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Novel catalyst design for multiphase reactions

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Abstract

The role of catalyst design and its integration with reactor design in multiphase reactions are examined according to the three main levels (nano-, micro- and macro-scale) at which catalyst design should be considered. The main concepts discussed are (i) control of the local effective concentration of reagents and possible deactivating molecules around the active sites by incorporating them into nanoporous cavities and by tuning the hydrophilic character of the support, (ii) possibilities offered by microstructuring catalyst composition (multilayer design and microassembled catalyst bodies) and (iii) opportunities offered by the use of macrostructured catalysts (monoliths, cloths and membranes). The various levels of design are not independent. They must be considered in an integrated view and in close relationship with reactor design.

Keywords: Catalyst design; Multiphase reactions; Structured catalysts; Nanocatalyst design; Multilayer catalysts

1. Introduction

Catalytic multiphase reactions are involved in many chemical processes ranging from refining to fine and specialty chemistry [1]. Recently, considerably interest was also focused on their use in the area of environmental protection and sustainable chemistry where the presence of concentration gradients influences considerably selectivity, activity and/or stability and therefore a proper reactor design is critical [1–3].

Different types of reactors are being used commercially in three-phase reactions. Of particular importance are bubble column and slurry or trickle bed reactors, each having advantages and limitations. The choice depends on various factors, such as the catalyst characteristics, mass- and heat-transfer limitations, scale-up, fluidodynamic and flow regimes, pressure drop and liquid holdup, etc. However, often there is a contrast between optimal conditions for efficient multiphase contact, high catalyst effectiveness and wetting efficiency, and low fouling/attrition and pressure drop. In these cases, a new type of reactors based on structured catalysts [4], such as monolithic catalysts [5,6], are an attractive alternative to conventional multiphase reactors, due to low-pressure drop, absence of a need for catalyst separation, and the large geometrical surface area. Other types of structured catalysts also have been proposed such as foam, membrane and cloth-type (fiber) catalysts. Use of these structured catalysts in the area of environmental protection and sustainable chemistry is currently increasing.

The behavior of multiphase catalytic reactions depends on several factors which may be broadly classified in terms of catalyst and reactor design and further subdivided according to the characteristic scale length of the control level (Fig. 1). In Table 1 some of the factors that are influenced by the relative level of control are also listed. Optimization of the performance

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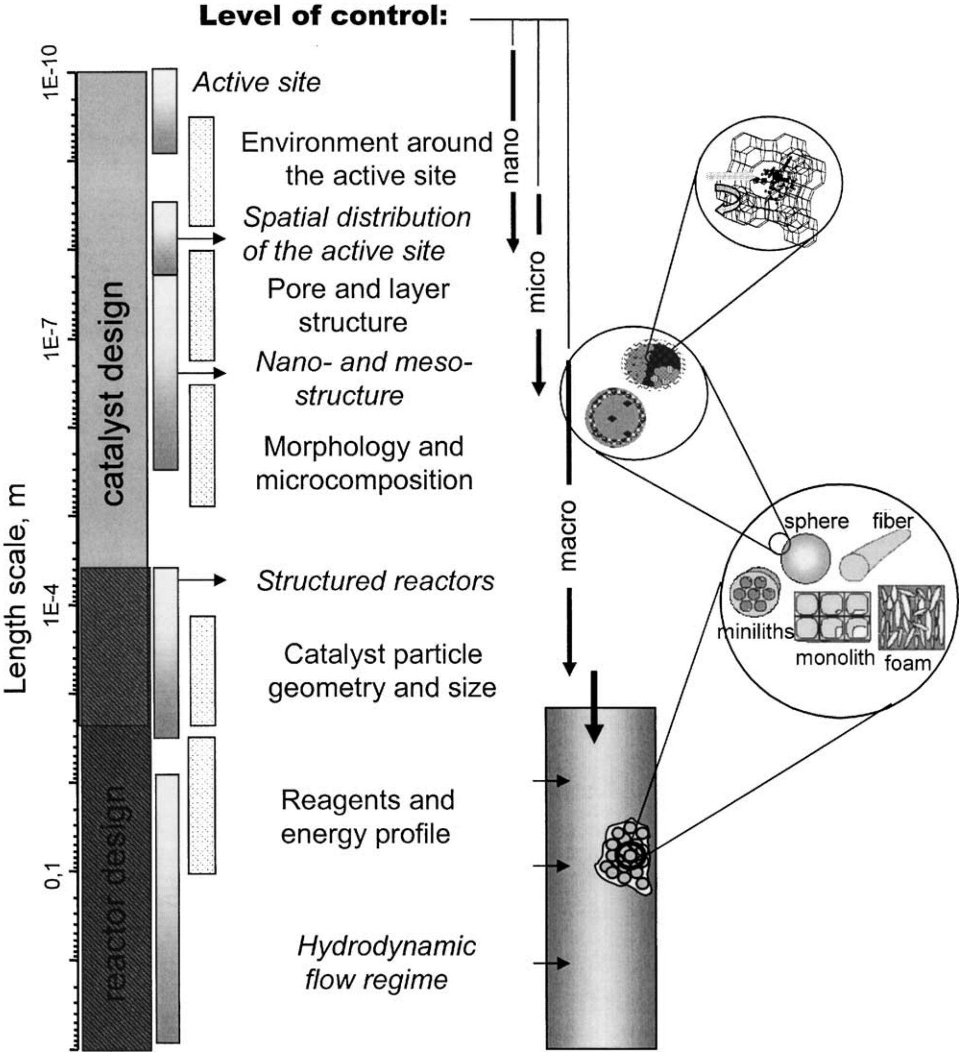

