Chapter 2
Synthesis of Novel Catalytic Materials: Titania Nanotubes and Transition Metal Carbides, Nitrides, and Sulfides

Davi Coelho de Carvalho, Josue Mendes Filho, Odair Pastor Ferreira, Alcineia Conceição Oliveira, Elisabete Moreira Assaf, and Yanet Villasana

2.1 Introduction and Scope

2.1.1 Overview

Catalysis is responsible for most of the advances in modern chemistry and industry. Food, fuels, chemical, pharmaceuticals, plastic, fibers, and fertilizers are examples of the impact of catalytic reactions on mankind, considering that chemical industry has been built after paramount advances in catalysis science and technology for the transformation of fossil and other resources into high-value products.

However, as the demand for efficient materials for catalytic processes has increased rapidly over the last century, this caused a huge growth in the search for new catalytic materials in comparison with the improvement of the traditional catalysts. Recently, much attention has been paid to the preparation of novel catalytic materials to address for challenging catalytic reactions and processes leading to

---

D. C. de Carvalho · A. C. Oliveira (✉)
Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará, Fortaleza, Ceará, Brazil
e-mail: alcineia@ufc.br

J. M. Filho (Deceased) · O. P. Ferreira
Departamento de Física, Universidade Federal do Ceará, Fortaleza, Ceará, Brazil

E. M. Assaf
Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos, SP, Brazil

Y. Villasana
Grupo I+D+i Biomass to Resources, Universidad Regional Amazónica IKIAM, Tena, Ecuador

Venezuelan Institute for Scientific Research, Caracas, Venezuela

© Springer Nature Switzerland AG 2019

J. M. Domínguez-Esquivel, M. Ramos (eds.), *Advanced Catalytic Materials: Current Status and Future Progress*, https://doi.org/10.1007/978-3-030-25993-8_2

environmental friendly technologies to meet current demand of products, energy, and services in a situation of social and economic sustainability. Properties of new catalytic materials depend on a large extent not only on the synthesis method, which defines the catalyst surface structure and porosity, but also on the final treatments such as calcinations which allow building their structures. The most important and widely used methods are sol–gel, precipitation, impregnation, chemical vapor deposition, mechanical mixtures, complexation, gelation, crystallization, hydrothermal treatment, and ion exchange, among others. Through these methods, innovative catalytic materials including metal organic framework (MOF), inorganic nanotubes (INT), carbon nanotubes (CNT), hydrotalcites (HT), zeolites, perovskites, pnictides, graphene, hierarchically porous materials, spinel oxides, hexaaluminates, composite oxides, carbides, nitrides, sulfides, and so on have been studied. Supports, precursors, promoters, and additives also have an essential role in catalytic material synthesis since they can modify acid-base properties, metal-support interactions, particle sizes and shapes, and surface species, and probably incorporate synergetic effect, which subsequently have an impact on catalytic performance, in terms of yields, stability, and selectivity.

Inorganic oxides have been used as catalytic supports due to their high thermal stability and also their ability to preserve or enhance the properties of the bulk active phase. Alumina, silica, titania, and zirconia are commonly used for an extensive variety of catalytic reactions as supports. Titanium functionalities generally provide redox and acid-base properties, which can enhance the interactions between the solid surface and hydrocarbon molecules, e.g., methane, carbon monoxide, and carbonyl compounds, among others. The possible structures of the titanium can be included in bulk TiO_2 in rutile or anatase phases and titanate nanotubes. Originally, interest in the latter materials has been mainly focused on their use as gas sensors, water treatment, solar energy cells, medicine, electrochemistry, hydrogen storage, and new catalysts or catalyst supports and in environmental protection, as well. In this aspect, titanate nanotubes with elevated textural properties are recently receiving a great deal of attention by virtue of their specific structures and unique properties in adsorption studies and catalytic supports. Since these solids were found to exhibit good catalytic activity in reactions, other inorganic nanotubes such as vanadates, sulfates, selenides, tungstates, molybdate nanotubes of silica, alumina, perovskites, ceria, and palladium have been widely investigated and utilized for polymerization, photocatalytic activity, anodization, Knoevenagel reaction, oxidations, acid-base reactions, as well as reduction of methyl orange and Cannizzaro reactions.

Furthermore, inorganic oxides with elevated surface areas have been widely used as supports of conventional catalysts for the upgrading and transforming of crude oil through hydrotreatment and hydrocracking reactions. Usually, these supports consist of alumina, silica-alumina, or zeolites with a surface area of about 200 m^2g^{-1}. Textural properties have significant incidence on the diffusion of reactants through pores and active sites, particularly for voluminous molecules, as those present in a complex matrix such as crude oil (resins and asphaltenes). On the other hand, the active phase of these conventional catalysts is commonly based on transition metal sulfides (TMS) of Mo, promoted with Co or Ni. However, processing of nonconventional crude oils (heavy or extra-heavy) differs substantially from processing of conventional crude oils (medium and light crude oil), due to the presence of large amounts of asphaltenes and high contents of S, N, and metals, which rapidly deactivate these conventional catalysts, by sintering, poisoning, and pore mouth clogging. As a consequence, some efforts have been made to improve deactivation resistance of hydrotreatment catalysts in terms of S, N, metals, and coke resistance, and also lifetime in the process, by changing active phases and textural properties of supports. In this regard, recently carbides and nitrides have been considered as an alternative for the hydrotreatment of heavy crude oils since they can successfully perform hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions and are more resistant to coke than conventional TMS.

For these reasons, the aim of this chapter is to discuss the synthesis of novel catalytic materials and their application in a variety of catalytic processes, emphasizing on the structure/function relationships obtained by titania nanotubes and also transition metal carbides and nitrides (TMC and TMN, respectively). These exciting modern advances are moving from the fundamental and practical setting to the pilot-plant stage. Thus, technologies are currently being developed that will enable us to use these materials in catalytic plants by replacing the traditional catalysts. The approaches for using titanate nanotubes as catalysts or catalyst supports include some of the advantages such as their low cost, environmentally friendly aspects, stability, and lifetime. TMC and TMN have shown to be resistant to severe deactivation and also being highly active during hydrotreatment and hydrocracking reactions due to their resemblance with noble metals in terms of electronic properties.

This chapter sets out to demonstrate that the synthesis of novel catalytic materials has driven the majority of the studies of catalysis up to now, rather than the improvement of the benchmark catalysts; there are significantly more investigations on the synthesis of new solids for catalytic reactions besides other applications. Section 2.2 discusses the overall forecast for new catalytic materials related to this approach. Section 2.2.1 discusses the methods of synthesis, as this provides the basis for how to design innovative catalytic materials. Conventional solids are synthesized by physical or chemical methods and these strategies are also widely utilized to obtain newly porous materials. Inorganic nanotubes including titanate nanotubes themselves are promising candidates to be industrial catalysts. Therefore, Sect. 2.2.2 considers the general aspects concerning the inorganic nanotubes, including their routes of production, which can be used as-synthesized or modified. Also, the types of inorganic nanotubes, their characterizations, and some applications will be emphasized. Section 2.2.2.1 discusses the synthesis routes to obtain titanate nanotubes describing their characterizations and their uses. Section 2.2.2.2 explains the reasons for what the as-synthesized titanate nanotubes can be applied in the production of valuable chemical intermediates through reactions such as polymerization, photocatalytic activity, anodization, Knoevenagel reaction, oxidation and reduction of methyl orange, Cannizzaro reaction, CO oxidation, hydroformylation of vinyl acetate, and phenol oxidation. On the other hand, Sect. 2.2.3 discusses about catalytic profile of TMC and TMN and their generalities; moreover, in next Sect. 2.2.3.1 synthesis, characterization, and applications are briefly described for bulk and supported TMC and TMN finally in Sect. 2.2.3.2 their specific application as catalysts for the hydrotreatment of model molecules and crude oil is discussed.

Finally, Sect. 2.3 provides the summary and conclusions for this chapter. Significantly, this manuscript describes the fundamental chemistry on the methods of synthesis to obtain catalysts, inorganic nanotubes, TMC, and TMN; their applications in catalytic reactions; and the needs for future new catalytic material development.

2.2 Forecast for New Catalytic Materials

The constantly growing world demand for materials to be applied as catalysts has shown that there is a need of improving the traditional catalysts or produce new solids for catalytic reactions. Coupling this with rising instability in the price of reactants, devices, preparation of the materials, and uncertainty of supply as well, many research groups have been encouraged to other drivers in the search for alternative routes to prepare materials. This search also includes a very important multidisciplinary research scope for novel strategies for material syntheses, as new catalytic materials [1–7]. Advances in computational chemistry and pursuit for a deep understanding of factors involved during catalytic reactions have motivated the development of methods to simulate an entire catalytic process considering thermodynamic parameters, leading to prediction of trends in reactivity and performance, and then tailoring of catalytic structure, this being transduced into savings in synthesis and catalytic tests [8–14], as it will be seen in other chapters of this book.

A close look in the search of new catalytic material theme over the past 10 years reveals that the researches typically focused on the synthesis of innovative materials to meet demand for experimental setups and technological aspects of the catalytic reactions. Moreover, an aggressive growth is expected to continue, driven primarily by investments in preparation of material domains after 2015 (Fig. 2.1).

If these growth speculations are met, new catalytic materials would account for more than 19,519 publications of the catalytic field search by 2015. In other words, hundreds of papers are expected to be published in this field. Noteworthy, the above-mentioned projections have arisen based on the development and design of new catalytic materials such as MOF, INT, CNT, hierarchically porous materials, HT, zeolites, pnictides, graphene, perovskites, spinel oxides, hexaaluminates, graphene, composite oxides, transition metal carbides, and nitrides [1–7, 11–17]. In addition, the search is associated to the development of synthetic routes throughout the methods involving sol–gel, precipitation, impregnation, chemical vapor deposition, mechanical mixtures, complexation, gelation, crystallization, nanocasting, hydrothermal treatment, temperature-programmed reaction with reactive gases, and ion exchange, among others [17–25].

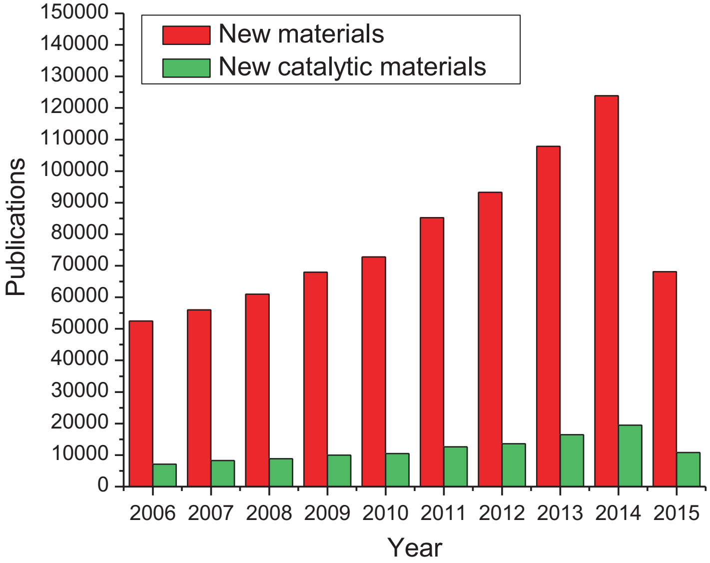


Fig. 2.1 Forecast for the applications of new catalytic materials. The period is 2006–2015

2.2.1 Methods of Synthesis to Design New Catalytic Materials

According to the Schwarz et al. [20], the catalytic materials exist in various forms and their preparations follow different protocols with a huge number of possible synthesis routes, frequently larger than the number of known catalysts. Hence, it is important to bear in mind that the new catalysts have been developed and shown promise in solving challenges encountered by the hydrocarbon transformation reactions in the industry. Therefore, as catalysis is the basis of the chemical industry [21], the improvement of properties and the discovery of new functionalities for the catalysts are achieved by a well-controlled and a better understanding of the preparation methods. Moreover, the idea of tailoring materials for specific applications has been widely spread as a consequence of the need for new materials that can handle challenging processes with a minimum of environmental impact, almost reaching zero by-products and using abundant materials in the world, with the vision of promoting the mitigation rather than adaptation to global climate change, especially on those processes identified by their highly negative impacts on the environment, as it occurs for the fuel and petrochemical industry [5, 26–31].

