sub> production at 573 K was improved in the order of Ni/Na-Y < Ni/K-Y < Ni/Cs-Y, according to the size of the cation in the zeolite and the amount of basic sites. Improvement of the catalytic performance was considered to be due to the increase of basic sites, which weaken the OH bond of ethanol adsorbed on the zeolite. In terms of elementary reactions, the dehydrogenation reaction of ethanol was accelerated by the basicity of the zeolite, whereas the dehydration reaction that produces ethylene was inhibited.

The basicity of the zeolite was found to be effective for the inhibition of coke deposition, because Ni/Cs-Y with higher H<sub>2</sub> production than Ni/Na-Y also exhibited higher resistance to carbon deposition. In summary, an increase of the zeolite basicity by cation exchange can selectively promote the dehydrogenation of ethanol by Ni on the zeolite and improve H<sub>2</sub> production and resistance to carbon deposition.

Ni and Co have been the active sites more studied in the SR of ethanol using zeolites as support. Nevertheless, other metals as Sn have been also found actives. Lee et al. [109] studied the production of hydrogen using Y zeolite promoted with Sn and K. They studied the effects of the Sn and K presence on the H<sub>2</sub> production and on the catalytic deactivation. They reported that the Sn component played an important role in the oxidation of the feed gases during ethanol reforming, while the addition of the K depressed the formation of CH<sub>4</sub> or others hydrocarbon intermediates. Based on the results of H<sub>2</sub>-TPR and NH<sub>3</sub>-TPD, they suggest that the reduction of Sn oxides (Sn<sup>4+</sup> to Sn<sup>0</sup>) on SnO<sub>2</sub>-K<sub>2</sub>O/Y catalyst at low temperatures easily occurs compared

TABLE 2: Reaction network for the steam reforming of bioethanol.

| Reaction                        | Equation   |
|---------------------------------|--|
| Reforming with excess of water  | $\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \longrightarrow 2\text{CO}_2 + 6\text{H}_2$   |
| Reforming with deficit of water | $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \longrightarrow 2\text{CO} + 4\text{H}_2$<br>$\text{CH}_3\text{CH}_2\text{OH} + 2\text{H}_2 \longrightarrow 2\text{CH}_4 + \text{H}_2\text{O}$   |
| Dehydrogenation                 | $\text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2$  |
| Acetaldehyde decomposition      | $\text{C}_2\text{H}_4\text{O} \longrightarrow \text{CH}_4 + \text{CO}$   |
| Acetaldehyde reforming          | $\text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O} \longrightarrow 3\text{H}_2 + 2\text{CO}$   |
| Dehydration                     | $\text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$  |
| Coke formation                  | $\text{C}_2\text{H}_4 \longrightarrow \text{polymeric deposits (coke)}$  |
| Decomposition                   | $\text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{CO} + \text{CH}_4 + \text{H}_2$<br>$2\text{CH}_3\text{CH}_2\text{OH} \longrightarrow \text{C}_3\text{H}_6\text{O} + \text{CO} + 3\text{H}_2$<br>$\text{CH}_3\text{CH}_2\text{OH} \longrightarrow 0.5\text{CO}_2 + 1.5\text{CH}_4$ |
| Methanation                     | $\text{CO} + 3\text{H}_2 \longrightarrow \text{CH}_4 + \text{H}_2\text{O}$<br>$\text{CO}_2 + 4\text{H}_2 \longrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$  |
| Decomposition of methane        | $\text{CH}_4 \longrightarrow 2\text{H}_2 + \text{C}$   |
| Boudouard reaction              | $2\text{CO} \longrightarrow \text{CO}_2 + \text{C}$  |
| Water gas shift reaction        | $\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$  |

FIGURE 5: Comparison of XRD patterns of the catalysts, Ni(10)/Ga(x)/Mg(30)/zeolite Y ( $x = 0, 10, 20, 30$ ), according to the reaction temperature, before and after reaction [107].

to conventional Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. In addition, the acidity of the Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst induced by the existing Al is higher than that presented in the SnO<sub>2</sub>-K<sub>2</sub>O/Y catalyst. Thus, the condensation of ethanol on the last catalyst is more difficult and consequently the formation of the coke is lower, and eventually the higher activity over SnO<sub>2</sub>-K<sub>2</sub>O/ZY catalyst is maintained.

