



## Review paper

# Impeded solid state reactions and transformations in ceramic catalysts supports and catalysts

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## Abstract

*Impeded chemical reactions and impeded polymorphous transformation in materials are discussed, as desired effects, for stabilization of ceramic catalyst supports and ceramic based catalysts. This paper gives a short overview about the possibilities of slowing down the aging processes in ceramic catalyst supports and catalysts. Special attention is given to alumina and titania based catalysts.*

**Keywords:** ceramic based catalysts, solid state reactions, polymorphous transformation

## Contents

1. Introduction .....	173
2. Chemical reactions and physical transformation in catalysts .....	174
3. Impeded chemical reactions between catalyst components .....	176
3.1 Steam reforming catalysts .....	176
3.2 Three-way automotive exhaust gas catalysts .....	178
4. Impeded polymorphous transformations and catalyst sintering .....	178
4.1 Steam reforming catalysts .....	178
4.2 Three-way automotive exhaust gas catalysts .....	179
4.3 Titania catalysts .....	179
5. Conclusions .....	180
References .....	181

## I. Introduction

Studies involving solids are important since they identify the factors governing the reactivity of solids, allowing synthesis of new solid materials with desired structures and properties [1]. Solid state reactions are chemical reactions in which solvents are not used. Sintering and phase transitions often follow chemical reactions, however, they cannot be considered as reactions in a chemical sense. From the standpoint of catalyst stability sintering deserves a special attention. Sintering results in the loss of catalyst's active surface area due to crystal growth. In the case of supported metal catalysts reduction of the active surface area is caused by agglom-

eration and coalescence of small metal crystallites into larger ones. Nevertheless, these processes are of similar importance as chemical reactions and that is why sintering and phase transitions are usually discussed simultaneously with chemical reactions in solid state.

Chemical reactivity of materials is regularly identified by their crystal structure (or more generally, by their microstructure) rather than by intrinsic chemical reactivity of reaction constituents. When the reactivity of materials is primarily controlled by their crystal structure instead of their chemical properties the reaction is said to be topochemically controlled. In topochemical reactions the atomic arrangement in the crystal remains largely unaffected during the reaction, except the changes in dimension in one or more directions [1]. Among several conditions under which solid state reactions can take place applying high temperatures to fa-

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cilitate reactions without solvents is the most common one. In extreme cases the reactants are melted together and reaction, at least partly, occurs in the liquid phase. Presence of different impurities or gases can accelerate or impede chemical reactions or physical transformations. In our previous papers we have reported about accelerated chemical reactions and physical transformation in materials [1–5]. In many fields of industrial chemistry (ceramic, refractory and construction materials) accelerated chemical reactions and solid state transformations are desirable because they can contribute to reduction of heat input, pollution and production time. Thus, at the industrial scale the chemical reaction between calcia and silica  $3\text{CaO} + \text{SiO}_2 \rightarrow 3\text{CaO}\cdot\text{SiO}_2$  is well known as the major phase in cement formation. The reaction proceeds very slowly even at 1650–1700 °C. In industrial conditions the reaction is catalysed by  $\text{CaF}_2$ ,  $\text{Na}_2\text{SiF}_6$  [6] or  $\text{CuO}$  and  $\text{CuF}_2$  [7] in order to accelerate the formation of  $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$ . In our recent work [8] we have reported on copper ions accelerating the polymorphous polymorphous transformations of transient aluminas leading to the sintering of the catalyst support. On the other hand, these polymorphous transformations impede  $\text{CuAl}_2\text{O}_4$  spinel formation enhancing the catalyst stability. Thermal and mechanical stability of the industrial catalyst is a warranty for its long life, corresponding to high activity and selectivity. Therefore this study is devoted to impeded solid state reactions and physical transformations which can take place in different heterogeneous catalysts.

## II. Chemical reactions and physical transformation in catalysts

During the synthesis and use of heterogeneous catalysts solid state reactions and physical transformations can proceed both in bulk and on the catalyst surface. Chemical reactions between catalyst components and phase transformations in catalyst supports can lead to the loss of catalyst activity and selectivity. These phenomena are known as catalyst aging. Catalyst aging represents a serious problem especially for catalysts applied at high temperatures, as is the case with methane steam reforming catalysts, three-way catalysts for the reduction of automobile exhaust gases emission, as well as catalysts for the reduction of volatile organic components (hydrocarbons, carbon monoxide, nitrogen

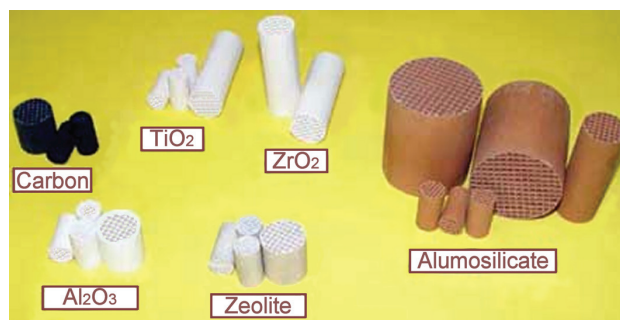


Figure 1. Monolithic honeycomb supports and catalysts [10]

oxides, ammonia, sulphur compounds) from industrial off-gases. Today, the production and development of heat- and mechanical-resistant catalysts represents one of the most important questions in the field of heterogeneous catalysis. In most of these cases heterogeneous catalysts using different supports for the positioning of an active phase are widely used. It ensures the stability of the active metal particle size, better mass and heat transfer in catalyst particles, appropriate acidity or basicity of the catalyst surface, and lower catalyst cost by reducing the loading of expensive active metal.