Thus, several methods have been developed in an attempt to attend these requirements including precipitation, impregnation, coprecipitation, sol–gel, chemical vapor deposition, mechanical mixtures, nanocasting, complexation, gelation, crystallization, hydrothermal treatment, and ion exchange, among others [1–7, 23, 32–39].

The most common methods used to prepare catalysts are divided into two families, the precipitation and impregnation procedures, as illustrated in Fig. 2.2.

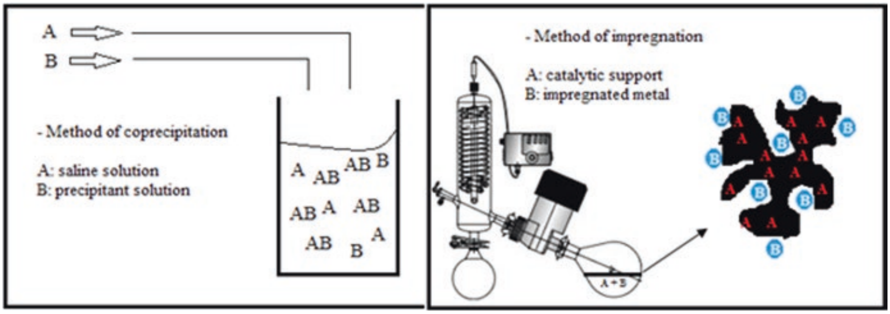


Fig. 2.2 Schematic representation of precipitation and impregnation routes to prepare catalysts

The precipitation from a homogeneous solution route is a technique based on the fact that one or more soluble salts, which contain the metal of interest, are neutralized by addition of a base for generation of precipitate or coprecipitate of the corresponding metal oxide gels [32]. As a result of the process, relative supersaturation is kept low with phase separation from the homogeneous liquid solution. The resulting precipitate is transformed into the following preparation stages into new solid phase through heating procedures, being the active catalyst. It has been claimed that the precipitation route includes the variant coprecipitation through two or more salt precursors used with ending calcination treatment steps, which transform amorphous precipitates to crystalline materials [20].

The classical impregnation route consists of the synthesis strategy whereby a certain volume of solution containing the precursor of the active element is contacted with the solid carrier material (silica, alumina, magnesia, active carbon, titania, etc.) [20, 32, 33]. The suspension is formed, being afterwards heated to remove the solvent and to disperse the metal on the carrier [32]. When the volume of the metal salt solution taken by the carrier is either identical or lesser than its pore volume, the technique is designed as incipient wetness [20]. The impregnation route also comprises different techniques such as ion exchange, deposition and grafting, among others.

The ion exchange consists of exchanging either hydroxyl groups or protons of the carrier with cationic and anionic species in solution [32]. The adjustment of the pH is a key factor to have an electronic interaction between the support and the metal precursor.

The traditional sol–gel method consists of the formation of a sol followed by the formation of gel [34]. This method is mainly based on the chemistry of hydrolysis and polymerization reactions and uses colloidal dispersion or inorganic precursors to produce novel materials. The method can use a wide variety of precursors, but the alkoxides are the most commonly used. Moreover, the alkoxides react with nucleophilic reagents giving rise to new precursors that exhibit different molecular structure, functionality, and reactivity [32, 34].

Other methods to prepare catalytic materials, for instance chemical vapor deposition, mechanical mixtures, nanocasting complexation, gelation, crystallization, hydrothermal treatment, and ion exchange, are well described in the literature [20–

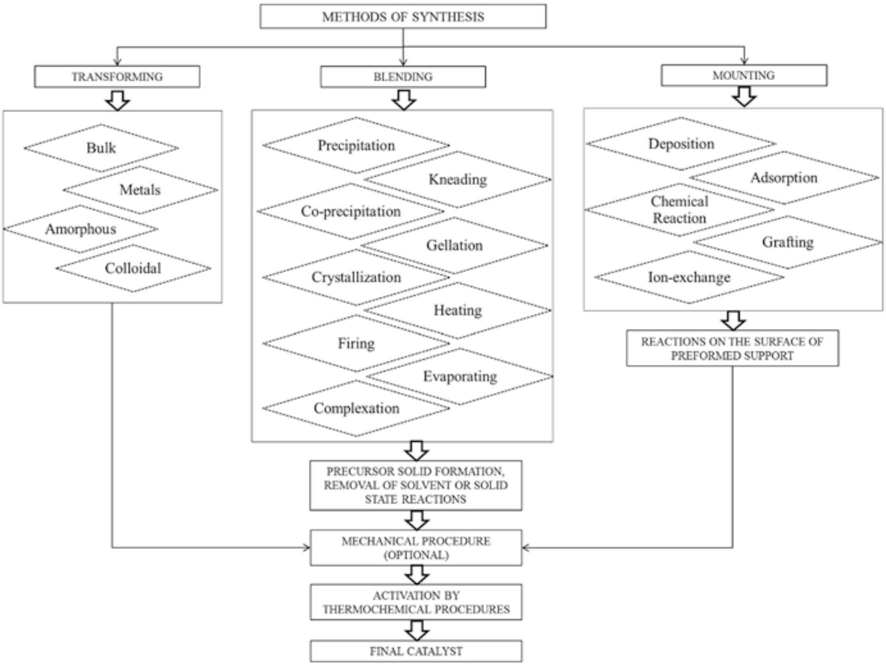


Fig. 2.3 Schematic diagram showing the methods of blending, transforming, and mounting the catalysts (adapted from ref. [20])

23, 32–43]. The main preparation routes are summarized in Fig. 2.3. These methods allow defining the properties of the catalyst via blending, transforming, and mounting steps to obtain the final catalyst to be applied in the reactions.

Importantly, through the abovementioned methods, novel materials such as metal organic framework (MOF), inorganic nanotubes (INT), carbon nanotubes (CNT), hierarchically porous materials, hydrotalcites (HT), picnides, zeolites, perovskites, spinel oxides, hexaaluminates, graphene, composite oxides, and so forth have been developed. The advantages and disadvantages of using these methods are shown in Table 2.1.

Despite these catalyst preparation methods producing materials with advantageous structural and porosity features, some of these synthetic routes require a sequence of several complex processes, many of them not completely understood.

2.2.2 Inorganic Nanotubes: General Aspects

Synthesis of inorganic nanotubes (INT) has recently drawn considerable interest in the research areas of solid-state chemistry and nanomaterials. The INTs are nanostructured materials derived from layered inorganic compounds possessing

Table 2.1 Distinct preparation methods to obtain new catalytic materials [20, 44–49]

Method of synthesis	Advantage	Disadvantage
Coprecipitation [20, 44, 46]	Convenient, simple process, provides a large range of scale, can be highly selective and virtually quantitative	Precipitate can be contaminated easily, can spend a long time to digest, to filter, or to wash the precipitate
Impregnation [20, 44, 45]	Fast process, the excess solvent is removed by drying easily and addition of active precursor into the porous carrier	Increasing the weight loading results usually in lower solution pH, carrying out support disruption and substitution of ions into the support lattice
Sol–gel [20]	Allows control of the textural properties, homogeneity, and chemical composition	Synthesis more complicated that requires greater energy expenditure
Chemical vapor deposition [20]	Fine-tuning of the pore size and using low-pressure conditions to allow direct deposition of the active material onto catalyst material	Surface poisoning, dissolution, and mainly redistribution of the active material during activation of the solid
Complexation [20]	The use of organic molecules with several chemical functionalities is important for formation of the three-dimensional network during the sol–gel step	The removal of the organic ingredient is very important during the catalysis activation
Crystallization [20]	Simple process and excellent purity obtained after the crystalline growth	Variation of temperature can cause instability and difficulty to the growth of the crystalline structure
Hydrothermal treatment [20, 49]	Low cost and simplicity of operation	Large amount of energy expended to produce a little sample
Ion exchange [20, 44]	Able to modify the size and way until achieving the internal pores	It is a prerequisite to keep the charge compensating ions for stability of the crystalline structure

structures comparable to those of graphite [43, 47]. For instance, Fig. 2.4 illustrates the MX_2 (M = Ta, Zr, Mo, W, Cd, Nb, Hf; X = S, Se) metal dichalcogenides, which are inorganic compounds with a metal-layered sandwiched structure between two chalcogen layers, with the metal in a trigonal pyramidal or octahedral coordination mode [43]. What makes these structures interesting is that they comprise unsaturated bonds at the edges of the layers, similar to that presented in graphite. It is important to figure out that especially in case of the dichalcogenide layers, there is instability towards bendings and these solids have a high propensity to roll into curved structures [43, 48].

In recent years, these INTs have moved towards being the subject of intense multidisciplinary studies in reason of their one-dimensional nanostructure, excellent physiochemical properties, and versatile applications such as sensors, adsorbents, solar cells, catalyst supports, medicine, photocatalysis, drug delivery, and electronics, among other applications [43, 47–52].

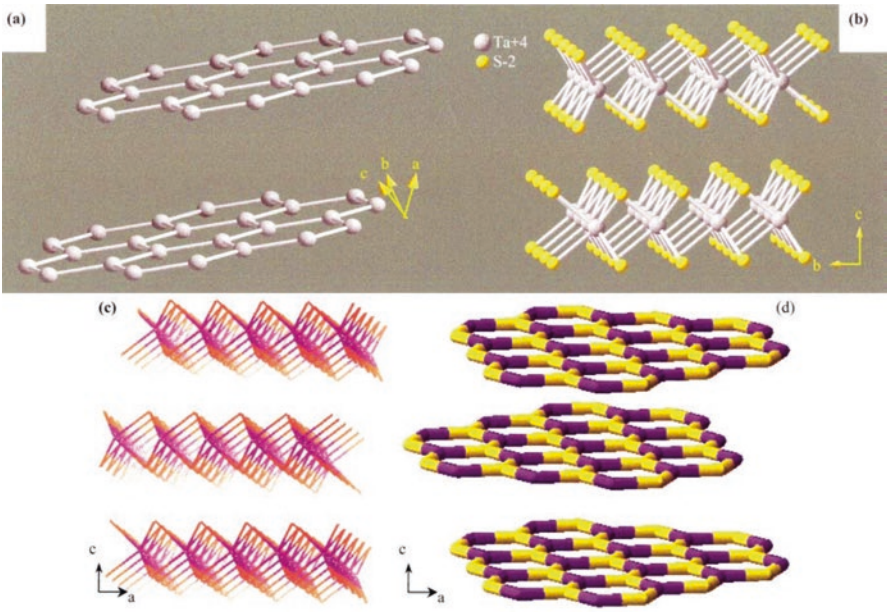


Fig. 2.4 Comparison of the structures of (**a**) graphite and inorganic layered compounds such as (**b**) NbS_2/TaS_2; (**c**) MoS_2; and (**d**) BN. In the layered dichalcogenides, the metal is in trigonal either prismatic (TaS_2) or octahedral coordination (MoS_2). (*Reproduced with permission from ref. [43]*)

Over the last two decades, the INTs have opened innovative research direction as a challenge for synthesis of new catalytic materials. The most used methods to produce INTs for catalytic applications are (1) the arc discharge and laser ablation, (2) sol–gel, (3) hydrothermal treatment, (4) assisted template method, and (5) electrochemical anodic oxidation. The main synthetic routes for INT production are summarized in Table 2.2. As it can be seen, the metal dichalcogenides (e.g., MoS_2, $MoSe_2$, and WS_2) can be easily fabricated through the arc discharge, laser ablation, as well as chemical reactions involving the stable oxides, such as MoO_3 and WO_3, upon heating [43]. The carbon nanotube template route is used to obtain INTs by adsorbing the precursors on the outer walls of CNTs and covering it with inorganic materials [51–53].