Considering all the above mentioned, it seems that the use of zeolites as metal support to prepare active and

stable reforming catalyst to produce hydrogen could be an attractive option since they have a high external surface area and can be prepared with neutral behaviors if they synthesized all silica, with high Si/Al ratios or exchanged with alkaline metals. However, pore opening of zeolites can limit their application to the reforming of large molecules. Thus, mesoporous molecular sieves with size-tunable mesopores have attracted a great deal of attention because of their controllable structure and composition [110, 111]. However,

unlike zeolites, the wall of the mesoporous is amorphous, not crystalline. Therefore, mesoporous aluminosilicates cannot exhibit the excellent catalytic properties unlike acidic zeolites. Moreover, their hydrothermal stability is especially low. To overcome this problem, one strategy has been the generation of mesoporosity on zeolites [112–114]. The presence of mesopores in the crystalline of the zeolite would be equivalent to increasing the external surface of the zeolites making a larger number of pore openings accessible to the large reactants [115–121]. On the other hand, the presence of mesoporous could improve the diffusion affecting the ion exchange processes and catalytic reaction [122–129]. Although ethanol is a small molecule from biomass processing, most part of the molecules from biomass susceptible to be reformed are large (i.e., glycerin, sugars, cellulose, lignin, hemicellulose, and so forth), making the mesopore-modified zeolites an attractive material to prepared hydrothermally stable steam reforming catalysts. In this line, da Costa Serra et al. [130] studied the effect of mesopores-modified mordenite zeolite promoted with Ni in the steam reforming of bioethanol. They reported the alkaline treatment of a commercial mordenite to generate mesoporosity (Figure 6). The idea was to generate mesoporosity in the commercial mordenite zeolite in order to improve the exchange of alkaline cation (to remove the acidity) and create good positions for the incorporation and stabilization of Ni metallic particles (active sites for steam reforming of bioethanol). They found that reforming activity of catalyst based on mesopores-modified mordenite was significantly higher than that shown by the commercial one (without mesopores). The lower size of the Ni metallic particles supported on mesopores-modified mordenite were the main factor responsible for this high activity.  $H_2$  selectivity and catalytic stability were also found higher for the mesopore-modified material. They reported that the formation of coke precursors (favored by acid sites) and the subsequent deposition of carbon was lower in the mesopore-modified mordenite. This effect is explained by the generated mesoporosity, which would improve first the Na exchange and thus, the neutralization of the acid sites, and second the diffusion of the reactants and products, avoiding the blockage of micropores. Indeed, for the same Na exchange conditions, the amount of Na exchanged was found higher in the mesopores-modified mordenite (4.2 wt.% against 2.9 wt.% for original mordenite), suggesting that the presence of mesopores would improve the exchange of protons (responsible of acid sites) by sodium cations. On the other hand, they observed a higher enlargement of the Ni metallic particles supported on not treated mordenite (without mesopores), suggesting that generated mesoporosity could be contributing to the generation of good position for the incorporation and stabilization of Ni metallic particles, avoiding or decreasing the Ni sinterization and thus, improving the catalytic activity and stability.

All the works mentioned above have been centered in the reforming of ethanol or bioethanol in gas phase. Nevertheless, in the literature the use of zeolites in the reforming of ethanol in liquid phase is also reported. Aqueous phase reforming (APR) has been recently reported by Dumesic et al. [131–133]. This process operates at low temperatures (<573 K), at

which the WGS reaction is also thermodynamically favored, making it capable of producing hydrogen with high yields. The low reaction temperature minimizes the decomposition reactions and, hence, avoids carbonization and catalyst deactivation. Tang et al. [134] studied the feasibility of platinum-loaded NaY zeolite catalysts for APR of methanol and ethanol. The feasibility of APR of ethanol was demonstrated on the Pt/NaY catalysts. The results were compared with the data on Pt/ $\gamma$ - $Al_2O_3$  catalysts. At 538 K, the 0.5 wt % Pt/NaY achieved higher  $H_2$  selectivity and lower alkane selectivity than the 3 wt % Pt/ $\gamma$ - $Al_2O_3$  catalyst with similarly high ethanol conversion of ~97% on both catalysts. The zeolite-based catalysts, with the advantages of high activity, reduced use of precious metal, and low cost of zeolite materials, deserve further investigations. They report that research is ongoing into the effect of substrate properties on the catalytic performance of platinum catalysts in APR reactions.