Catalyst supports can be prepared from various materials, including ceramics. Oxide based ceramics have great importance in catalysis due to the fairly high mechanical strength, thermal and thermal shock resistance and resistance against corrosive media. Their capability to operate at elevated temperatures in various atmospheres, combined with the possibility of making products with various configurations, porosity, acidity, activity, macro-, micro- and nano-structures make oxide based catalyst very useful and prosperous. The appropriate macrostructure, porosity, strength, and heat resistance of ceramic catalyst supports can be selected by varying the calcination temperature and other conditions [9]. Ceramic catalysts and their supports can be used in the form of granules, cylinders, rings, tubes with one or more holes, as well as in the form of monolithic units with a honeycomb or cellular structure (Fig. 1). Ceramic based catalysts can withstand high mechanical load, harsh corrosive environments and high temperatures better than most other materials. Oxides of refractory metals aluminum, zirconium, titanium, hafnium and molybdenum have outstanding resistance to oxidation and corrosion at elevated temperatures in different atmospheres.

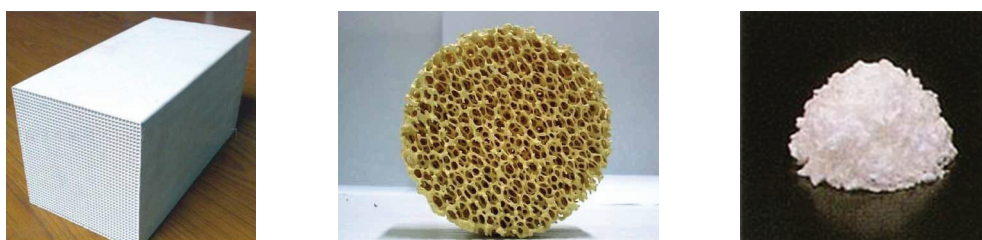


Figure 2. The structure of honeycomb, foam, and mineral wool supports [13,14]

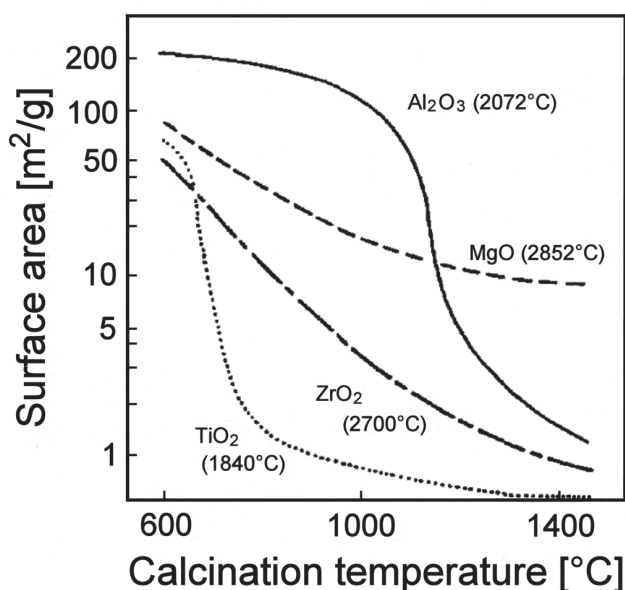


Figure 3. Specific surface area of different ceramic supports (melting point is shown in parenthesis) [15]

Ceramic foams possess also good structural characteristics that make them suitable as supports for heterogeneous catalysts. These features include high porosity with a significant degree of interconnectivity that results in low pressure-drop, while the convection in mega-pores provides enhanced mass and heat transfer (Fig. 2) [11,12].

Different ways have been devised to improve the resilience and stability of materials applied in catalysis. For example, chemical additives and surface coatings are incorporated to enhance the oxidation resistance and limit grain coarsening. Stabilization of iron on magnesia catalyst is attributed to the “skin” effect of alumina which

“covers” a part of iron oxide [16]. Stabilisation of the active iron sites on the catalyst surface represents a significant contribution and benefit of the alumina promoter. Silica and many other oxide based ceramics (MgO, CaO, BeO, HfO<sub>2</sub>, ThO<sub>2</sub>, ZrO<sub>2</sub> and Cr<sub>2</sub>O<sub>3</sub>) are chemically inert at very high temperatures and may be used either as catalyst support or promoter to improve mechanical and thermal resistance of the catalyst. Many of these oxides are very brittle, susceptible to thermal shock, or have other limitations. For example, MgO, CaO, Cr<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub> all have high melting points but also high evaporation rates [11]. In addition, MgO and CaO are hygroscopic and degrade through moisture absorption [11]. The melting point of Al<sub>2</sub>O<sub>3</sub> is lower than the melting point of MgO or ZrO<sub>2</sub>. However, its surface area is higher than the surface area of the two previously mentioned oxides up to 1200 °C (Fig. 3), therefore alumina supported catalysts are very commonly used both in the chemical industry and in the field of pollution abatement catalysis. Specific surface area dependence of Al<sub>2</sub>O<sub>3</sub> on its polymorph forms is given in Fig. 4 [15] and Fig. 5 [17]. The use of additives such as lanthanum, silicon, barium, etc., is a promising way to improve the thermal stability of alumina-based support materials. The preparation routes also influence the surface area and the pore structure at operating temperatures.