Fig. 1. Length scale in the catalyst and reactor design for multiphase reactions.

depends on the proper integrated reactor and catalyst design [2,7,8], but limited attention has been usually given to catalyst design itself.

Some aspects in catalyst design in multiphase reactions are discussed here from the general perspective of the dimensional scale at which catalyst design should be considered (Fig. 1), in order to show in an integrated view all the different aspects which should be considered for a proper catalyst design integrated with reactor design.

Examples are focused especially on the area of environmental protection and sustainable chemistry applications, because there is a special need for novel catalyst design for multiphase reactions in these area. The approach used in the discussion is to exemplify with specific cases/applications the relevance of one of the aspects discussed along the general concept of multiple dimensional levels of catalyst design, but is out of the scope a systematic discussion of the factors relevant for catalyst design or an in-depth discussion of each specific example. It should be noted, however, that often catalyst design is discussed in terms mainly of molecular aspects of the active site(s) [9], and also catalyst engineering aspects such as porosity, catalyst

Table 1
Influence of the level and related parameters of control in catalyst design on the main properties and performances of the catalysts

Level of control[a]	Parameter	Influence on
Molecular	Active sites	Intrinsic activity
Nano	Environment around the active sites	Selectivity, deactivation, local environment, wettability
	Spatial distribution of the active sites	Deactivation, activity, multiphase contact
Micro	Pore and layer structure	Diffusion, mechanical strength, multiphase contact, micromixing, transport mechanism
	Nano- and meso-structure	Catalyst effectiveness, deactivation, mechanical strength and transport, diffusion
Macro	Morphology and microcomposition	Fluidizability, mechanical strength, control of the reactivity, composition gradients, multifunctionality, recovery
	Structured reactors catalyst particle geometry and size	Pressure drop, interphase diffusion, fluidizability, mechanical strength, fouling, phase contact, backmixing and concentration gradients, products separation
Reactor	Reagents and energy profile	Concentration and temperature profile, transport-kinetic interaction, productivity
	Hydrodynamic flow regime	Flow regimes, pressure drop, interfacial areas, multiphase contact, productivity

[a] Here the italics words indicates the levels of control.

shape, micro-structure and composition, etc. are considered separated and not integrated aspects of a combined catalyst and reactor design.

2. Catalyst design at a nanoscale level

The local environment around the active sites plays an important role in determining catalytic performances especially in multiphase reactions, although often not enough attention is given to this aspect. Using nanostructured materials based on the active components located in ordered microporous materials such as zeolites, it is possible to change the local environment "seen" by the active sites and thus change their reactivity and/or stability.