## 2.2. Zeolites as Constituents of Photocatalysts for the Sustainable Production of Hydrogen via Water Splitting

### 2.2.1. Solar Energy and Water Splitting Reaction.

The incidence of solar energy on the surface of the earth (180.000 TW) by far exceeds all human energy needs [135]. Thus, it is easy to understand that the solar energy could be considered one of the most important renewable energy sources potentially available on earth.

Undoubtedly, solar energy is the largest renewable carbon-free resource amongst all other renewable energy options. However, to make use this energy by the currently human technology, solar energy must be captured, converted, and stored in order to assure a continuous supply of energy and to overcome the diurnal cycle and the intermittency of the terrestrial solar resource.

Among the different energy carriers capturing the solar energy, hydrogen from photocatalytic water splitting is considered as one of the most promised carriers since it allows storing solar energy in the form of chemical energy and makes available solar energy for 24 hours a day, 7 days a week.

In the photocatalytic water splitting, hydrogen is produced from water using sun light and specialized semiconductors. The semiconductor uses light energy to directly dissociate water molecules into hydrogen and oxygen. The water splitting takes place when the semiconductor is irradiated with light in the presence of an electron donor and acceptor, oxidizing  $OH^-$  ions to produce  $O_2$  and reducing  $H^+$  ions to  $H_2$ . Specifically, the electrons in the valence band of the photocatalyst are excited to the conduction band, while the holes are left in the valence band. This, therefore, creates the negative-electron ( $e^-$ ) and positive-hole ( $h^+$ ) pairs. This stage is referred to the semiconductor's "photo-excited" state, and the energy difference between the valence band and the conduction band is known as the "band gap." This must correspond to the wavelength of the light for it to be effectively absorbed by the photocatalyst. After photoexcitation, the excited electrons and holes separate and migrate to the surface of the photocatalyst. In the photocatalytic water-splitting reaction, they are used as a



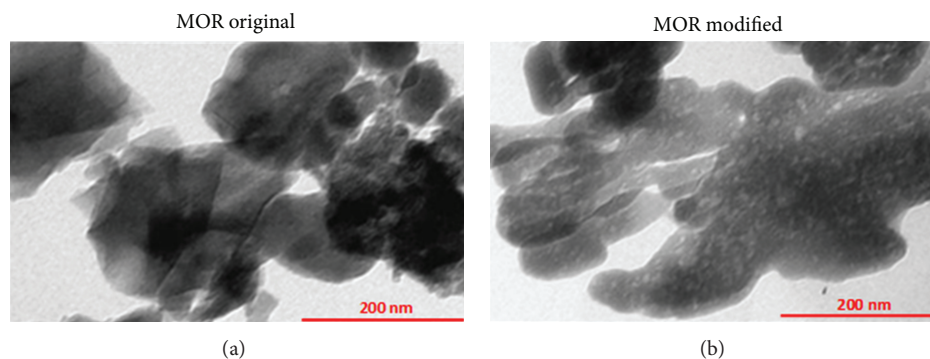
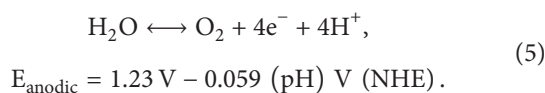
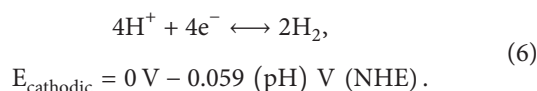


FIGURE 6: TEM microphotographs of original and alkaline treated mordenite to generate mesoporosity. Adapted from [130].

reducing agent and oxidizing agent to produce  $H_2$  and  $O_2$ , respectively. A schematic representation of the principle of the photocatalytic system for water is shown in Figure 7 [136]. As it can be seen, first, that O–H bonds of two water molecules need to be broken with the simultaneous formation of one O=O double bond as follows [137]:



Since this reaction requires a high oxidizing potential, 1.23 V versus NHE (normal hydrogen electrode) (pH = 0), the top level of valence band has to be more positive than this potential, so that the photogenerated holes have enough energy to oxidize water. This reaction releases four protons ( $H^+$ ) and four electrons ( $e^-$ ), which need to be combined to form two  $H_2$  molecules, as follows [136]:



Therefore, the conduction band of the semiconductor has to be more negative than water reduction potential (0 V versus NHE (pH = 0)). Thus, water molecules are oxidized by the holes to form  $O_2$  and are reduced by the electrons to form  $H_2$  for overall water splitting. Therefore, the theoretical minimum band gap for water splitting is 1.23 eV that corresponds to light wavelength of about 1000 nm.