The limitations of beryllium and thorium oxides (BeO, ThO<sub>2</sub>) are in their toxicity and radioactivity [11]. Oxides of hafnium and zirconium (HfO<sub>2</sub>, ZrO<sub>2</sub>) have high melting points (2900 °C and 2770 °C, respectively) and low tendency to vaporize, but both suffer from poor thermal shock resistance [11]. Both of these oxides undergo a solid state phase transformation that leads to large volume changes, residual stresses, cracking, and failure. Frequently, additives such as CaO, MgO and Y<sub>2</sub>O<sub>3</sub> are incorporated in ZrO<sub>2</sub> and HfO<sub>2</sub> to stabilize their crystal structure and prevent transformations and volume changes, but these additives also tend to lower their melting and softening temperatures, thus limiting their high temperature use [14]. Sulphur slows the transformation of active to inactive crystal form of zirconium oxide [18].

Titanium dioxide (TiO<sub>2</sub>) is also very often used in catalysis. Titanium dioxide occurs in nature as the minerals anatase, rutile, brookite, octahedrite, and ilmenite [19]. Anatase can be converted in hydrothermal conditions into delaminated anatase forming nanotubes and nanoribbons (Fig. 6) [20]. Titanium dioxide in the anatase form is a photocatalyst under ultraviolet (UV) light ( $h\nu \geq E_g = 3.2$  eV) [21,22]. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals, and can oxidize organic compounds directly into H<sub>2</sub>O and CO<sub>2</sub> [22,23]. The key problem of preparing of the titania based catalyst is the relatively low temperature of phase transition of the catalytically active crystalline form of TiO<sub>2</sub>, anatase, to its poorly active form, rutile. This problem will be discussed in a later chapter.

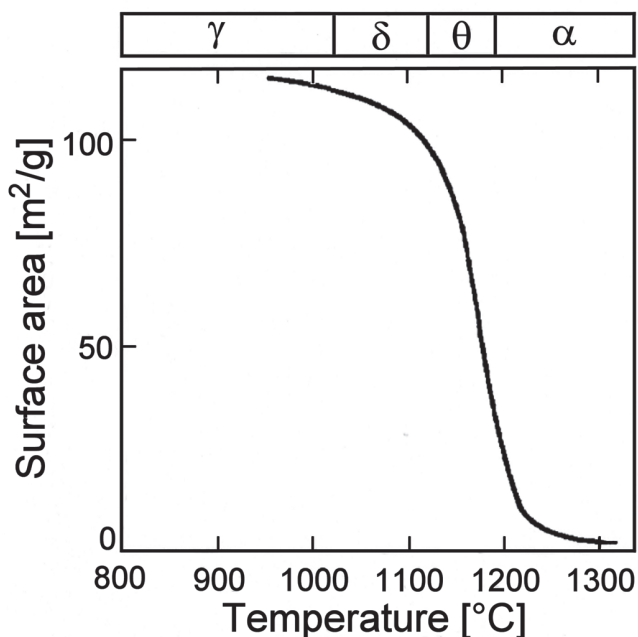


Figure 4. Phase transformations and specific surface area of alumina [15]



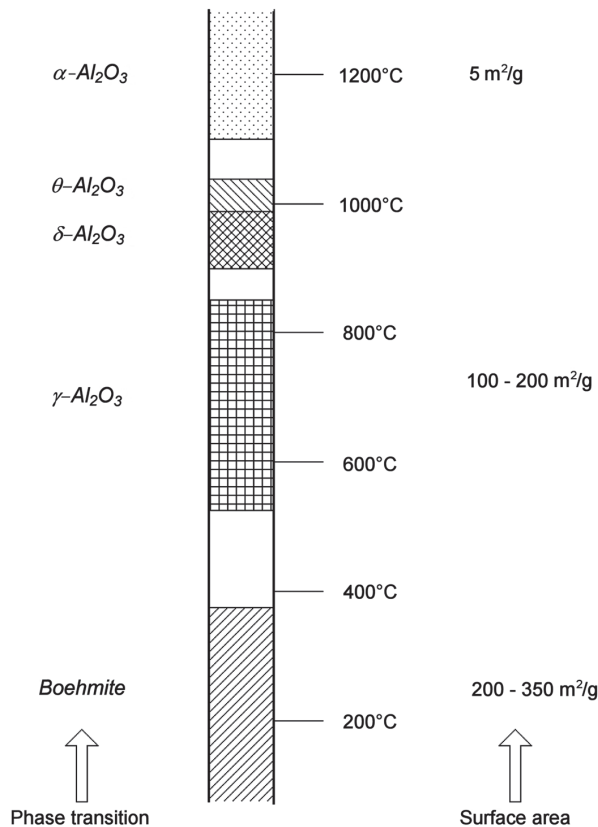


Figure 5. Phase transitions and specific surface area of alumina (starting from boehmite) [17]