In case of the hydrothermal treatment method, it has been used for synthesizing nanotubes from several metal oxides such as SiO_2, Al_2O_3, $Na_2Ti_3O_7{\cdot}nH_2O$, V_2O_5, ZnO_2, $PbTiO_3$, and $BaTiO_3$ [54–56].

The sol–gel method provides a new approach to the preparation of INTs, as for silica, TiO_2, Ga_2O_3, and In_2O_3. Besides, the strategy based on the sol–gel route is that of the oxide gels in the presence of surfactants or suitable templates form nanotubes. The coating of the CNTs with oxide gels is performed and then burning off the carbon provides the formation of nanotubes and nanowires of a variety of metal oxides including ZrO_2, SiO_2, and MoO_3 [54]. Another method is the layer-by-layer

Table 2.2 Types of INTs produced by different routes [64–69]

Type of nanotubes	Synthetic strategy	Refs.
Al_2O_3	(1) Chips were electropolished to anodization in a solution containing ethanol and $HClO_4$ (2) H_2SO_4 was used in the first anodization step (3) After the pulses in H_2SO_4 electrolyte, the remaining aluminum substrate was removed by wet chemical etching	[64]
CeO_2	(1) $K_{1.33}Mn_8O_{16}$ nanowires and $Ce(NO_3)_3$ were transferred into Teflon-lined, during hydrothermal treatment process (2) Product was rinsed with ethanol and deionized water, and dried in air	[65]
$PdCl_2$	(1) Aqueous $PdCl_2$ was slowly added in solution containing Ag nanowires and NaCl, under vigorous stirring (2) Product was washed with ethanol and water for removing AgCl and NaCl (3) Finally, reminiscent Ag was removed with addition of H_2O_2 solution	[66]
SiO_2	(1) TEOS was added to the solution containing glycyldodecylamide (GDA) and ethanol and stirred at room temperature (2) Product was washed with ethanol to remove the surfactant (3) Aminopropyltriethoxylsilane (APTES) was added to a suspension of toluene-containing silica nanotubes (4) Solution was heated under reflux	[67]
$Na_2Ti_3O_7{\cdot}nH_2O$	(1) TiO_2 (rutile) was added in NaOH aqueous solution (2) Mixture was placed into Nalgene flask during 20 h at 110 °C (3) Product was treated with distilled water and then centrifuged to separate the powder (titanate nanotube)	[68]
MoS_2	(1) Large-surface-area MoS_2 atomic layers (2) Synthesized on SiO_2 substrates by chemical vapor deposition using MoO_3 and S powders as the reactants	[69]

(LBL) assembly of the precursors on CNT templates in combination with subsequent calcination that has been developed to prepare porous SnO_2 and In_2O_3 nanotubes [57].

Furthermore, the sol–gel chemistry can also be used to obtain oxide nanotubes in the pores of alumina membranes. Through this method, MoS_2 nanotubes are also synthesized by the decomposition of a precursor in the pores of an alumina membrane [43, 55]. Also, cobalt, iron, nickel, and copper nanotubes have been synthesized using polycarbonate membranes as templates [58].

The use of precursors via direct decomposition has been reported as a vastly applied method to obtain the disulfide nanotubes. The selenide nanotubes are obtained through H_2Se reactions whereas the sulfide nanotubes are prepared from MoS_3, WS_3, NbS_2, and HfS_2. Both molybdenum and tungsten dichalcogenides can also be obtained through the decomposition of the precursor ammonium salt, such as $(NH_4)_2MX_4$ (X = S, Se; M = Mo, W) [43]. The types of INTs produced by different routes are summarized in Table 2.2.

The metal oxide nanotubes can also be prepared by the surfactant-assisted synthesis combined with sulfidizing/selenidizing agent, with CdSe and CdS nanotubes being good examples of the use of such method [59]. Nanotubes of other oxides such as Er, Tm, Yb, and Lu have been prepared by the aforesaid template-mediated reactions using dodecyl sulfate assemblies [60].

Importantly, the transition metal halides, oxides, and nitrides in layered structures as well as GeO_2 and GaN nanotubes are reported to be prepared by heating of their salt precursors in air to vanish the water of crystallization, with the heating under nitrogen flow being the final step to prepare the solids [59]. Moreover, nanotubes of both $PbTiO_3$ and $BaTiO_3$ can be better discussed elsewhere [61]. Boron nitride nanotubes have also been prepared by coprecipitation and annealing routes and striking an electric arc between HfB_2 electrodes in nitrogen atmosphere as well [62, 63]. The polysiloxane nanotubes were synthesized via trifunctional organosilanes, as reported elsewhere [63].

Similar morphologies of the INTs including nanowires, nanorings, nanowhiskers, nanofilaments, nanorods, and nanobelts have begun to emerge through the use of the abovementioned methods [43, 63].

Among the discussed methods of synthesis, hydrothermal treatment is attractive, since it allows the preparation by a simple route and is of low cost to design catalysts.

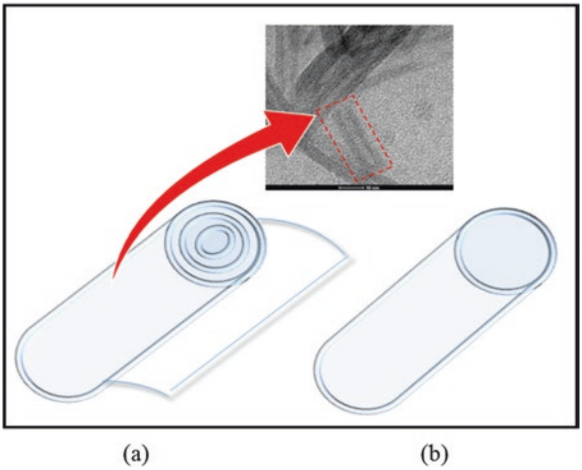
Numerous investigations have been reported to ascertain how the INT synthesis conditions affect their properties and thereby affect their catalytic performance. Therefore, suitable characterizations of the crystal and/or textural structure features of the INTs are essential in understanding their physicochemical properties. The conventional measurements by TEM, SEM, Raman and FTIR spectroscopy, XRD, TGA/DSC/DTA, and nitrogen physisorption isotherms give deep insight into the structure, texture, and surface morphologies of the synthesized INTs [49–51, 53–63]. Other techniques such as temperature-programmed desorption of CO, CO_2, or O_2 (TPD); temperature-programmed reduction of hydrogen (H_2-TPR); extended X-ray absorption fine structure (EXAFS); and X-ray photoelectron spectroscopy (XPS) give information on the reducibility, defects, and oxidation state of metal and oxygen elements of the INTs, which are indispensable properties to justify the efficiency (inefficiency) of the catalysts in the reactions.

Despite the fact that INTs have not yet been applied in industry up to now and there is still a long way to walk on before their commercialization, the easy availability, their potential for extensive applications, and tuneable physicochemical properties make them bouncy materials for catalytic studies.

2.2.2.1 Titanate Nanotubes: Preparation, Characterization, and Applications

Titanate nanotubes blossomed since the turn of the twentieth century led by pioneers such as Kasuga and coworkers [70, 71]. TNTs are 1D nanostructures consisting of a layered structure with a hollow cavity (Fig. 2.5). The scrolling of an

Fig. 2.5 Types of TNTs: (**a**) single-layer nanosheets and multilayer nanosheets (**b**)



exfoliated layered titanate nanosheet is formed in the nanotube structure through hydrothermal treatment by folding nanosheets [71]. According to the figure, there are two types of nanosheets that is to say, single-layer nanosheets, which are isolated (100) planes of titanates (Fig. 2.5a), or multilayer nanosheets (Fig. 2.5b), which are several conjugated (100) planes of titanates [71]. Additionally, both types of nanosheets are very thin and could be found in both planar and curved shapes. The TNTs can be prepared by the sol–gel, hydrothermal treatment synthesis, anodization, atomic layer deposition, template assisted, and supercritical media, providing access to the fabrication of morphologically diverse TiO_2 nanomaterials [72–75].

The hydrothermal treatment of TiO_2 is the simplest synthetic tool to obtain the TNTs with low cost and harnesses and requiring neither expensive apparatus nor special chemicals. The advantages of this technique are indeed enormous, since the TNT's unusual morphology and unique physicochemical properties can be easily and flexibly controlled. The nanosheets are usually observed in the early stage of preparation of TNTs or as a small impurity in the final product obtained via the alkaline hydrothermal treatment [71]. Moreover, dimensions and morphology can be controlled by adjusting the temperature and pressure parameters as well as the alkaline concentration and synthesis time [76–78].

Many applications of the TNTs have burgeoned since then in photocatalysts, gas sensors, photoluminescence, dye-sensitized solar cells, electrochemical capacitors, water treatment, proton conduction, lithium inserting, hydrogen storage, catalysts or catalyst carriers, medicine, proton transport, and adsorbents. The TNTs have charted progress in these areas that have indeed become prosperous fields in the discovery of new TiO_2-nanotube materials [49, 70–76, 79].

This likely pursues from the certain degree of porosity associated with the high surface areas of the solids in relation to the more straightforward understanding of the superior adsorption capacities and thereby catalytic properties of the TNT nanomaterials.

2.2.2.2 Heterogeneous Catalysis Using Titanate Nanotubes

Titanium functionalities give redox and acid-base properties making the interactions between the solid surface and hydrocarbons molecules easy. The structures derived from titanium functionalities are TiO_2 in rutile or anatase phases and titanate nanotubes. The catalytic applications of TNTs date back over 15 years and the evolution of the chemistry of the TNTs, until very recently, has been more gradual. Most of the studies on application of the titanate nanotubes in catalysis field are devoted towards their uses as catalysts or catalyst carriers.

As catalysts, the moderate acid-base property can be considered as one of the earlier attempts to use protonated titanate nanotubes in Friedel-Crafts alkylation of toluene with benzyl chloride, photocatalysis, hydroxyalkylation/alkylation of 2-methylfuran and *n*-butanal from lignocelluloses, esterification, dye oxidation, and hydrolysis of 2-chloroethyl ethyl sulfide [71, 80–83]. Despite that highly active Lewis acid catalyst with active Brønsted acid sites is often found, the TNTs provide the drawback of being not reusable for several times. Also, they have a much lower catalytic activity than the traditional catalyst applied in title reactions.