**2.2.2. Semiconductors and Zeolites for Water Splitting.** Currently, the photocatalytic water splitting over semiconductor materials is an area of great interest due to the potential of hydrogen as a clean-energy fuel source. Since the initial works of Fujishima and Honda [138], who discovered that water can be photoelectrochemically decomposed into hydrogen and oxygen using a semiconductor ( $TiO_2$ ) electrode under UV irradiation, an extensive variety of materials ( $TiO_2$ , CdS, ZnO,  $ZrO_2$ , titanates, niobates, and tantalates) [139–151] have been reported to be effective for the photocatalytic decomposition of water.

Initial efforts in this area involved large bandgap ( $E_g > 3.0 \text{ eV}$ ) semiconductors that used only UV light. Currently,

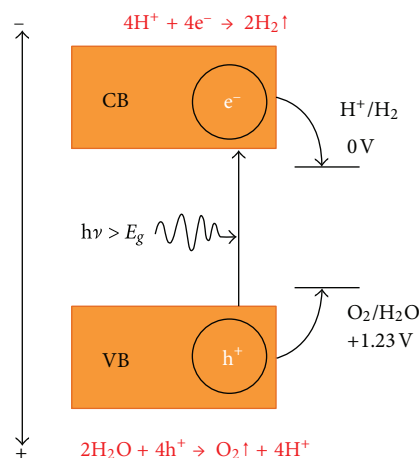
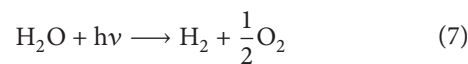
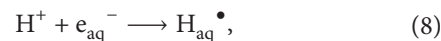


FIGURE 7: Schematic diagram of band edge requirements for water splitting reaction. Adapted from [137].

the most important efforts are being focused on using visible light as the energy source [152–170] as the ultimate goal to produce hydrogen fuel using solar energy. While the overall redox potential of the reaction



is only  $-1.23 \text{ eV}$  (1000 nm) at pH 7, the crucial reaction for hydrogen production is believed to be the initial one-electron transfer to  $H^+$  ion



where  $E_H = -2.5 \text{ V}$  at pH 7, which falls energetically within the visible region of light.

Taking into account the basic mechanism and reactions of photocatalytic water splitting process, the photocatalysts should meet several characteristics with respect to semiconducting and electrochemical properties [171–175] as follows: (1) narrow band gap ( $1.23 \text{ eV} < E_g < 3.0 \text{ eV}$ ) and band edge potentials suitable for overall water splitting to be activated under visible light, (2) successive separation of photoexcited electrons from reactive holes, (3) minimum energy losses associated with charge transport and recombination

of photo-excited charges, (4) corrosion and photocorrosion resistivity in aqueous mediums, (5) facilitated electron transfer properties from photocatalyst surface to water, and (6) low production cost.

To meet part of the above mentioned expectations, extensive studies have been performed based on the use of support where effective photocatalysts have been impregnated [176–183]. The major incentives for implementing the supported photocatalyst idea are (1) inhibition of the back electron transfer as limiting parameter in redox systems, (2) taking advantage of nanosized semiconductors while using them in easily separable micro-sized level of the support, (3) utilizing the support to add more solid chemical promoters, and (4) structural and chemical characteristics of the support by itself.

Among the different supports used to prepare efficient water splitting photocatalysts, zeolites are presented as promising materials. Zeolites exhibit high surface area, unique nanoscaled porous structure, and ion exchange properties which can be used in the design of highly efficient photocatalysts [184]. Unique photocatalytic properties, which cannot be realized in normal catalytic systems, have been observed recently in such modified spaces [185–190]. It is important to note that zeolites can also provide specific photophysical properties such as the control of charge transfer and electron transfer processes [191–194] which is very important in photocatalytic reactions.

There are several advantages that zeolites afford as support or host of semiconductor particles. For example, the pore sizes of the host support material control the resulting particle size of the supported semiconductor. Particle size is a crucial factor in the dynamics of electron/hole recombination processes, especially in semiconductor nanomaterials, and that the movement of electrons and holes is primarily governed by the well-known quantum confinement [195]. Generally, a decrease in particle size could be expected to lead to a higher efficiency in photocatalysis [196–201]. This was because the bulk charge recombination of photogenerated electrons and holes, dominant in the well-crystallized large semiconductor particles, was reduced by decreasing particle size. Reduction in particle size could also lead to a larger surface area and an increased available surface active sites [202–204].