### III. Impeded chemical reactions between catalyst components

Chemical reactions are such processes which lead to the transformation of one set of substances to another. The state of matter (atoms, ions) in materials largely determines the chemical changes, *i.e.* there are marked interdependences between the structure of materials (crystal form and its parameters) and their reactivity. Besides chemical affinity of materials and the reaction parameters the reaction rate depends also on the migration velocity of atoms or ions, and lattice defects of reactants. There are many other parameters which govern solid state reactions, such as metal dispersion, particle size distribution, number and volume of contacting surfaces, presence of impurities, preparation technique, etc. Every listed parameter can either accelerate or decelerate solid state reaction depending on reactants and the producer's desire. The impeded chemical reactions between catalyst components will be described with two characteristic examples.

#### 3.1 Steam reforming catalysts

Nickel supported on alumina represents a conventional steam reforming catalyst [24–27]. At high temperatures (700–1100 °C) in the presence of a nickel catalyst steam reacts with methane to yield carbon monoxide and hydrogen. Metallic nickel is the active form

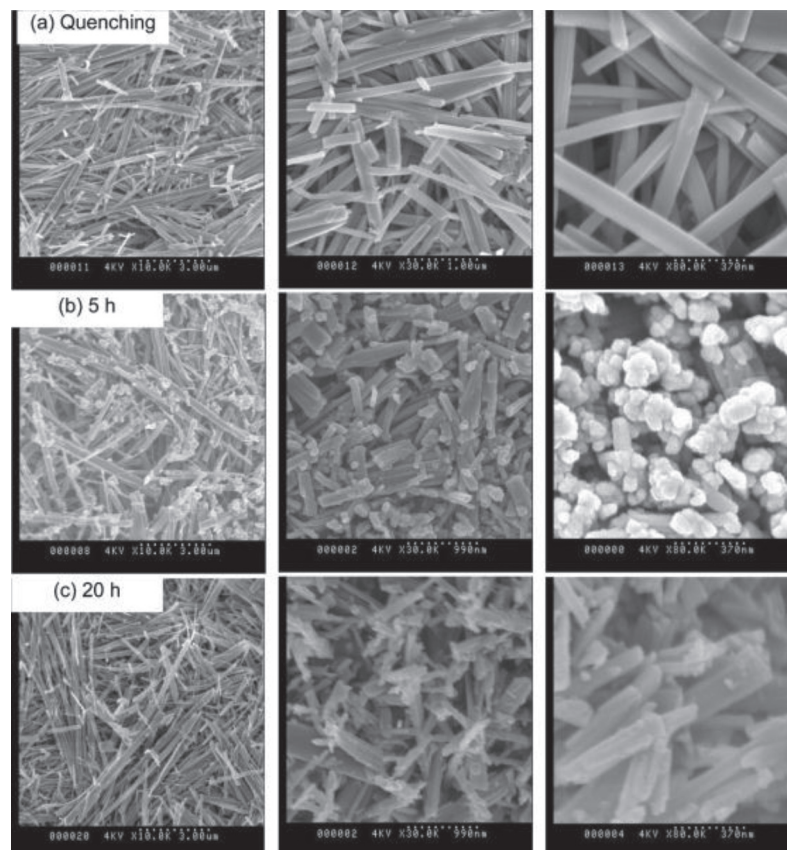


Figure 6. SEM images of titanate samples treated by: a) quenching in an ice bath, b) aging at room temperature for 5 h, or c) aging at room temperature for 20 h [20]

**Table 1.** Phase composition and textural properties of the NiO-Al<sub>2</sub>O<sub>3</sub> binary systems with  $\approx 8$  wt.% of nickel prepared by co-precipitation, impregnation and mechanical powder mixing, thermally treated at 400, 700 and 1100 °C in air [36,37]

Sample characteristics	Calcination	Co-precipitation	Impregnation	Mechanical mixing
Phase composition	400 °C	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; NiO
Surface area [m <sup>2</sup> /g]	400 °C	428	438	269
Aver. pore radius [nm]	400 °C	2.3	2.0	4.3
Phase composition	700 °C	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; NiAl <sub>2</sub> O <sub>4</sub> *	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; NiAl <sub>2</sub> O <sub>4</sub> *	$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ; NiO
Surface area [m <sup>2</sup> /g]	700 °C	186	181	174
Aver. pore radius [nm]	700 °C	8.8	5.1	11.5
Phase composition	1100 °C	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> ; NiAl <sub>2</sub> O <sub>4</sub>	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> ; NiAl <sub>2</sub> O <sub>4</sub>	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> ; NiAl <sub>2</sub> O <sub>4</sub>
Surface area [m <sup>2</sup> /g]	1100 °C	12	1.2	5.6
Aver. pore radius [nm]	1100 °C	73.1	401.9	89.9