The use of TNTs as catalyst carriers has been investigated for water gas shift reaction, reduction of methyl orange, Knoevenagel reaction, isomerization of allylbenzene polymerization of methyl methacrylate, Cannizzaro reaction, CO oxidation, hydroformylation of vinyl acetate and phenol oxidation, NO_x storage/reduction, and hydrotreating for ring opening of tetralin, among others [48, 64, 71–80, 84]. Some of them are depicted in Fig. 2.6. Another interesting feature is that the as-synthesized titanate nanotubes can be *in situ* transformed into active centers for supported catalysts.

Thus, the unique physicochemical properties of TNTs seem to be imperative to attend these reactions. In this sense, TNT materials with remarkable catalytic performance have been obtained by virtue of the intercalation of metal cations in TNTs and/or decoration of metal oxide nanoparticle procedures [71]. Thereby, the majority of the studies reported on these reactions have demonstrated that the TNTs decorated with CuO, La_2O_3, RuO_2, NiO, ZnO, CeO_2, NiO, MoO_x, MnO_x, Cs_2O, and SnO_2, doped with boron or nitrogen nanoparticles, have outstanding performance as acid-base catalysts. Indeed, insights into the redox ability of TNTs is displayed, when the nanotubes contain Fe_2O_3, ZnO, Au, Cr, As, Cd, Pd, Cu, Ce, Ru, Ni, and Pt [42, 80–83, 85–93].

It is quite necessary to study the physicochemical features of the TNTs and their effect on the reaction mechanisms. Though not addressed here, the disadvantages associated to deactivation of TNTs in the reaction media due to diverse aspects as pore blocking and/or coke formation are still in debate.

Of the applications available in catalysis, photocatalysis degradation of contaminants by TNTs has been widely investigated [71, 73, 94]. One remarkable advantage of the TNTs is the elevated photocatalytic activity over counterparts of TiO_2 nanoparticles. This is due to the shape-dependent structure of the TNTs associated with their high surface-to-volume ratio and superior physicochemical properties [95]. However, the usage of TNTs in photocatalytic applications suffers from intrin-

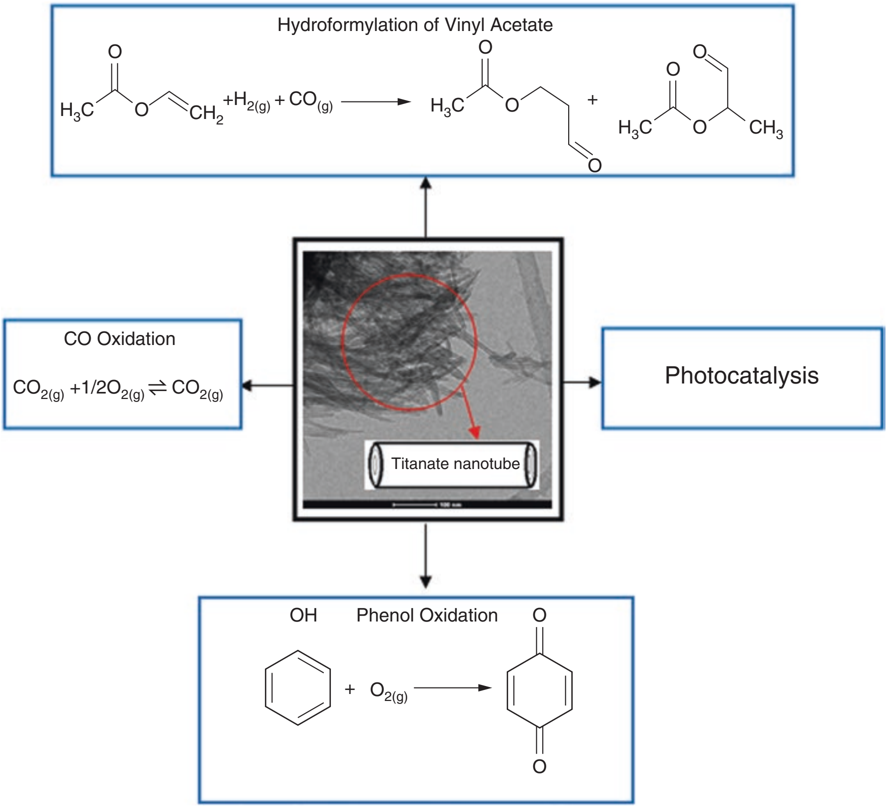


Fig. 2.6 Some reported catalytic reactions using TNTs

sic disadvantages of photocorrosion, which greatly decreases their photoactivity and photostability.

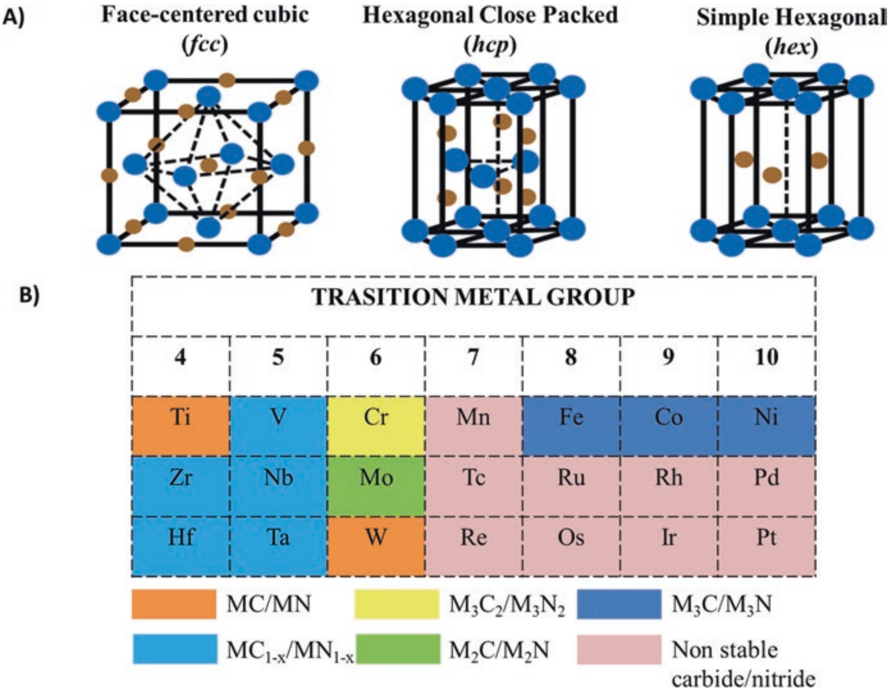
Clearly, the methods for synthesizing TNTs need to be optimized to develop the technology for an active, selective, and stable catalyst and lastly a long-standing challenge for their commercialization successfully. It should be kept in mind that the capital cost savings can be gained through the preparation of large amounts of TNT catalysts. The environmental friendly aspect is another factor that limits the discarding needs of the industrial plants and also enhances the economic feasibility of these materials as heterogeneous catalysts.

2.2.3 Transition Metal Carbides and Nitrides: General Aspects

TMC and TMN are known to be interstitial compounds where nonmetal atoms are located at big interstitial sites of the cubic and octahedral prismatic structure of metals. These materials follow Hägg's rule which establishes that the formed structure depends on the atomic ratios of metal and nonmetal elements [96].

Moreover, regarding structure and composition, it is important to mention that carbon and nitrogen form compounds with all transition metals except late metals of the second and third rows of the periodic table. TMC and TMN exhibit a variety of structures depending on metals involved, varying from *fcc* to *hex* and *hcp*. These structures are mainly determined by their electronic properties and their trends have been found to be similar to those found for metals by the Engel-Brewer theory [97, 98]. Group 6 metals form structures similar to M_2X (X = C, N), while groups 3–5 form structures like MX. It is also notable that compounds formed with early transition metals show structures such as MX and M_2X, but in the late transition metals the M_3X and M_4X stoichiometry prevailed (see Fig. 2.7). This increase in M/X ratio when moving to the right of the periodic table represents a C and N rejection of the metal and reflects a decrease in carbides and nitride stability in comparison to their parent metals [99].

The discovery of new phases with unique properties has permitted to use TMC and TMN in diverse areas, such as that reported by Yu et al. [99] in which an oxynitride of V-Mo has more activity in the HDN of quinoline under industrial conditions than the pure V or Mo nitrides, or a conventional NiMoS catalyst.



4	5	6	7	8	9	10
Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

Fig. 2.7 (**a**) Crystalline structures of TMC and TMN compounds. ● (Blue) = Metal; ● (Brown) = C o N. (**b**) TMC and TMN compound stoichiometry. Reproduced with permission of refs. [100–102]

2.2.3.1 Synthesis, Characterization, and Applications

Many methods have been developed for the synthesis of TMCs and TMNs, which can be used to obtain materials with different physical properties, such as high or low surface area. Also, bulk or supported materials can be prepared. For catalytic applications, usually high-surface-area materials are desirable, being prepared at moderate temperatures (see Table 2.3). Temperature-programmed reaction is a method that consists of the treatment of a precursor compound with a stream of reactive gas while increasing temperature uniformly (until around 700–800 °C). Oxides, sulfides, nitrides, or other compounds can be used as precursors in this method, while the reactive gas can be a mixture of a hydrocarbon (e.g., methane) and hydrogen in order to obtain carbides, and ammonia for obtaining nitrides. This reaction is usually carried out in a packed bed flow reactor with the precursor in the form of powder or pellets, using a program for temperature which enables to balance synthesis and sintering, giving products with high specific surface areas [25, 103–106]. A better control of textural properties (surface area and pore size distribution) and use of the active phase can be achieved by means of a support. Well-dispersed phases of carbides and nitrides have successfully been prepared by impregnation method to obtain oxidic precursors (as it was described earlier in Sect. 2.2.2) and then applying the temperature-programmed reaction method [15, 25, 103–107].