Decreasing particle size has a known beneficial effect on catalyst efficiency [205–208]. Furthermore, encapsulation into a porous structure should provide some protection against surface-mediated reactions that corrode the catalyst, as exposed surface area will be limited. In addition, a major factor that limits the efficiency of the most part of the photocatalysts is electron-hole recombination.

The incorporation of photocatalysts into the micropore structure of zeolite in order to prepare nanoparticles is an attempt to improve their photocatalytic activity and photostability. Small nanoparticles show a higher photocatalytic activity compared to the bulk materials due to changes in the surface area, band gap, morphology, and generation of surface defects [209, 210]. In addition, the incorporation of photocatalyst into solid matrices as zeolites is reported to suppress photocorrosion and improve the activity for water reduction. The incorporated nanoparticles, whose sizes are

determined by the nanometric size of zeolite cages, show some novel physical properties such as blue shift of optical absorption spectra, increased photooxidation potentials, and third-order nonlinear optical properties. In this line, Sathish et al. [211] reported the preparation of cadmium sulphide (CdS) nanoparticles by precipitation process using different zeolite matrices as templates (H-Y, HZSM5 and H- $\beta$ ). In this study, the micropores of zeolites were used as molds to prepare nanoparticles of CdS with different sizes. After the removal of zeolite phase, the CdS nanoparticles were used as catalysts for the photocatalytic decomposition of water. The hydrogen evolution rate was found higher than that presented by the bulk samples which correlated quite well with the particle size and surface area.

Of particular interest is the use of zeolites as support, because of the well-defined microporous structure and ion-exchange properties, as was mentioned before. One of the first works reported in the literature about the use of zeolites as support to produce hydrogen by water splitting process was carried out by Fox and Pettit [209]. They studied the photocatalytic hydrogen evolution on zeolite-supported CdS particles modified by surface modification with an appropriate hydrogen evolution catalyst (Pt or ZnS). Particles formed within the zeolite cavities aggregate upon exposure to water, and small clusters were isolated within individual cavities only in nonaqueous solvents at low CdS loading levels (<3%). Sustained hydrogen evolution required the presence of an added sacrificial donor ( $S^{2-}/SO_3^{2-}$ ). Platinum deposited on the photoactive CdS surface is exclusively found inside the cavity, where it was inaccessible to large anionic reagents.

Ryu et al. [212] also studied the water splitting activity of CdS particles supported on several micro- and mesoporous silicas (zeolites: Y and L, mesoporous: SBA-15). Specifically, they studied the hydrogen production from water/ethanol solutions using visible light. All catalysts were active in the photocatalytic water splitting with the following order of photoreactivity: zeolite-Y > SBA-15 > zeolite-L. They found that optimization of reaction conditions (i.e., pH, ionic strength, and water-to-alcohol ratios) was critical to achieve a high level of hydrogen production. Preventing loss of CdS during the course of the photoreaction is also paramount to create a stable, long-term use catalyst. Specifically, they found that there was an efficient dispersion of CdS nanoclusters into the cages and micropores of zeolite Y, and the quantum confinement of hydrated CdS increased the reduction potential for the bound proton to hydrogen atom electron transfer, and finally the confined CdS supercluster in a more efficient chromophore in the visible portion of the spectrum.

The water splitting activity with visible light using CdS nanocomposites (quantum-sized (Q-sized) CdS, CdS nanoparticles embedded in zeolite cavities (CdS/zeolite), and CdS quantum dots (Q-CdS) deposited on  $KNbO_3$  (CdS/ $KNbO_3$  and Ni/ $NiO/KNbO_3/CdS$ )), was also investigated by Ryu et al. [213]. They reported that the rate of  $H_2$  production in alcohol/water mixtures and other electron donors at  $\lambda \geq 400$  nm was clearly higher in the hybrid catalysts, including zeolite-based photocatalyst. The relative order of reactivity as a function

of catalyst is  $\text{Ni}(0)/\text{NiO}/\text{KNbO}_3/\text{CdS} > \text{Ni}(0)/\text{KNbO}_3/\text{CdS} > \text{KNbO}_3/\text{CdS} > \text{CdS}/\text{NaY-zeolite} > \text{CdS}/\text{TiY-zeolite} > \text{CdS}$ , while the reactivity order with respect to the array of electron donors is  $2\text{-propanol} > \text{ethanol} > \text{methanol} > \text{sulfite} > \text{sulfide}$ .