NiAl<sub>2</sub>O<sub>4</sub>\* in traces

of the catalyst, therefore strong catalyst component interactions, like the one leading to the inactive spinel, NiAl<sub>2</sub>O<sub>4</sub>, have to be avoided. The simplest way to achieve this is to use the most thermodynamically stable form of alumina support,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The rate of nickel spinel formation on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is two orders of magnitude lower than on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [28]. Similar results on low spinel formation were obtained using zinc, magnesium and copper on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, in contrast to the reactions using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a support [29]. Main mechanisms which are responsible for such behaviour are: topotactic effect, Hedvall effect, contacts between the active metal and support, and mass transport in the reaction zone. Topotactic effect is based on the resemblance between the dimensions of cubic spinel lattices of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (0.790 nm), and corresponding spinel of Mg- (0.808 nm), Zn- (0.808 nm) and Cu- (0.806 nm). Hedvall effect is produced by a series of polymorphous transformation of alumina leading to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ( $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$ ). The speed of the polymorphous transformations of thermodynamically unstable aluminas could be affected by a variety of different ion species. Usually Ca<sup>2+</sup>, Be<sup>2+</sup>, Cr<sup>2+</sup>, La<sup>3+</sup>, Th<sup>4+</sup>, Ce<sup>4+</sup>, and Zr<sup>4+</sup> hinder, while Fe<sup>3+</sup>, Mn<sup>3+</sup>, Co<sup>3+</sup> and Mo<sup>6+</sup> accelerate the transformation [30,31]. Polymorphous transformations could be facilitated by high surface area of the initial porous alumina too [30].

High surface area of porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (100–200 m<sup>2</sup>/g) provides better dispersion of nickel, easier mass transport and higher reaction rate in methane steam reforming reaction compared to the catalyst prepared on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support with a low surface area of  $\approx 5$  m<sup>2</sup>/g. However, the thermodynamically most stable form,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, with a very compact structure, high density and low surface area shows very good resistance against the nickel-spinel formation. Support is a fundamental part of the catalyst and cannot be considered separately. Other refractory oxides, like  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, MgO, MgAl<sub>2</sub>O<sub>4</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub>, are also often used as catalyst supports. These supports should have good porosity, which results in proper contact time between reactants and catalyst en-

hancing its activity [32]. High active surface area can be achieved by adding rare earth promoters, like zirconium and lanthanum oxides [33]. Lanthanum oxide, La<sub>2</sub>O<sub>3</sub>, is one of the best stabilizers of the textural properties of alumina [34]. Rare earth metals addition to the nickel catalyst show generally positive effect to its thermal stability and raise resistance to catalyst coking [31]. Arai and Machida papers [15,35] were devoted to the thermal stabilization of catalyst supports. They have demonstrated high effectiveness of BaO, La<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and K<sub>2</sub>O in preserving the high surface area of alumina due to the limitation of surface and volume diffusion which has an effect on the phase transformation too. Barium oxide addition to alumina support causes stabilization of the textural properties of steam reforming catalysts. Barium oxide stabilizes the surface area of alumina support, being especially effective after holding the catalyst at temperature of 1050–1100 °C. Potassium oxide, K<sub>2</sub>O, has stronger interactions with nickel phase than with the support and causes its stabilization on the surface of the reforming catalyst [15,35].

The catalyst preparation procedure also significantly influences the creation of nickel spinel in the steam reforming catalyst. The data listed in Table 1 shows the phase composition and the textural properties of the NiO-Al<sub>2</sub>O<sub>3</sub> binary model systems of steam reforming catalyst, prepared by co-precipitation, impregnation and mechanical powder mixing, thermally treated at 400, 700 and 1100 °C in air [36,37]. Interaction between catalyst components is clearly the weakest when the system is prepared by mechanical mixing of catalyst components. Free NiO phase in this system is present at 400 °C, and even in the sample treated at 700 °C. In contrast, for the systems prepared by co-precipitation and impregnation, the nickel compounds were not observed after calcination temperatures as low as 400 °C. This can be explained by the excellent distribution of nickel oxide in the alumina bulk and on the alumina surface, which is certainly one of the most important prerequisites for the spinel formation.

### 3.2 Three-way automotive exhaust-gas catalysts

Support for three-way catalysts for CO and hydrocarbon residues reduction from automobile exhaust gases is usually made from cordierite,  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ . The monolith support is made by means of a precise extrusion process, which allows the production of channels of various shapes and sizes. Cordierite possesses an extremely low thermal expansion coefficient and low thermal conductivity. The main characteristics of the catalyst support are: low thermal expansion coefficient (about  $10^{-6} \text{ }^\circ\text{C}^{-1}$ ); high heat resistance (capability to withstand local and general heating up to  $1000 \text{ }^\circ\text{C}$  without changes in the composition, structure, and properties); low gas-dynamic resistance (no more than  $26.66 \text{ kPa}$  at an exhaust flow rate of  $200 \text{ nm}^3/\text{h}$ ); fairly high mechanical strength (crushing strength of up to  $7\text{--}10 \text{ MPa}$  per product), including under vibration; resistance to water vapour, vapours of sulphurous, phosphorous, and chlorous compounds, soot, etc.; a rather high porosity (about  $40\%$ ) and activity, and the pore size should be of the order of  $4\text{--}6 \text{ }\mu\text{m}$  [9,38].