This concept can be demonstrated by the case of Ti-silicalite (TS-1), catalyst for the selective oxidation of various substrates using H_2O_2 [10]. Although TS-1 has approximately the same composition as that of the Shell catalyst based on titania supported on amorphous silica used to synthesize propene oxide from propene, TS-1 makes selectively the reaction using H_2O_2, while hydroperoxides (for example, ethylbenzene hydroperoxide) are necessary in the case of the Shell catalyst. Recent studies ([10], discussion) have shown than the different behaviour do not depend on the different nature of Ti ions, but on the differences in the local environment around the Ti active sites. TS-1 is hydrophobic and therefore water molecules do not diffuse (or only in minor amounts) inside the channels of TS-1 zeolite where the Ti ions are localized. This is different from the case of the Shell catalyst where the Ti ions are accessible to water molecules, being supported over the silica. TiO_2–SiO_2 is able to epoxidize 1-hexene with H_2O_2, if a "water-sponge" is present which scavenges the H_2O formed during the reaction. TS-1 also remains active in aqueous solutions of H_2O_2 (usually a water/methanol solvent is used), because the hydrophobic character of the local environment around the active sites (nano-environment) creates a local water-free-like solvent.

The differences in the hydrophobic character between silicalite (TS-1) and silica (Shell catalyst) derives from the presence of a well ordered structure which created an ordered array of channels (therefore, minimizing defects) in the first case, while defects in amorphous or crystalline silica creates hydroxyl groups (silanols) or hydroxyl nests which induces some degree of hydrophilic character in the Shell catalyst. These hydroxyl groups under acid catalyzed conditions (acidity is generated by oxidation of the solvent) causes ring opening to the corresponding glycol in the soon formed epoxide. In addition, the water adsorbed on the surface limits the accessibility of the alkene towards the active centre. Partially hydrophobic materials can been obtained by anchoring TiF_4 on silica [11] or by anchoring alkyl (alkoxy) groups to the silica surface [12]. The amorphous microporous titania–silica in which pendant alkyl groups make the surface hydrophobic can epoxidize alkenes with H_2O_2 [13].

Therefore, the hydro-phobic/philic character of the catalyst is as essential component for the design of these catalyst and may be estimated using competitive adsorption or diffusion experiments. The concept demonstrated by these examples is that the catalytic performances do not depend only from the active site (coordination of the Ti ions, for example), but also from the nano-environment around the active sites which modify the effective local concentration of the reactants.

The concept of nano-environment is not often properly taken into account for catalyst design, but it is the basis of various multiphase applications in the area of environmental protection:

- The removal of volatile organic compounds (VOCs) in dilute, high volume humid streams or the removal of VOCs during automotive cold starts requires to use of high silica hydrophobic zeolites, while more hydrophilic zeolites rapidly deactivate due to water absorption [14].
- By tuning the hydrophobic character of zeolites it is possible to promote three-phase reactions such as the hydrodehalogenation of chlorinated hydrocarbons [15]. Reported in Fig. 2 is the comparison of the reaction rates in the hydrodechlorination of the model compound 1,2-dichlorobenzene (DCB) for three Pd-containing zeolites with different Si/Al ratios [15]. The results refer to tests in deionized water in the presence or absence of sodium sulfite, chosen as a model compound to test the resistance to deactivation of the catalyst by anions which usually rapidly deactivate Pd-supported catalysts for the reaction of hydrodehalogenation.

In the absence of sulfite the hydrophobic Y zeolite (Si/Al ratio of 200) shows a considerably higher reaction rate than the same type of catalyst, having a more hydrophilic character (Si/Al ratio of 6 or 15), due to the preferential accumulation of the organic contaminant inside the pores of the zeolite. Other hydrophobic materials, such as MCM-41 show an even higher reaction rate [15], due to better accessibility (pore diameter about 2.6 nm versus 0.74 nm for Y zeolite) and higher surface area.