Titanium exchanged zeolites have been also studied in the water splitting reaction. Yue and Khan [214] were one of the first reporting the use of titano-zeolites to produce hydrogen by water splitting. In their study, the Ti was exchanged and incorporated into the framework of zeolite A. Specifically, they studied the effect of several variables on the photoassisted production of hydrogen over this titanium-exchanged zeolite. During the reaction, oxygen tended to react with titanium ions exchanged on zeolite forming titanium oxides ultimately leaving the zeolite surface thereby creating vacant sites. These vacant sites were occupied by hydrogen, after the absorbed hydrogen was successfully displaced from the zeolite structure by the addition of base.

Zeolites containing titanium in their framework have been also used as support of CdS nanoparticles. In this line, Guan et al. [215, 216] studied the water splitting activity of CdS encapsulated on ETS-4 and ETS-10 titanosilicalite zeolite. They found a stable photocatalytic activity under visible light irradiation ( $\lambda > 420 \text{ nm}$ ) in aqueous solution containing  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$  as electron donors. Specifically, the catalytic activity for the zeolite-based photocatalysts was found higher than that for CdS bulk (17.5 and 13.3  $\mu\text{mol H}_2/\text{h/g}$  catalyst for CdS/ETS-4 and CdS/ETS-10. resp., and, 8.3  $\mu\text{mol H}_2/\text{h/g}$  catalyst for CdS bulk). These results seem to indicate that the encapsulation of CdS in these titanosilicalite zeolites is effective for separating charge-carriers photogenerated in CdS and for improving the activity as well as the stability.

Dubey et al. [217] reported the use of zeolite Y to prepare highly efficient water splitting catalysts under visible light. They reported the incorporation in the zeolite Y of titanium dioxide ( $\text{TiO}_2$ ), heteropolyacid (HPA), and transition metals like cobalt (Co). They got a photocatalyst where the  $\text{TiO}_2$  was effectively dispersed and stabilized on the zeolite surface. The high efficiency of the composite photocatalyst was explained by the synergetic work of  $\text{TiO}_2$  with Co and heteropolyacid, which made the material active in visible light for photoreduction of water to hydrogen. They also reported that the aluminosilicate framework of zeolite also contributed towards delayed charge separation.

In the previous studies, zeolites have been used for the separated incorporation of nanoparticles of CdS and titanium (as titanium oxide particles ( $\text{TiO}_2$ ) or  $\text{Ti}^{3+}$  taking part of the zeolite framework). In this way improved water splitting catalysts were obtained. Recently works carried out by White et al. [218] report the incorporation of both semiconductors in zeolite Y. They observed improvements in  $\text{H}_2$  evolution rates of  $\sim 300$  for CdS/ $\text{TiO}_2$  zeolite Y over  $\text{TiO}_2$  zeolite Y and  $\sim 18$  for CdS/ $\text{TiO}_2$  zeolite Y over CdS zeolite Y. These improvements exceed colloidal binary systems reported in the literature. On the other hand, improvements in the  $\text{H}_2$  evolution rate of the ternary system Pt/CdS/ $\text{TiO}_2$ -zeolite Y was not as marked, as compared to the best colloidal ternary systems reported in the literature. They proposed an interesting model to explain the colocalization of the

$\text{TiO}_2$  and CdS nanoparticles supported on zeolite Y. This model explains quite well the high activity of binary system (CdS/ $\text{TiO}_2$ , zeolite Y) and also why the incorporation of Pt did not improve the catalytic activity of the ternary system (Pt/CdS/ $\text{TiO}_2$ , zeolite Y). The main reason was that Pt needed to be associated only with  $\text{TiO}_2$  for best  $\text{H}_2$  evolution, and the zeolite promoted self-assembly did not provide a route for positioning the Pt only on the  $\text{TiO}_2$  particles. New strategies for the incorporation of Pt will be required in order to promote the association of Pt only with  $\text{TiO}_2$ .