Table 2.3 Synthesis methods for obtaining TMCs and TMNs with low surface areas (adapted from ref. [108])

Reaction of metals or metallic compounds with reactive gases	Carbides	$M + 2C \rightarrow MC + CO_2$	Cr_3C_2, Mo_2C, TcC, Fe_3C, Fe_5C_2, Co_2C, Ni_3C
	Nitrides	$MO + NH_3 \rightarrow MN + H_2O + 1/2H_2$	Mo_2N, TiN, ZrN, HfN, VN, NbN, W_2N
Decomposition of metal halide vapors	Carbides	$MCl + H_xC_y \rightarrow MC + HCl + \ldots$	TiC, TaC, HfC
	Nitrides	$MCl + N_2/H_2 \rightarrow MN + HCl + \ldots$	TiN, VN, Re_2N, Fe_2N, Fe_4N, Cu_3N
Decomposition of metal compounds	Carbides	$W(CO)_n + H_xC_y \rightarrow WC + H_2O + CO$	HfC, VC, WC
	Nitrides	$Ti(NR_2)_4 + NH_3 \rightarrow TiN + \ldots$	TiN, Zr_3N_4
Temperature-programmed methods	Carbides	$MoO_3 + CH_4 + H_2 \rightarrow Mo_2C + \ldots$	Mo_2C, MoC_{1-x}, WC, WC_{1-x}, NbC
	Nitrides	$WO_3 + NH_3 \rightarrow W_2N + \ldots$	Mo_2N, MoN, VN
Utilization of high-surface-area supports	Carbides	$Mo(CO)_6/Al_2O_3 \rightarrow Mo_2C/Al_2O_3$	Mo_2C/Al_2O_3
	Nitrides	$TiO_2/SiO_2 \rightarrow TiN/SiO_2$	TiN/SiO_2
Reaction between metal oxide vapor and solid carbon	Carbides	$M + C \rightarrow MC$	Mo_2C, W_2C
	Nitrides	$M + 1/2N_2 \rightarrow MN$	CoN, Ni_3N_2, TiN, LaN

Furthermore, Volpe and Boudart [104] used the temperature-programmed reaction method to transform MoO_3 and WO_3 with NH_3 as a new path for the preparation of bulk Mo_2N and W_2N with high surface areas (220 and 91 m^2/g, respectively). They revealed that this transformation is topotactic, since the (1 0 0) planes of Mo_2N are parallel to (0 1 0) planes of the MoO_3, resulting in platelets of a highly porous nitride that is pseudomorph of the MoO_3. Later Boudart with Lee et al. [106] synthesized Mo carbide with a mixture or CH_4/H_2, starting from bulk MoO_3 and Mo_2N, obtaining β-Mo_2C (*hcp*; 50–100 m^2/g) and α-MoC_{1-X} (*fcc*; 200 m^2/g). These materials also exhibited pseudomorphism with precursors and topotactic changes. Later, Ramanathan and Oyama [109] prepared a series of Mo, W, V, Nb, and Ti carbides and nitrides by this method starting from metallic oxides and using CH_4/H_2 (20% v/v mixture) and NH_3 (100%).

Extensive studies regarding synthesis condition effect over active sites of these materials were carried out by Nagai and coworkers [110–114]. Nitriding temperature variations conduct to a distribution of species γ-Mo_2N, β-$Mo_2N_{0.78}$, metallic Mo and unreacted MoO_2. Low temperatures lead to high amounts of γ-Mo_2N. Increasing temperature promotes γ-Mo_2N transformation to β-$Mo_2N_{0.78}$ and metallic Mo. Also, it was noticed that the gaseous environment used during cooling to room temperature may affect product properties, since catalysts cooled in NH_3 resulted in a more active catalyst than that obtained when cooling with He. Surface properties of these materials are influenced by synthesis conditions [115], and it has to be taken into account that these materials are pyrophoric; thus, after their preparation, they must be passivated in a mixture that contains 1% or less of O_2 with a noble gas [116].

TMC and TMN have many technological applications due to their great strength and stability; they have been used as tools and they can handle severe conditions of temperature and pressure (for example in rocket nozzles). Also, they can perform optical, electronic, and magnetic functions [117–120]. These materials have also been proven to be good catalysts for ammonia synthesis, hydrogenation, Fischer-Tropsch, and reactions involving hydrogen adsorption, activation, and transfer, such as hydrotreatment reactions (HDN, HDS, and others) [104]. They have also been described to have similarities with noble metals and in some cases have resulted to be more active, selective, stable, and resistant to deactivation and poisoning [104].

Due to earlier described properties, they have been attracting attention in research and development for interesting applications in catalysis, electronics, and optics. In this chapter, specific applications as catalysts for hydrotreatment of model molecules and crude oil are discussed.

2.2.3.2 Applications as Catalysts for Hydrotreatment of Model Molecules and Crude Oil

Hydrotreatment is a process that involves different reactions and carries out the removal of S, N, and more, in the presence of hydrogen and an active catalyst. This process is widely used in the oil industry and other chemical processes. Recently, TMCs and TMNs have been considered as alternative catalysts for hydrotreatment since they are highly active and also resistant to high contents of S and N in feedstocks [16, 121–126]. Some efforts have been made to understand the active sites responsible for this behavior, most of them based on hydrogen adsorption ability [127, 128]. Also, particle size and temperatures have been considered for several authors to be determining for the adsorption-activation-transfer of hydrogen and catalytic performance of Mo and W carbides and nitrides. Noteworthy, in contrast to conventional sulfide-based catalysts, researchers have found that TMCs and TMNs with lower surface areas (large particle sizes) could lead to more active catalysts [122, 128]. Furimsky [116] discussed a mechanism proposed by Li and coworkers [129] for the adsorption activation and transfer of hydrogen over a surface of Mo nitride (due to an extensive availability of data for nitrides in contrast to carbides). This mechanism is summarized in Fig. 2.8.

First, heterolytic dissociation occurs over sites with Mo-N pairs, where blue box represents N deficiency in a surface Mo atom. It should be noticed that these deficiencies could be eliminated during passivation step and also be regenerated during reduction (or activation) with H_2. According to Nagai and coworkers [112, 113] Mo_2N prepared at high temperatures has low surface area and a high amount or N-deficient Mo atoms on the surface. In addition, Guerrero-Ruiz and colleagues [131] reported that hydrogen adsorption increases when particle size increases (and surface area decreases) in the same Mo nitride. On the other hand, high amount of surface Mo could lead to homolytic dissociation, obtaining Mo–H species, where hydrogen can be easily transferred to reactant molecules due to the low strength of the Mo–H bond. In this point, a migration of H into the subsurface and/or interstices can occur, motivated by the force of the N–H bond [122]. Similarly, this behavior could occur in the surface of Mo carbide since the bonding strengths of N–H and C–H are in the same range [132].

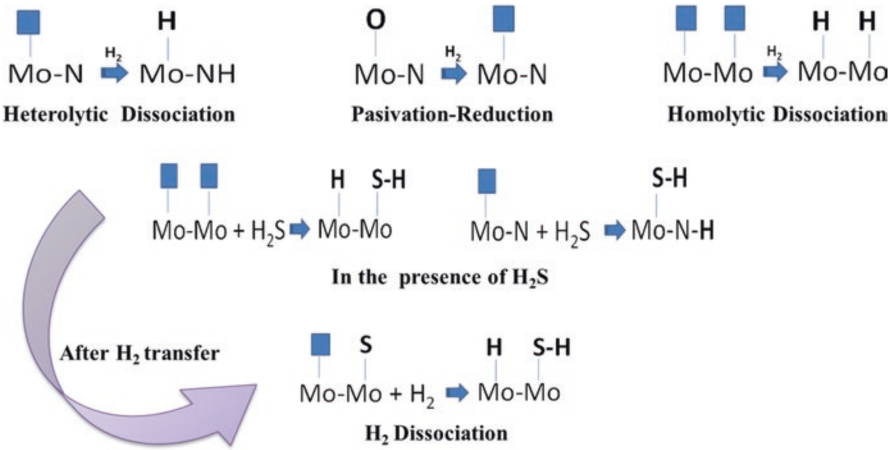


Fig. 2.8 Hydrogen activation and transfer over Mo nitride surface (adapted from refs. [116, 129, 130])

Moreover, TMC and TMN have shown interesting surface properties during hydrotreatment reactions, due to the presence (or formation) of H_2S, which have led to a surface modification obtaining a so-called sulfo-carbided or sulfo-nitrided species, showing good performances, as it was reported by several research groups [16, 133–135]. Additionally, MoS_2 slabs have been found in samples of passivated, presulfided and promoted carbides and nitrides as it was reported by Villasana et al. (see Figs. 2.9 and 2.10).

Scarcer information is available regarding the role of promoting metals in hydrogen adsorption, activation, and transfer over these materials. However, some studies have shown that promoted carbide and nitride catalysts have shown better performances than un-promoted compounds [136–139].

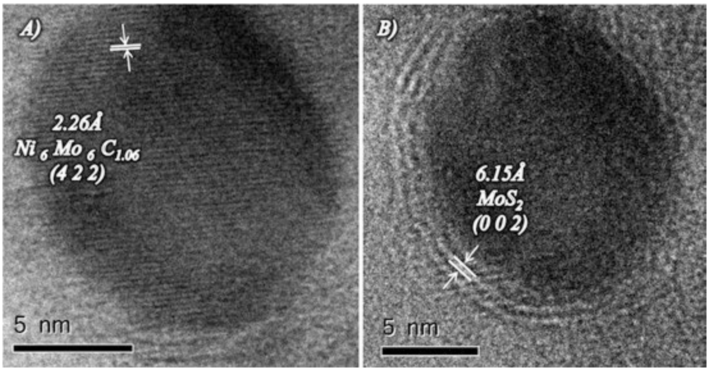


Fig. 2.9 HRTEM images of NiMo carbide (Ni/(Ni + Mo) = 0.33) after presulfiding: (**a**) NiMo carbide particle and (**b**) MoS_2 slabs coverage over NiMo carbide particle (reproduced from ref. [16])

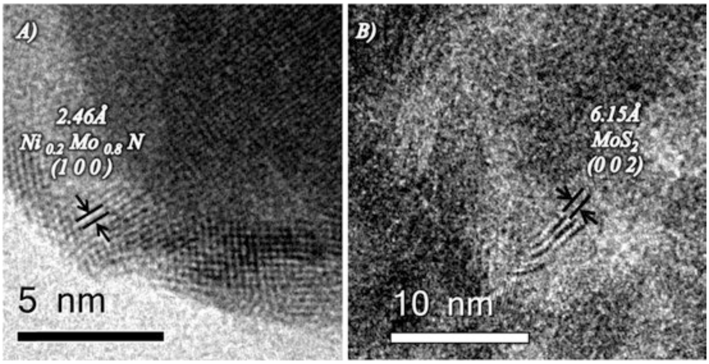


Fig. 2.10 HRTEM images of NiMo nitride (Ni/(Ni + Mo) = 0.33) after presulfiding: (**a**) NiMo nitride particle, (**b**) MoS_2 slabs in a particle agglomerate of particles in the NiMo nitride catalyst (reproduced from ref. [16])

Support role in the catalytic activity of these materials has yet to be investigated and it could be compared to earlier reports of transition metal sulfides, in terms of hydrogen migration, as it has been compared as a hydrogen reservoir [140, 141].

In these sense, Villasana [142] sustained earlier proposals of Furimsky [116], by also suggesting that during passivation process a surface monolayer of transition metal carbides and nitrides could be oxidized, and later, being sulfided (during a presulfiding step), thus being converted into MoS_2 and WS_2, based on results of XRD, ECA, SEM, and HRTEM analysis, and also thiophene HDS and crude oil hydrotreatment tests [15, 16, 143, 144]. Hence, it could have a key role in the activation and transfer of hydrogen to reactant molecules such as thiophene (model molecule) or asphaltenes (real feed), considering that both C and N attract hydrogen to the inside of particles, due to earlier mentioned C–H and N–H bond strengths, which could serve as hydrogen reservoir and promote catalytic performance. This was corroborated by the results almost simultaneously reported by Oliveira et al. [145] in which experimental and theoretical methods revealed the occlusion of hydrogen inside the bulk of Mo carbide during synthesis and reactivity tests.

TMC and TMN have been proven during hydrotreatment of diesel, light and heavy gas oil, and medium and extra-heavy crude oil, also with Carabobo crude oil (Venezuelan extra-heavy crude oil) and Maya crude oil (medium crude oil) showing good performances. Earlier reports revealed interesting results related to residue conversion, change in asphaltene and resin content and nature, sulfur and metal content, viscosity, API gravity, apparently due to cracking, HDS, and hydrogenation over these materials [16, 107, 142–144, 146–148].