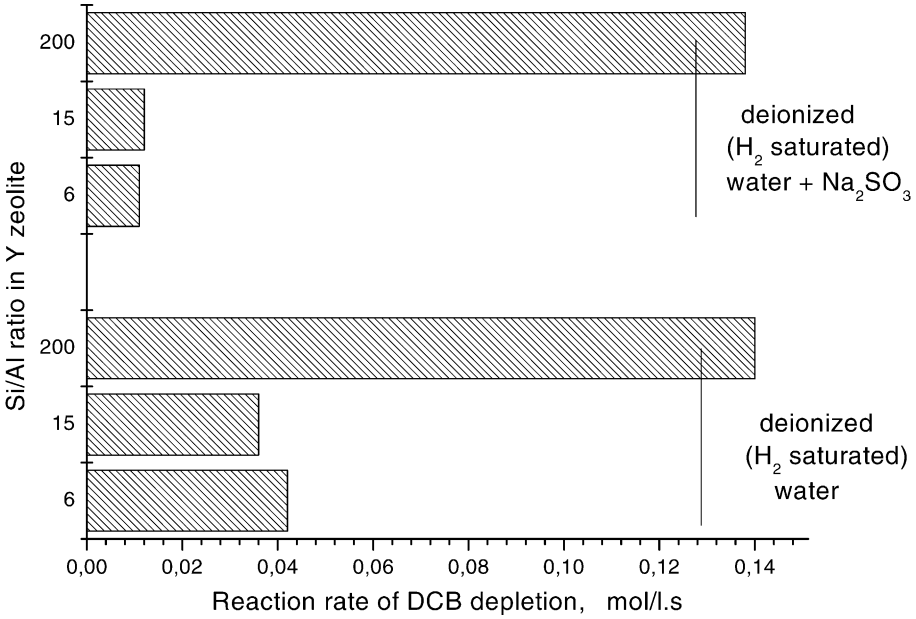

Fig. 2. Reaction rate of DCB hydrodehalogenation with 1% (w/w) Pd/Y zeolites having different Si/Al ratios. Tests made at room temperature and pressure using H_2 saturated solutions of DCB in deionized water in the absence or presence of 30 mg/l Na_2SO_3 [15].

However, in the presence of sulfite anions MCM-41 based catalysts as well as all Pd-supported catalysts (such as Pd/alumina) nearly completely deactivate. Pd/Y also slightly deactivates, but much less than the other analogous catalysts, due to limitations on the diffusion of the anions inside the zeolite channels. There is a synergetic effect between hydrophobicity and diffusional limitations, because the Pd/Y(200) zeolite is much less influenced by deactivation than the analogous Pd/Y(15) and Pd/Y(6) zeolites (Fig. 2) [15].

- Zeolites also may be used in permeable catalytic barriers (PCBs) used to avoid contamination of wells by methyl *tert*-buthyl ether (MTBE) [16]. The zeolites adsorb MTBE and catalyze its hydrolysis, enhancing the rate of bioremediation, because the products of hydrolysis (methanol and *tert*-buthyl alcohol) are biodegraded much faster. Since hydrolysis is an acid-catalyzed reaction and since the amount of acid sites in a zeolite increase with decreasing Si/Al ratio, it may be expected that the reaction rates will decrease with increasing Si/Al ratio. However, the opposite behavior is found (Fig. 3), because increasing the Si/Al ratio increases the hydrophobicity of the zeolite cavities and thus changes the effective local composition inside the zeolite cavities. There is also in this case a synergetic effect between diffusivity inside the zeolite channels and hydrophobicity of the zeolite.