### 3. Conclusions

The intense exploitation of fossil fuels to satisfy the globally growing energy demand has caused an increase of  $\text{CO}_2$  in the atmosphere and, therefore, a significant global warming (green-house effect). Furthermore, the reserves of fossil fuels on earth are finite and no matter how long they will last, a cleaned and renewable energy alternative independent of fossil fuels has to be developed for the future. Hydrogen could be a good option because it exhibits the greatest heating value (39.4 kWh/kg) of all chemical fuels. Its combustion to heat or power is simple and clean. When combusted with oxygen, hydrogen forms water and no pollutants are generated or emitted. About 95% of the hydrogen we use today comes from reforming natural gas. But to realize the full benefits of a hydrogen economy, increased energy security, diverse energy supply, and reduced air pollution, hydrogen must be produced cleanly, efficiently, and affordably from available renewable resources. Thus, renewables are a desired energy source for hydrogen production. However, there are many challenges to produce hydrogen from renewables and probably the major one is developing new catalytic process to produce sustainable hydrogen and reducing the cost to be competitive with the current fuels (gasoline and diesel).

Zeolites are presented as excellent catalysts and support of catalysts due to their very special physicochemical properties.

- (i) High surface area.
- (ii) Molecular dimensions of the pores.
- (iii) High adsorption capacity.
- (iv) Partitioning of reactant/products.
- (v) Possibility of modulating the electronic properties of the active sites.
- (vi) Possibility for preactivating the molecules when in the pores by strong electric fields and molecular confinement.

Currently, new scientific applications have been developed for these materials. Among them, the production of green fuels from renewable sources is the focus of a large part of the research efforts.

Two different routes to produce sustainable hydrogen using zeolites have been described and revised in this paper. One of them is based on the biomass conversion via indirect thermochemical conversion to intermediate products. The indirect thermochemical option is related to the conversion



of biomass to biofuels (bioethanol, biodiesel, biogas), followed by catalytic steam reforming of them to hydrogen. An advantage of this approach is that the biofuels, as an intermediate product, have a higher energy density than the biomass feedstock and can be transported more easily. Specifically, this paper has considered the steam reforming of bioethanol.

Renewable bioethanol is an interesting hydrogen source through steam reforming, but its C–C bond promotes parallel reactions, mainly coke and by-products formation. In this way, good ethanol reforming catalysts are still needed. The use of zeolites has been able to improve the catalytic activity, selectivity, and stability of the bioethanol steam reforming catalysts. It has been reported that zeolites play an important role in the preparation of highly active and selective ethanol steam reforming catalysts since they help in the dispersion of metal active sites and enhance their activity via metal-support interactions. Specifically, it has been found that high surface areas of the support improve the catalytic activity and that the particular topology or crystalline structure of one support can affect the metal dispersion of the metallic particles improving their stability against sinterization.

Another interesting option analyzed in this paper, with enormous potential but requiring more development time, has been the photocatalytic decomposition of water using solar energy, which is also called water splitting. In the photolysis of water, solar photons area is used to produce hydrogen directly via electrochemical systems. This method involves the dissociation of water into hydrogen and oxygen directly at the surface of a semiconductor through the irradiation of the semiconductor by solar photons. The photovoltaic semiconductor material acts as a catalyst to produce hydrogen directly at the semiconductor and water interface.

It has been shown that among the different supports used to prepare efficient water splitting, photocatalysts zeolites are presented as promising materials. Zeolites exhibit high surface area, unique nanoscaled porous structure, and ion exchange properties which can be used in the design of highly efficient photocatalyst. In addition, zeolites can also provide specific photophysical properties such as the control of charge transfer and electron transfer processes which are very important in photocatalytic reactions.

It has been seen that there are several advantages that zeolites afford as support or host of semiconductor particles. For example, the pore sizes of the host support material control of the resulting particle size of the supported semiconductor. Semiconductors such as  $\text{TiO}_2$  and CdS have been incorporated in zeolites in order to improve their photocatalytic activity and photostability. Small nanoparticles of these semiconductors incorporated in zeolites have been reported to show a higher photocatalytic activity compared to the bulk materials due to changes in the surface area, band gap, morphology, and generation of surface defects. In addition, the incorporation of photocatalyst into zeolites helps to suppress photocorrosion and improve the activity for water reduction. Although the studies presented here using zeolites can be considered promising, the major problem to solve would be to find a semiconductor material that had the right

photoelectrochemical properties, while being economical and robust enough to withstand the severe chemical and physical environment.

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