The catalyst support contains a large number of small channels, each about  $1 \text{ mm}$  in diameter. The washcoat is impregnated on these channel walls. The thickness of the washcoat layer is  $20\text{--}60 \text{ }\mu\text{m}$  and it has a large surface area of approximately  $50\text{--}200 \text{ m}^2/\text{g}$ . The main compounds in the washcoat are base-metal oxides, such as aluminum, cerium and zirconium. Cerium is present in high quantities in the form of  $\text{CeO}_2$  ( $\sim 20 \text{ wt.}\%$  of washcoat  $\text{Al}_2\text{O}_3$ ) [39]. In addition to these oxides, minor washcoat compounds are  $\text{CaO}$  and  $\text{MgO}$ , as well as the oxides of rare earth elements, such as  $\text{La}_2\text{O}_3$ . These compounds are used as promoters and stabilizers, i.e. they increase the catalytic activity and stabilize the catalyst structure. Precious metals like Pt, Pd and Rh make the active component of this catalyst, with usual loading of  $\sim 1\text{--}2 \text{ wt.}\%$  of the washcoat. Their task is pretty demanding as reduction and oxidation reactions have to be performed simultaneously. Thus rhodium has proven to be an efficient catalyst for  $\text{NO}_x$  reduction, whereas palladium and platinum metals are used in CO and hydrocarbon oxidation reactions. Therefore, commercially-used three-way catalysts for gasoline engines are often a bi-metallic combination of the precious metals, such as Pt-Rh or Pd-Rh [39]. The role of ceria is to act as oxygen reservoir, providing just enough for oxidation without interfering with reduction part of the reaction.

## IV. Impeded polymorphous transformations and catalyst sintering

Polymorphous transformations imply processes whereby physico-chemical properties of a substance are altered by a rearrangement of the atoms in the initial crystal substance. Polymorphism refers to the ability of a solid material to exist in more than one crystalline form. The change that takes place between crystal struc-

tures of the same chemical compound is called polymorphic transformation. Different polymorphs have different arrangements of atoms within the unit cell, and this can have a very significant effect on the properties of the catalysts. According to Gibbs' rules of phase equilibrium, the crystalline phases are dependent on the extensive variables such as pressure and temperature. Understanding the mechanisms of phase transformations is fundamental to catalysis as, in many cases, only one of the crystalline phases has significant catalytic activity or selectivity. In some other cases catalysts perform with maximum activity only at the temperature of polymorphous transformation of its constituents. That is the reason to have a catalyst in a strictly determined crystalline form as well as to insure stable process conditions such as pressure, temperature, etc.

The impeded polymorphous transformations and catalyst sintering will be described with three characteristic examples.

### 4.1 Steam reforming catalysts

As mentioned above it is very important to impede reaction between the components in the conventional steam reforming catalyst (nickel supported on alumina). It is equally important, however, to control phase composition of the alumina support in the same catalyst. Schaper *et al.* are among the first authors who have reported that addition of lanthanum stabilizes  $\gamma\text{-Al}_2\text{O}_3$  by preventing its phase transformation into  $\alpha\text{-Al}_2\text{O}_3$  [40–42]. Addition of lanthanum oxide increases the transformation temperature by  $100 \text{ }^\circ\text{C}$ . The results indicate that the phase transformation does not contribute significantly to the loss of surface area at high temperatures [40]. In addition, the stability of the  $\gamma\text{-Al}_2\text{O}_3$  was improved by the presence of lanthanum in steam-containing atmospheres at high pressures and temperatures [41]. Addition of lanthanum oxide decreases the rate of surface diffusion by the formation of lanthanum aluminate surface layers resulting in decrease of the rate of catalyst sintering [40]. This phenomenon was observed for both  $\gamma$ - and  $\theta\text{-Al}_2\text{O}_3$  at high temperatures ( $800\text{--}1100 \text{ }^\circ\text{C}$ ) [42]. According to Chen *et al.* [33] the formation of  $\text{LaAlO}_3$  mainly retards the surface area loss resulting from the  $\alpha$  phase transformation. Lanthanum aluminate is a member of a class of ceramics known as perovskites. The stability of perovskites depends on crystal field stabilization energy of transient metal ions that is embedded in its crystal structure [44]. Borowiecki and Ryczkowski observed high efficiency of lanthanum oxide as a stabilizer of nickel on alumina catalyst up to  $1100 \text{ }^\circ\text{C}$ . According to these authors surface area of this catalyst is higher than the surface area of the sample without lanthanum by a factor of four. The promoting effect of lanthanum addition has an influence on nickel, too. Thermal treatment in the temperature range  $1000\text{--}1100 \text{ }^\circ\text{C}$  in the presence of lanthanum causes growth of the nick-



el active surface area [34]. Lanthanum oxide, or oxides of rare earth metals are very often proposed as promoters or additives for nickel catalysts applied in reforming processes. The promoter mechanisms may be various, and authors report on its influence on structure, thermal stability, activity and resistance to coking [34].