Finally, due to their easy and low-cost synthesis method, transition from conventional catalysts to TMC and TMN catalysts could be done relatively quick, since they can be easily obtained by using common streams in the petrochemical industry (i.e., CH_4, H_2, and NH_3) and will also be suitable in an already installed industrial structure, since they have shown to be stable during severe conditions as industrial processes demand [109].

2.3 Summary and Conclusions

This chapter provides a summary of the synthesis of novel catalytic materials focused on titanate nanotubes and transition metal carbides and nitrides. Throughout the discussion, the primary objective has been to describe the forecasts and the method of synthesis to obtain innovative catalytic materials such as INTs, MOF, picnides, graphene, hierarchically porous materials, spinel oxides, hexaaluminates, composite oxides, and zeolites. The aims also included the aspects concerning the fundamental chemistry of precipitation, sol–gel, impregnation, and ion exchange, among other methods, for designing new catalytic materials. Among the INTs, special attention was given to the titanate nanotubes, whose unique properties allow them to be applied in a variety of catalytic processes, e.g., polymerization, photocatalytic activity, anodization, Knoevenagel reaction, oxidations, reduction of methyl orange, and acid-base and Cannizzaro reactions, and as as-synthesized catalysts or carriers. Also, the technical challenges of the synthesis that need to be overcome to enable the commercial deployment of future novel catalytic materials have been emphasized. Also, transition metal carbide and nitride synthesis, properties, and applications are discussed mainly focusing on their application in hydrotreatment reactions.

In conclusion, the consolidated methods of synthesis of catalytic materials are mature assessments, despite some remaining questions about the best method to develop the exact solid properties to attend the mechanism of a specific reaction. Interest in the use of inorganic "nanotubes," TMC and TMN appears to be increasing since these compounds are versatile as catalysts. Among the wide range of methods discussed for the TNTs, the hydrothermal treatment one is largely applied. Moreover, the TNTs are active selectives to the desired products and seem to have stability for some reactions due to their high specific surface area, redox and acid-base properties, and ion-exchange capacities. Nevertheless, there are still limitations in the industrial use of TNTs in catalytic process at severe conditions such as low recyclability, coking, and phase transformations. In order to overcome these drawbacks, efforts have been made in synthetic strategies based on the need to reduce total capital costs by developing processes with high product yields and conversions.

On the other hand, TMC and TMN are promising materials in the petroleum industry since they can accomplish several reactions over their non-fully understood active sites, and also some recent modifications of surface species (Mo and W sulfide slabs) and the incorporation of promoters (such as Fe, Ni, and Co) could enhance their performance in hydrotreating. This could lead to savings in operation and handling of heavy feedstocks in terms of time manageability, solvent consumption, catalyst poisoning, deactivation avoiding, and more, but there is still much work to do in the understanding of reaction mechanism and their physical and chemical surface behavior during hydrotreatment.

Acknowledgements The support by CNPq (473568/2012-8, 470793/2013-9) and CAPES/Funcap (23038.008860/2013-92) is greatly acknowledged. Also, Villasana wants to thank the technical support offered by Joaquín L. Brito, Franklin J. Méndez, and Yelisbeth Escalante from the Venezuelan Institute for Scientific Research and Edgar Cañizalez from PDVSA Intevep.

References

1. J. Wang, G. Cao, J. Domínguez, Advances in new catalytic materials, in *Advanced Materials Research*, ed. by J. Wang, G. Cao, J. Domínguez, (Trans Tech Publications, Stafa-Zurich, 2009), pp. 1–300
2. A. Corma, Preparation and catalytic properties of new mesoporous materials. Top. Catal. **4**, 249–260 (1997)
3. K. Wilson, A. Lee, M. Ecormier, D. Macquarrie, J. Clark, New catalytic materials for clean technology: structure-reactivity relationships in mesoporous solid acid catalysts, in

Nanotechnology in Catalysis, ed. by B. Zhou, S. Hermans, G. Somorjai, vol. 1, (Springer, New York, 2004), pp. 293–312

4. C. Pham-Huu, M.-J. Ledoux, Carbon nanomaterials with controlled macroscopic shapes as new catalytic materials. Top. Catal. **40**, 49–63 (2006)
5. K. Wilson, A.F. Lee, M.A. Ecormier, D.J. Macquarrie, J.H. Clark, *New Catalytic Materials for Clean Technology Structure-Reactivity Relationships in Mesoporous Solid Acid Catalysts*, vol 1 (Kluwer Academic/Plenum, New York, 2004), pp. 293–312
6. G. Busca, Heterogeneous catalytic materials: solid state chemistry, surface chemistry and catalytic behaviour, in *Heterogeneous Catalytic Materials: Solid State Chemistry, Surface Chemistry and Catalytic Behaviour*, (Newnes, Oxford, 2014)
7. G.L. Haller, New catalytic concepts from new materials: understanding catalysis from a fundamental perspective, past, present, and future. J. Catal. **216**, 12–22 (2003)
8. G.A. Gonzalez, M. Alvarado, M.A. Ramos, G. Berhault, R.R. Chianelli, Transition states energies for catalytic hydrodesulfurization reaction in Co9S8/MoS_2 theoretical interface using computer-assisted simulations. Comput. Mater. Sci. **121**, 240–247 (2016)
9. M. Ramos, G. Berhault, D.A. Ferrer, B. Torres, R.R. Chianelli, HRTEM and molecular modeling of the MoS2-Co9S8 interface: understanding the promotion effect in bulk HDS catalysts. Cat. Sci. Technol. **2**, 164–178 (2012)
10. M. Ramos et al., In-situ HRTEM study of the reactive carbide phase of Co/MoS_2 catalyst. Ultramicroscopy **127**, 64–69 (2013)
11. I.V. Parvulescu, E. Kemnitz, in New Materials for Catalytic Applications, vol 1 (Elsevier Amsterdam 2016) pp. 1–386
12. A. Tiwari, S. Titinchi, in Advanced Catalytic Materials, (Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusett 2015) pp. 1–446
13. ACS Publications. http://pubs.acs.org/action/doSearch?AllField=new+materials&target=default&targetTab=std&startPage=&dateRange=%3E. Accessed 20 May 2015
14. W. Moser *in* Advanced Catalysts and Nanostructured Materials (Elsevier, Amsterdam 1996) pp. 1–596
15. Y. Villasana et al., Atomic ratio effect on catalytic performance of FeW-based carbides and nitrides on thiophene hydrodesulfurization. Fuel **110**, 259–267 (2013)
16. Y. Villasana et al., Maya crude oil hydrotreating reaction in a batch reactor using alumina-supported NiMo carbide and nitride as catalysts. Catal. Today **220–222**, 318–326 (2014)
17. B. Dhandapani, T. St. Clair, S.T. Oyama, Simultaneous hydrodesulfurization, hydrodeoxygenation, and hydrogenation with molybdenum carbide. Appl. Catal. A Gen. **168**, 219–228 (1998)
18. J.M. Cameron, R.W. Hughes, Y. Zhao, D.H. Gregory, Ternary and higher pnictides; prospects for new materials and applications. Chem. Soc. Rev. **40**, 4099–4118 (2011)
19. L. Kőrösi, S. Papp, I. Dékány, Synthesis, structure, and photocatalytic activity of titanium dioxide and some of its surface-modified derivatives. L.Guczi, A. Erdôhely (eds). Catal. Altern. Energy Gener, 459–489 (2012). https://doi.org/10.1007/978-1-4614-0344-9
20. J.A. Schwarz, C. Contescu, A. Contescu, Methods for preparation of catalytic materials. Chem. Rev. **95**, 477–510 (1995)
21. J. Allouche, Synthesis of Organic and Bioorganic Nanoparticles: An Overview of the Preparation Methods, in *Nanomaterials*, (Springer, London, 2013). https://doi.org/10.1007/978-1-4471-4213-3
22. B. Grzybowska-Swierkosz, J. Haber, Chapter 11. Catalysis. Annu. Rep. Sect. C **91**, 395–439 (1994)
23. F.F. de Sousa et al., Nanostructured Ni-containing spinel oxides for the dry reforming of methane: effect of the presence of cobalt and nickel on the deactivation behaviour of catalysts. Int. J. Hydrog. Energy **37**, 3201–3212 (2012)
24. R.B. Levy, M. Boudart, Platinum-like behavior of tungsten carbide in surface catalysis. Science **181**, 547–549 (1973)
25. S.T. Oyama, Preparation and catalytic properties of transition metal carbides and nitrides. Catal. Today **15**, 179–200 (1992)

26. J. Ancheyta, M.S. Rana, E. Furimsky, Hydroprocessing of heavy petroleum feeds: Tutorial. Catal. Today **109**, 3–15 (2005)
27. J.K. Norskov, T. Bligaard, J. Rossmeisl, C.H. Christensen, Towards the computational design of solid catalysts. Nat. Chem. **1**, 37–46 (2009)
28. A. Kafizas, C.J. Carmalt, I.P. Parkin, CVD and precursor chemistry of transition metal nitrides. Coord. Chem. Rev. **257**, 2073–2119 (2013)
29. M.S. Rana, J. Ancheyta, S.K. Maity, P. Rayo, Heavy crude oil hydroprocessing: a zeolite-based CoMo catalyst and its spent catalyst characterization. Catal. Today **130**, 411–420 (2008)
30. X. Song, E. Yang, R. Ma, H. Chen, Y. Zhao, Sodium dodecyl sulfate-assisted synthesis of CoWO4 nanorods. J. Nanopart. Res. **10**, 709–713 (2008)
31. D. Astruc, Transition-metal nanoparticles in catalysis: from historical background to the state-of-the art, in *Nanoparticles and Catalysis*, (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2008), pp. 1–48. https://doi.org/10.1002/9783527621323.ch1
32. R.D. Gonzalez, T. Lopez, R. Gomez, Sol–gel preparation of supported metal catalysts. Catal. Today **35**, 293–317 (1997)
33. D. Barkhuizen et al., Experimental approaches to the preparation of supported metal nanoparticles. Pure Appl. Chem. **78**, 1759–1769 (2006)
34. D.A. Ward, E.I. Ko, Preparing catalytic materials by the sol-gel method. Ind. Eng. Chem. Res. **34**, 421–433 (1995)
35. S. Li, J. Gong, Strategies for improving the performance and stability of Ni-based catalysts for reforming reactions. Chem. Soc. Rev. **43**, 7245–7256 (2014)
36. K. Omata, H. Mazaki, H. Yagita, K. Fujimoto, Preparation of nickel-on-active carbon catalyst by CVD method for methanol carbonylation. Catal. Lett. **4**, 123–127 (1990)
37. A. Magrez, J.W. Seo, R. Smajda, M. Mionić, L. Forró, Catalytic CVD synthesis of carbon nanotubes: towards high yield and low temperature growth. Materials (Basel) **3**, 4871–4891 (2010)
38. A.C. Oliveira, N. Essayem, A. Tuel, J.-M. Clacens, Y.B. Taarit, Studies on MeAPSO-5: an investigation of physicochemical and acidic properties. Catal. Today **133**, 56–62 (2008)
39. J. Livage, Sol–gel synthesis of heterogeneous catalysts from aqueous solutions. Catal. Today **41**, 3–19 (1998)
40. S. Tait, J. Tamis, B. Edgerton, D.J. Batstone, Anaerobic digestion of spent bedding from deep litter piggery housing. Bioresour. Technol. **100**, 2210–2218 (2009)
41. J. Geus, Production of supported catalysts by impregnation and (Viscous) drying, in *Catalyst Preparation*, (CRC Press, Boca Raton, 2006), pp. 341–372. https://doi.org/10.1201/9781420006506.ch15
42. Z. Guo et al., Recent advances in heterogeneous selective oxidation catalysis for sustainable chemistry. Chem. Soc. Rev. **43**, 3480–3524 (2014)
43. C.N.R. Rao, M. Nath, Inorganic nanotubes. Dalton Trans. **1–24**, (2003). https://doi.org/10.1039/B208990B
44. J. Haber, J.H. Block, B. Delmon, Manual of methods and procedures for catalyst characterization (Technical Report). Pure Appl. Chem. **67**, 1257–1306 (1995)
45. S.-Y. Lee, R. Aris, The distribution of active ingredients in supported catalysts prepared by impregnation. Catal. Rev. **27**, 207–340 (1985)
46. M. Behrens, Coprecipitation: an excellent tool for the synthesis of supported metal catalysts—from the understanding of the well-known recipes to new materials. Catal. Today **246**, 46–54 (2015)
47. M. Sunkara, M. Meyyappan, *Inorganic nanowires: applications, properties, and characterization* (CRC Press, Boca Raton, 2009). https://doi.org/10.1201/b13579-2
48. R. Tenne, Recent advances in the research of inorganic nanotubes and fullerene-like nanoparticles. Front. Physiol. **9**, 370–377 (2014)
49. N.M. dos Santos et al., Metal cations intercalated titanate nanotubes as catalysts for α,β unsaturated esters production. Appl. Catal. A Gen. **454**, 74–80 (2013)