  By analyzing zeolites with different pore dimensions [17] it has been observed that the activity does not correspond with that expected on the basis of the kinetic diameter of the MTBE molecule in solution, and that the solvation molecules should also be considered. With increasing hydrophobic character of the zeolite, the energy necessary to break the solvation bonds of the organic molecules which enter into the zeolite channels decreases, differently from the case of inorganic anions.
- The degradation of organic contaminants in water using H_2O_2 as the oxidant [18] is a technology of increasing interest in wastewater treatments. H_2O_2 is a very clean reactant, but should be activated by generating hydroxyl radicals which are the effective powerful oxidizing species for the total oxidation of organic pollutants. Photolytic dissociation is the most common method, but costly due to the use of ultraviolet lamps. Iron ions in solution is an alternative method to catalyse hydroxyl radicals generation from H_2O_2 (Fenton mechanism). Fe^{2+} ions react with H_2O_2 giving rise to hydroxyl radicals and anions plus Fe^{3+} ions which by reaction with

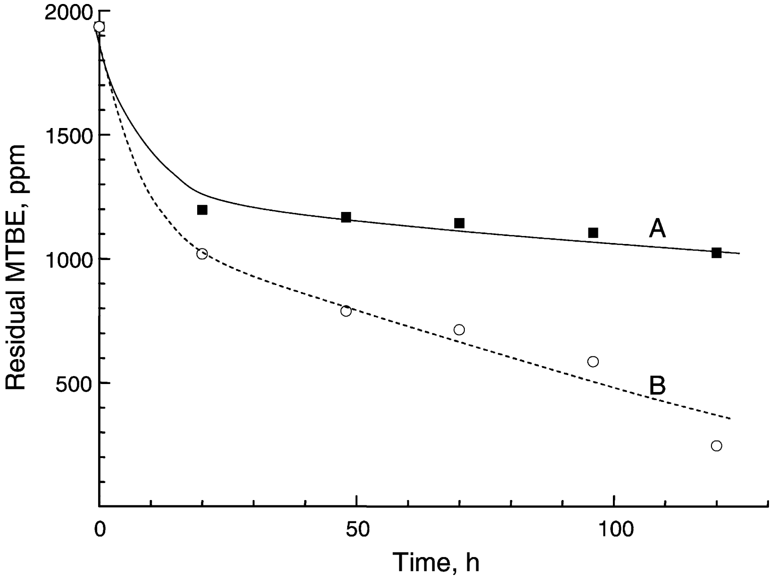

Fig. 3. Behavior of H-ZSM-5 zeolites in the hydrolysis at room temperature of MTBE in aqueous solution (no stirring) [16]: (A) Si/Al = 25; (B) Si/Al = 80.

H_2O_2 form again Fe^{2+} ions, protons and peroxo radicals. However, the complexation of these iron ions (for example, the products of the oxidative degradation of organic molecules, such as oxalic acid are high effective in complexing the iron ions) or their precipitation as hydroxides are two main side reactions which limit the effectiveness of this methodology.

Following the concept of nano-environment outlined before, limiting access of solvating molecules to iron ions and creating a local acidic environment which buffers changes of pH are two possible actions to improve the performances. In Fe/ZSM-5 catalyst, iron ions are localized inside the zeolite channels where strong acid groups are also present and therefore there is the potential to fulfil above indications. Although other reactions strongly depend on the nature of iron ions present in the zeolite, this is not a critical aspect in the application for wastewater treatment.

In comparison with the behavior of iron ions in solution where the activity stops (batch-type reactor) after some time due to complexation/precipitation of all iron ions, Fe/ZSM-5 show effectively improved performances. Oxalic acid (or of other complexing agents) diffusion inside the cavities of zeolites is slow, allowing thus to preserve activity for longer times [18]. In addition, a wider range of pH for which reaction rate is maximum was experimentally observed [19].

These examples taken from different type of multiphase reaction applications show that the concept of nano-environment around the active sites in terms of both tuning the local concentration of the reactants/solvent or pH and limiting the accessibility to active sites of some deactivating molecules (accessibility also depends on the characteristics of the environment in the nanocavities) offers several opportunities to promote performance in multiphase reactions by proper catalyst design at a nanoscale level.