#### 4.2 Three-way automotive exhaust-gas catalysts

Three-way catalyst have to work at temperatures higher than 1000 °C, however, the thermal degradation of this catalyst begins in the temperature range between 800–900 °C. Sometimes even lower temperatures are of interest since sintering of precious metals becomes significant above 600 °C. Catalyst deactivation appears as the consequence of: i) the loss of catalytic surface area due to crystal growth of the precious metal particles, ii) the loss of washcoat area due to a collapse of the pore structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and/or iii) chemical transformations of catalytic active phases to non-catalytic phases. The first two processes are typically referred to as sintering and the third as the solid-solid phase transition at high temperatures [45]. The nature of the sintering process is more physical than chemical, while the polymorphous transition is a typical physical process. That is the reason why solid state reactions, sintering and polymorphous transformations have different thermal dependences. Location of the active phase on the support, i.e. its closeness to particular sites, may contribute to the prevention of catalyst sintering. The presence of additives, such as CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and BaO, contributes to the catalyst stabilization and reduces the catalyst sintering. Ceria, as a structural promoter can stabilize precious metal particles on the catalyst surface and reduces alumina sintering by preventing its particle growth. Ceria reduces polymorphous transformation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> into inactive  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> form. Highly dispersed lanthanum species formed by interaction of La<sub>2</sub>O<sub>3</sub> with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> retard both sintering and phase transformations, as well as associated surface area loss. Formation of lanthanum perovskite, LaAlO<sub>3</sub>, retards polymorphous transformation of  $\gamma$ -alumina  $\rightarrow$   $\alpha$ -alumina and accompanied surface area decrease [33,43]. Stabilization of transitional alumina is achieved by nucleating a cubic LaAlO<sub>3</sub> structure on the surface of the alumina support. The structural transition to corundum is inhibited by strong surface interactions between the thermally stable cubic perovskite compound and alumina. The strength of the interaction is a result of structural analogies of LaAlO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, both holding *fcc* crystal framework [46]. Chandradass *et al.* [47] explained the transformation of different thermodynamically unstable aluminas into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by the fact that these transitional aluminas differ from each other only in the degree of ordering of the oxygen lattice. The formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> from transitional aluminas involves the rearrangement of the oxygen lattice from a more or less

distorted cubic array to a hexagonal close packed structure. Following this transformation, the cations occupy the octahedral sites and there is an increasing ordering of the cation vacancies. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase forms by a nucleation and growth process. When zirconia as a dopant is concerned, it more readily dissolves in transitional aluminas than in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> because of the cubic spinel structure with a considerable number of defects and disorder. During the transformation to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the zirconium ions come out of the cubic lattice and enter the vacant and interstitial sites causing expansion of the lattice along the *a*-axis. The zirconium ions probably exert a dragging force on the diffusion of aluminium ions. Hence, the transformation to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> occurs at higher temperatures in the presence of zirconia [47]. Barium oxide addition into alumina support causes stabilization its textural properties [34]. In addition, increased thermal stability is explained by the stabilization of transitional alumina ( $\theta$ -Al<sub>2</sub>O<sub>3</sub>) by formation of barium aluminate, BaAl<sub>2</sub>O<sub>4</sub>, as a surface layer [48].

#### 4.3 Titania catalysts

Titanium dioxide occurs in nature as minerals rutile (tetragonal), anatase (tetragonal, where the vertical axis of the crystals is longer than in rutile) and brookite (orthorhombic). In addition there are two high pressure forms, a monoclinic baddelevite-like form and an orthorhombic  $\alpha$ -PbO<sub>2</sub>-like form [49]. The most common is rutile, which is also the most stable form of titania. Anatase and brookite both convert to rutile upon heating. Following the heat-treatment of hydrous TiO<sub>2</sub> powders, obtained from TiCl<sub>4</sub> precursor by precipitation with aqueous ammonia under different pH values, reveals that the anatase-to-rutile transition starts with brookite-to-anatase one. Figure 7 shows the volume fraction of rutile as a function of pH synthesis and treatment temperature, indicating that the powders obtained at the lowest pH values had the lowest transition temperatures. The anatase-to-rutile transformation was almost completed for all the samples below 900 °C [50].