50. A.R. Adini, M. Redlich, R. Tenne, Medical applications of inorganic fullerene-like nanoparticles. J. Mater. Chem. **21**, 15121–15131 (2011)
51. D.V. Bavykin, J.M. Friedrich, F.C. Walsh, Protonated titanates and TiO_2 nanostructured materials: synthesis, properties, and applications. Adv. Mater. **18**, 2807–2824 (2006)
52. R. Tenne, Inorganic nanotubes and fullerene-like nanoparticles. Nat. Nanotechnol. **1**, 103–111 (2006)
53. P. Nguyen, H.T. Ng, M. Meyyappan, Catalyst metal selection for synthesis of inorganic nanowires. Adv. Mater. **17**, 1773–1777 (2005)
54. I. Kiricsi et al., Synthesis, characterization and catalytic application of inorganic nanotubes. Stud. Surf. Sci. Catal. **130**, 1115–1120 (2000)
55. H. Nefzi, F. Sediri, Vanadium oxide nanotubes VOx-NTs: hydrothermal synthesis, characterization, electrical study and dielectric properties. J. Solid State Chem. **201**, 237–243 (2013)
56. S. Kim, M. Kim, S.-H. Hwang, S.K. Lim, Enhancement of photocatalytic activity of titania–titanate nanotubes by surface modification. Appl. Catal. B Environ. **123**, 391–397 (2012)
57. H. Chu, L. Wei, R. Cui, J. Wang, Y. Li, Carbon nanotubes combined with inorganic nanomaterials: preparations and applications. Coord. Chem. Rev. **254**, 1117–1134 (2010)
58. C.N.R. Rao, A. Govindaraj, F.L. Deepak, N.A. Gunari, M. Nath, Surfactant-assisted synthesis of semiconductor nanotubes and nanowires. Appl. Phys. Lett. **78**, 1853 (2001)
59. G. Tourillon, L. Pontonnier, J.P. Levy, V.L. Electrochemically, Synthesized Co and Fe nanowires and nanotubes. Electrochem. Solid-State Lett. **3**, 20 (1999)
60. M. Yada, M. Mihara, S. Mouri, M. Kuroki, T. Kijima, Rare earth (Er, Tm, Yb, Lu) oxide nanotubes templated by dodecylsulfate assemblies. Adv. Mater. **14**, 309–313 (2002)
61. B.A. Hernandez, K.-S. Chang, E.R. Fisher, P.K. Dorhout, Sol−gel template synthesis and characterization of BaTiO3 and $PbTiO_3$ nanotubes. Chem. Mater. **14**, 480–482 (2002)
62. A. Loiseau, F. Willaime, N. Demoncy, G. Hug, H. Pascard, Boron nitride nanotubes with reduced numbers of layers synthesized by arc discharge. Phys. Rev. Lett. **76**, 4737–4740 (1996)
63. A. Stojanovic, S. Olveira, M. Fischer, S. Seeger, Polysiloxane nanotubes. Chem. Mater. **25**, 2787–2792 (2013)
64. Y. Wang, A. Santos, A. Evdokiou, D. Losic, Rational design of ultra-short anodic alumina nanotubes by short-time pulse anodization. Electrochim. Acta **154**, 379–386 (2015)
65. J. Wu et al., Chemically controlled growth of porous CeO_2 nanotubes for Cr(VI) photoreduction. Appl. Catal. B Environ. **174**, 435–444 (2015)
66. H. Hu, Z. Jiao, J. Ye, G. Lu, Y. Bi, Highly efficient hydrogen production from alkaline aldehyde solutions facilitated by palladium nanotubes. Nano Energy **8**, 103–109 (2014)
67. Y.-H. Seo, S.-C. Han, S.-E. Park, Amino functionalized silica nanotube for base catalyzed reaction. Stud. Surf. Sci. Catal. **174**, 1081–1086 (2008)
68. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Titania nanotubes prepared by chemical processing. Adv. Mater. **11**, 1307–1311 (1999)
69. Y.-H. Lee et al., Synthesis of large-area MoS_2 atomic layers with chemical vapor deposition. Adv. Mater. **24**, 2320–2325 (2012)
70. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, Formation of titanium oxide nanotube. Langmuir **14**(123), 160–3163 (1998). https://doi.org/10.1021/LA9713816
71. D.V. Bavykin, F.C. Walsh, P. O'Brien, H. Craighead, H. Kroto, *Titanate and Titania Nanotubes* (The Royal Society of Chemistry, London, 2009). https://doi.org/10.1039/9781849730778
72. A. Nakahira, T. Kubo, C. Numako, TiO_2-derived titanate nanotubes by hydrothermal process with acid treatments and their microstructural evaluation. ACS Appl. Mater. Interfaces **2**, 2611–2616 (2010)
73. P. Akhter, M. Hussain, G. Saracco, N. Russo, Novel nanostructured-TiO_2 materials for the photocatalytic reduction of CO_2 greenhouse gas to hydrocarbons and syngas. Fuel **149**, 55–65 (2015)
74. M. Myahkostupov, M. Zamkov, F.N. Castellano, Dye-sensitized photovoltaic properties of hydrothermally prepared TiO_2 nanotubes. Energy Environ. Sci. **4**, 998–1010 (2011)

75. H. Wang, S. Cao, C. Cen, X. Chen, Z. Wu, Structure–activity relationship of titanate nanotube-confined ceria catalysts in selective catalytic reduction of NO with ammonia. Catal. Lett. **143**, 1312–1318 (2013)
76. A. Elsanousi et al., Hydrothermal treatment duration effect on the transformation of titanate nanotubes into nanoribbons. J. Phys. Chem. C **111**, 14353–14357 (2007)
77. J. Edisson Morgado et al., Characterization of nanostructured titanates obtained by alkali treatment of TiO_2-anatases with distinct crystal sizes. Chem. Mater. **194**, 665–676 (2007). https://doi.org/10.1021/CM061294B
78. Y. Lan et al., Titanate nanotubes and nanorods prepared from rutile powder. Adv. Funct. Mater. **15**, 1310–1318 (2005)
79. B.C. Viana et al., Alkali metal intercalated titanate nanotubes: a vibrational spectroscopy study. Vib. Spectrosc. **55**, 183–187 (2011)
80. H. Li et al., Templated synthesis of TiO2 nanotube macrostructures and their photocatalytic properties. Nano Res. **8**, 900–906 (2015)
81. M. Kitano, K. Nakajima, J.N. Kondo, S. Hayashi, M. Hara, Protonated titanate nanotubes as solid acid catalyst. J. Am. Chem. Soc. **132**, 6622–6623 (2010)
82. A. Kleinhammes et al., Decontamination of 2-chloroethyl ethylsulfide using titanate nanoscrolls. Chem. Phys. Lett. **411**, 81–85 (2005)
83. S. Li et al., Protonated titanate nanotubes as a highly active catalyst for the synthesis of renewable diesel and jet fuel range alkanes. Appl. Catal. B Environ. **170**, 124–134 (2015)
84. K. Zhu, H. Gao, G. Hu, Z. Shi, A rapid transformation of titanate nanotubes into single-crystalline anatase TiO_2 nanocrystals in supercritical water. J. Supercrit. Fluids **83**, 28–34 (2013)
85. Y. Shi et al., Synthesis and characterization of TiO_2 nanotube supported Rh-nanoparticle catalysts for regioselective hydroformylation of vinyl acetate. RSC Adv. **4**, 62215–62222 (2014)
86. D.J.M. de Vlieger, L. Lefferts, K. Seshan, Ru decorated carbon nanotubes - a promising catalyst for reforming bio-based acetic acid in the aqueous phase. Green Chem. **16**, 864–874 (2014)
87. S.Y. Lee et al., Kinetics of styrene polymerization to syndiotactic polystyrene over metallocene catalyst on flat surface, silica nanotube reactors and porous silica particles. Macromolecules **44**, 1385–1392 (2011)
88. B. Zhu et al., Synthesis of metal-doped TIO_2 nanotubes and their catalytic performance for low-temperature co oxidation. React. Kinet. Catal. Lett. **88**, 301–308 (2006)
89. S.K. Parayil et al., Photocatalytic conversion of CO_2 to hydrocarbon fuel using carbon and nitrogen co-doped sodium titanate nanotubes. Appl. Catal. A Gen. **498**, 205–213 (2015)
90. P. Hernández-Hipólito et al., Novel heterogeneous basic catalysts for biodiesel production: sodium titanate nanotubes doped with potassium. Catal. Today **250**, 187–196 (2015)
91. D. Nepak, S. Darbha, Selective aerobic oxidation of alcohols over Au–Pd/sodium titanate nanotubes. Cat. Com. **58**, 149–153 (2015)
92. C.H. Campos et al., Immobilised chiral inducer on Pt-based mesoporous titanate nanotubes as heterogeneous catalysts for enantioselective hydrogenation. J. Mol. Catal. A Chem. **398**, 190–202 (2015)
93. Y. Wang, W. Liu, T. Wang, J. Ni, Arsenate adsorption onto Fe-TNTs prepared by a novel water–ethanol hydrothermal method: Mechanism and synergistic effect. J. Colloid Interface Sci. **440**, 253–262 (2015)
94. X. Sun, J. Zhang, G. Zhang, X. Pan, T. Huang, Preparation and characteristics of TiO_2 nanotube catalysts used in hybrid photocatalysis/membrane process. Cat. Com. **18**, 76–80 (2012)
95. F.-X. Xiao, Construction of highly ordered ZnO–TiO_2 nanotube arrays (ZnO/TNTs) heterostructure for photocatalytic application. ACS Appl. Mater. Interfaces **4**, 7055–7063 (2012)
96. G. Hägg, Gezetsmassigkeiten im Kristallbau bei Hydriden, Boriden, Karbiden und Nitriden der Ubergangselemente. Z. Phys. Chem. **12**, 33–56 (1931)
97. L. Brewer, A most striking confirmation of the Engel metallic correlation. Acta Metall. **15**, 553–556 (1967)

98. N. Engel, Copper, copper alloys and the electron concentration concept. Acta Metall. **15**, 557–563 (1967)
99. C.C. Yu, S. Ramanathan, F. Sherif, S.T. Oyama, Structural, surface, and catalytic properties of a new bimetallic V-Mo oxynitride catalyst for hydrodenitrogenation. J. Phys. Chem. **98**, 13038–13041 (1994)
100. Y. Zhong et al., Transition metal carbides and nitrides in energy storage and conversion. Adv. Sci. **3**, 1500286 (2016)
101. Y. Liu, T.G. Kelly, J.G. Chen, W.E. Mustain, Metal carbides as alternative electrocatalyst supports. ACS Catal. **3**, 1184–1194 (2013)
102. D.J. Ham, J.S. Lee, Transition metal carbides and nitrides as electrode materials for low temperature fuel cells. Energies **2**, 873–899 (2009)
103. J.S. Lee, S.T. Oyama, M. Boudart, Molybdenum carbide catalysts: I. Synthesis of unsupported powders. J. Catal. **106**, 125–133 (1987)
104. L. Volpe, M. Boudart, Compounds of molybdenum and tungsten with high specific surface area: I. Nitrides. J. Solid State Chem. **59**, 332–347 (1985)
105. L. Volpe, M. Boudart, Compounds of molybdenum and tungsten with high specific surface area: II. Carbides. J. Solid State Chem. **59**, 348–356 (1985)
106. J.S. Lee, L. Volpe, F.H. Ribeiro, M. Boudart, Molybdenum carbide catalysts: II. Topotactic synthesis of unsupported powders. J. Catal. **112**, 44–53 (1988)
107. Y. Villasana et al., Maya crude oil hydrotreating reaction in a batch reactor using alumina-supported NiMo carbide and nitride as catalysts. Catal. Today **220**, 318–326 (2014)
108. S.T. Oyama, Introduction to the chemistry of transition metal carbides and nitrides, in *The Chemistry of Transition Metal Carbides and Nitrides*, ed. by S. T. Oyama, (Springer, Netherlands, 1996), pp. 1–27. https://doi.org/10.1007/978-94-009-1565-7_1
109. S. Ramanathan, S.T. Oyama, New catalysts for hydroprocessing: transition metal carbides and nitrides. J. Phys. Chem. **99**, 16365–16372 (1995)
110. M. Nagai, Transition-metal nitrides for hydrotreating catalyst—synthesis, surface properties, and reactivities. Appl. Catal. A Gen. **322**, 178–190 (2007)
111. H. Tominaga, M. Nagai, Mechanism of thiophene hydrodesulfurization on clean/sulfided β-Mo_2C(0 0 1) based on density functional theory—cis- and trans-2-Butene formation at the initial stage. Appl. Catal. A Gen. **343**, 95–103 (2008)
112. M. Nagai, Y. Goto, O. Uchino, S. Omi, TPD study and carbazole hydrodenitrogenation activity of nitrided molybdena–alumina. Catal. Today **45**, 335–340 (1998)
113. M. Nagai, Y. Goto, O. Uchino, S. Omi, TPD and XRD studies of molybdenum nitride and its activity for hydrodenitrogenation of carbazole. Catal. Today **43**, 249–259 (1998)
114. M. Nagai et al., Temperature-programmed reduction and XRD studies of ammonia-treated molybdenum oxide and its activity for carbazole hydrodenitrogenation. J. Catal. **182**, 292–301 (1999)
115. Y.-J. Zhang, Q. Xin, I. Rodriguez-Ramos, A. Guerrero-Ruiz, Simultaneous hydrodesulfurization of thiophene and hydrogenation of cyclohexene over dimolybdenum nitride catalysts. Appl. Catal. A Gen. **180**, 237–245 (1999)
116. E. Furimsky, Metal carbides and nitrides as potential catalysts for hydroprocessing. Appl. Catal. A Gen. **240**, 1–28 (2003)
117. M. Erola, J. Keinonen, A. Anttila, J. Koskinen, TiN films prepared by nitrogen implantation on Ti-coated fused SiO_2. Sol. Energy Mater. **12**, 353–359 (1985)
118. C. Ernsberger, J. Nickerson, A. Miller, D. Banks, Contact resistance behavior of titanium nitride. J. Vac. Sci. Technol. A **3**, 2303–2307 (1985)
119. I. Suni, M. Maenpaa, M.A. Nicolet, M. Luomajarvi, Thermal stability of hafnium and titanium nitride diffusion barriers in multilayer contacts to silicon. J. Electrochem. Soc. **130**, 1215–1218 (1983)
120. M. Wittmer, Properties and microelectronic applications of thin films of refractory metal nitrides. J. Vac. Sci. Technol. A **3**, 1797–1803 (1985)
121. C.W. Colling, J.-G. Choi, L.T. Thompson, Molybdenum nitride catalysts: II. H2 temperature programmed reduction and NH3 temperature programmed desorption. J. Catal. **160**, 35–42 (1996)

122. J.-S. Choi, G. Bugli, G. Djéga-Mariadassou, Influence of the degree of carburization on the density of sites and hydrogenating activity of molybdenum carbides. J. Catal. **193**, 238–247 (2000)
123. J.-G. Choi, H.J. Lee, L.T. Thompson, Temperature-programmed desorption of H_2 from molybdenum nitride thin films. Appl. Surf. Sci. **78**, 299–307 (1994)
124. J.-G. Choi et al., Synthesis and characterization of molybdenum nitride hydrodenitrogenation catalysts. Catal. Today **15**, 201–222 (1992)
125. J. Ancheyta, Properties of catalysts for heavy oil hydroprocessing, in *Deactivation of heavy oil hydroprocessing catalysts*, (John Wiley & Sons, Inc., New Jersey, 2016), pp. 31–87. https://doi.org/10.1002/9781118769638.ch2
126. S.M. Hunter, *Molybdenum Nitrides: Structural and Reactivity Studies.* Ph.D. thesis (College of Science and Engineering, School of Chemistry, 2012)
127. K. Miga, K. Stanczyk, C. Sayag, D. Brodzki, G. Djéga-Mariadassou, Bifunctional behavior of bulk mooxny and nitrided supported nimo catalyst in hydrodenitrogenation of indole. J. Catal. **183**, 63–68 (1999)
128. S.T. Oyama, G.L. Haller, *Catalysis, Specialist Periodical Review*, vol 5 (Royal Society of Chemistry, London, 1982), p. 333
129. X. Li, Y. Chen, Y. Zhang, C. Ji, Q. Xin, Temperature-programmed desorption and adsorption of hydrogen on Mo_2N. React. Kinet. Catal. Lett. **58**, 391–396 (1996)
130. X.S. Li et al., Irreversible hydrogen uptake on Mo_2N catalyst. React. Kinet. Catal. Lett. **57**, 177–182 (1996)
131. A. Guerrero-Ruiz, Q. Xin, Y.J. Zhang, A. Maroto-Valiente, I. Rodriguez-Ramos, Microcalorimetric study of H2 adsorption on molybdenum nitride catalysts. Langmuir **15**, 4927–4929 (1999)
132. Z. Wei, Q. Xin, P. Grange, B. Delmon, TPD and TPR studies of molybdenum nitride. J. Catal. **168**, 176–182 (1997)
133. J.C. Schlatter, S.T. Oyama, J.E. Metcalfe, J.M. Lambert, Catalytic behavior of selected transition metal carbides, nitrides, and borides in the hydrodenitrogenation of quinoline. Ind. Eng. Chem. Res. **27**, 1648–1653 (1988)
134. E. Puello-Polo, J.L. Brito, Effect of the activation process on thiophene hydrodesulfurization activity of activated carbon-supported bimetallic carbides. Catal. Today **149**, 316–320 (2010)
135. E. Puello-Polo, J.L. Brito, Effect of the type of precursor and the synthesis method on thiophene hydrodesulfurization activity of activated carbon supported Fe-Mo, Co-Mo and Ni-Mo carbides. J. Mol. Catal. A Chem. **281**, 85–92 (2008)
136. Y. Li et al., The modification of molybdenum nitrides: the effect of the second metal component. Catal. Lett. **48**, 239–245 (1997)
137. E.J. Markel, J.W. Van Zee, Catalytic hydrodesulfurization by molybdenum nitride. J. Catal. **126**, 643–657 (1990)
138. J. Trawczyński, Comparison of HDS of dibenzothiophene and HDN of quinoline over supported Mo and CoMo nitrided and sulfided catalysts. React. Kinet. Catal. Lett. **69**, 293–298 (2000)
139. W. Yuhong, L. Wei, Z. Minghui, G. Naijia, T. Keyi, Characterization and catalytic properties of supported nickel molybdenum nitrides for hydrodenitrogenation. Appl. Catal. A Gen. **215**, 39–45 (2001)
140. M. Breysse, P. Afanasiev, C. Geantet, M. Vrinat, Overview of support effects in hydrotreating catalysts. Appl. Catal. **86**, 5–16 (2003)
141. M. Breysse, E. Furimsky, S. Kasztelan, M. Lacroix, G. Perot, Hydrogen activation by transition metal sulfides. Catal. Rev. Eng. **44**, 651–735 (2002)
142. Y. Villasana, *Carburos, Nitruros Y Sulfuros De Mo Y W Promovidos Con Fe, Co Y Ni, Y Su Aplicación Como Catalizadores En Hidrotratamiento De Crudos Pesados* (Venezuelan Institute for Scientific Research, Mérida and Zulia, 2014)
143. Y. Villasana et al., *Nanometric CoMo carbide and nitride as heavy oil hydroprocessing catalysts: application to an Orinoco Oil Belt crude* (NANOSUR, Miami, 2014)

144. Y. Villasana et al., Quality improvement of Carabobo heavy crude oil with Al_2O_3-supported CoW carbide and nitride nanoparticles, in International Material Research Congress (2016)
145. R.R. Oliveira Jr., A.S. Rocha, V. Teixeira da Silva, A.B. Rocha, Investigation of hydrogen occlusion by molybdenum carbide. Appl. Catal. A Gen. **469**, 139–145 (2014)
146. P. Da Costa, C. Potvin, J.-M. Manoli, B. Genin, G. Djéga-Mariadassou, Deep hydrodesulphurization and hydrogenation of diesel fuels on alumina-supported and bulk molybdenum carbide catalysts. Fuel **83**, 1717–1726 (2004)
147. V. Sundaramurthy, A.K. Dalai, J. Adjaye, Comparison of P-containing γ-Al_2O_3 supported Ni-Mo bimetallic carbide, nitride and sulfide catalysts for HDN and HDS of gas oils derived from Athabasca bitumen. Appl. Catal. A Gen. **311**, 155–163 (2006)
148. Y. Villasana, S. Ramírez, J. Ancheyta, J.L. Brito, Effect of hydrotreating reaction conditions on viscosity, API gravity and specific gravity of Maya Crude Oil, in *Computational and Experimental Fluid Mechanics with Applications to Physics, Engineering and the Environment*, ed. by L. D. G. Sigalotti, J. Klapp, E. Sira, (Springer International, New York, 2014), pp. 423–430. https://doi.org/10.1007/978-3-319-00191-3_28