Firing of ceramic catalysts based on anatase is especially complicated since the temperature is limited to 500–550 °C because of the polymorphous transformation of anatase to rutile, as titanium dioxide in the rutile form has a considerably lower activity than anatase does. According to the results obtained by Hu *et al.*, [50] anatase obtained at higher pH values shows higher stability toward undesired polymorphous transformation than the samples synthesized at lower pH values. For nanocrystalline anatase samples with less dense particle packing, both interface nucleation and surface nucleation control the anatase-to-rutile transformation between 620 and 690 °C. Below 620 °C, or in the range 620–680 °C for nanocrystalline anatase samples with denser particle packing, interface nucleation dominates the transformation. At very high temperatures

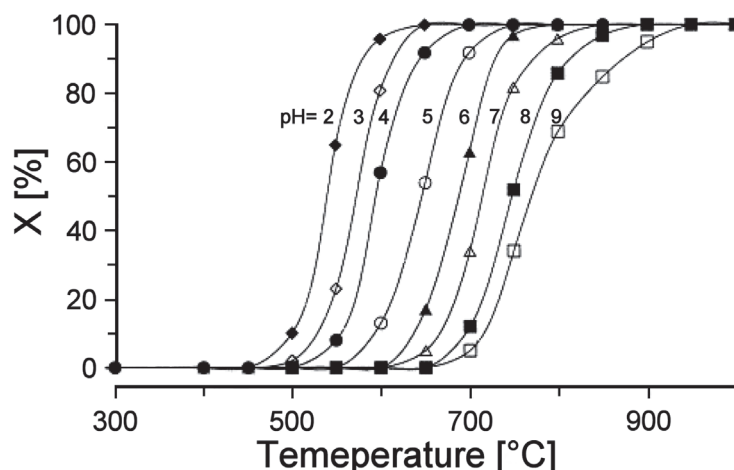


Figure 7. Correlation between the anatase-to-rutile transformation fraction in (%) and the temperatures of heat treatment for the precipitated powders [50]

(1150 °C), transformation proceeds mainly through bulk nucleation. Mixed alumina particles can largely affect the interface nucleation in nanocrystalline anatase samples. The temperature and particle packing, determined by the sample preparation and/or by the introduction of a second phase (promoter, stabilizer), can be employed to control the phase transformation and particle coarsening of nanocrystalline particles in order to obtain the desired microstructures and, thus, the optimized material properties [51]. Phosphate content in titania (0.1–0.5 mass %  $P_2O_5$ ) causes the anatase-to-rutile transformation ratio to drop 2 to 10 times. Moreover, the presence of phosphates restricts the unfavourable growth of anatase and rutile crystallites. In fact, their crystallites size was found 2–3 times lower relative to the crystallites size without phosphates [52]. Beside catalytic activity the catalyst should have good strength, heat resistance, porosity, etc. Anatase can be converted by hydrothermal synthesis to delaminated anatase - inorganic nanotubes and titanate nanoribbons which are of potential interest as catalytic supports and photocatalysts [53–55]. Porous nanostructured titania catalysts which can be used at relatively higher temperatures are of great importance, as it is more practical to carry out chemical reactions at elevated temperatures. The initial surface area of such catalysts is relatively high, even over 100 m<sup>2</sup>/g, and its stabilization is necessary during high-temperature treatments. When nanosized (5 to 10 nm) particles are prepared by the sol-gel route, the least stable phase is precipitated first. In the case of titania that is anatase, the metastable phase is formed first and upon heat treatment it will convert to the stable catalytically inactive rutile form. During any metastable-to-stable phase transformation, there is a drastic reduction in surface area because of faster densification due to the enhanced mass transport. The level of packing and higher particle coordination number (particle neighbours with physical contact) influence thermal stability of catalyst supports and ceramic membranes. Coordination num-

ber has a direct influence on the sintering and crystallite growth. Sintering and crystallite growth are successfully manipulated by doping titania with lanthanum and ruthenium oxide. Most effective techniques for porous nanocomposite formation are the stabilization of titania in the alumina matrix phase [56].

## V. Conclusions

Impeded chemical reactions in materials can be achieved by proper selection of ceramic support, both in terms of chemical composition and the polymorphic form of catalyst components. Properly chosen method and process parameters of catalyst synthesis contribute to catalyst stabilization. Different additives/promoters can significantly contribute to catalyst stabilization too. Stabilization of the catalyst active phase can be achieved by stronger interaction of promoter with catalyst active component than with catalyst support.

Another example of catalyst stabilization is the “skin” effect of promoter, which “covers” a part of active component on the support surface hindering its sintering. Rare earth metals, especially lanthanum, react with alumina forming an extremely stable perovskite,  $LaAlO_3$ , which retards the surface area loss resulting from phase transformation of the support. Oxides like  $BaO$ ,  $La_2O_3$ ,  $SiO_2$  etc. show high effectiveness for preserving high surface area of alumina due to limitation of surface and volume diffusion which has an effect on the phase transformation too. Different additives can decelerate polymorphous transformation of other typical ceramic supports, e.g. sulphur slows down the phase transformation of zirconium oxide, or phosphorus that affects titanium oxide. Effective catalyst stabilization can be achieved by the dispersion of dopants into supports, like titania in the alumina matrix. Resulting phase transformation deceleration slows down catalyst supports sintering.

The method of catalyst preparation also significantly influences the catalyst stability. Interaction between catalyst components is usually the weakest when catalyst is



prepared by mechanical mixing of its components. On the other hand, catalysts prepared by co-precipitation show high capacity to achieve good catalyst components interactions and excellent distribution of the active component within the support. Impregnation of the catalyst support with the solution which contains ions of the active component can provide a stabile catalyst with satisfactory catalyst component distribution on the surface of the catalyst support. It is recommended to first prepare the support with a desired structure and texture, and then to introduce the active component on it.

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