3. Catalyst design at a microscale level

Microscale level of catalyst design indicates the possibility of developing catalytic materials having non uniform composition at a microscale level, in order to develop multifunctional materials, create protective barriers to reduce deactivation or have specific activity profiles inside the catalyst pellets. Nano- and micro-scale catalyst design levels may also be combined. For example, zeolites and other micro- or meso-porous materials may grow over various surfaces and often are used as a selective diffusion layer (for example, in gas-selective sensors). This is an example of multilayer functional materials, but the hydrophobic or hydrophilic character of the zeolite (depending on the specific application; the zeolite hydrophobicity can be increased by increasing the Si/Al ratio) is also a determining factor to maximize performances, evidencing the link between nano- and micro-scale levels of design of these advanced materials. The use of multilayer microstructured catalysts has become of increasing importance in recent years and various new generation industrial catalysts for multiphase reactions are based on this concept [20].

An old, although still relevant example of catalyst design at a microscale level is the development of catalyst pellets having a specific profile of activity within the pellet. The optimal spatial distribution of active sites/species in catalyst pellets is usually focused on finding the best compromise between activity and stability by locating the active components in different zones of the catalyst pellet [7]. Impregnation in the presence of coadsorbing ions (for example, the adsorption of $PtCl_4{}^{2-}$ in the presence of citric acid) allows catalysts to be obtained with different preferential localizations of the active component (for example, an egg-shell or egg-white distribution). Non-uniform active sites distribution can be advantageous when the main reaction is accompanied by an irreversible poisoning reaction [7]. The main factors determining the best type of activity distribution are the Thiele moduli for both the main and poisoning reactions, which also allow the development of a catalyst selection chart for the optimal choice of the spatial distribution of active sites in spherical catalyst pellets [2]. Egg-shell type catalysts are instead preferable when significant heat and mass transfer intraparticle limitations are present [21].

Modification of the distribution of the active component in the catalyst particle also may allow interesting performances to be obtained in three-phase reactions such as the hydrogenation of carbohydrates which is a process of major importance in the fine chemical and food industries. Van Gorp et al. [22] observed that the hydrogenation of large molecules such as maltose occurs only when the active sites are located at the pore mouths, while for smaller molecules, such as glucose the activity is nearly independent of the location of the active sites. Based on this concept, it is possible to develop catalysts having or not having preferential hydrogenation activity on some molecules based on dimensional recognition.

The further extension of this concept is microstructuring the catalyst composition (for example, using multiple layers with different compositions) in order to improve performance. An example is given by catalysts for the reduction of NO by hydrocarbons in the presence of O_2. Supported noble metals are active only in a very restricted temperature window, while catalysts for car exhaust emissions should operate efficiently in a wider temperature range. However, the temperature window of operation may be extended significantly using microstructured catalysts (Fig. 4) based on multiple layers having different activities and temperature ranges. The most active catalyst is located in the bottom layer.

A different concept of catalyst design at a micro level is given by the synthesis of microassembled catalyst bodies. Microscopic catalysts and colloids often show markedly different catalytic properties in comparison with macroscopic catalysts, but their practical use is often hindered by the difficulties in their recovery and easy contamination of the outcoming effluents. Various solutions have been recently developed in order to overcome this problem. Hähnlein et al. [23] incorporated Pd colloids stabilized by polyvinyl pyrrolidone into the hollow fibers of a dialiser module. Hollow fibers are commercially used in water and gas treatments as well as in various health applications. The diameter is usually small (around 200 mm) with a membrane thickness of 20–50 mm and can host inside relatively small catalyst particles allowing at the same time good access of reactants through the porous membrane. Due to the limited thermal stability, this solution is limited to reactions occurring near to room temperature, but has been effectively applied to the reduction of nitrate in water by H_2 [23]. Very small particles are required, because the presence of intraparticle diffusional limitations has a considerable influence on the selectivity in nitrate reduction. A similar concept was also reported by Prüsse et al. [24] which evidenced the possibility of preparing homogeneous or egg-shell type mono- and bimetallic catalysts supported on microsized alumina pellets encapsulated in hydrogel beads of polyvinyl alcohol. The egg-shell catalysts show a higher activity and better selectivity in nitrite and nitrate reduction in water, avoiding at the same time the problems of leaching present when the catalysts are not encapsulated in the polymeric beads.

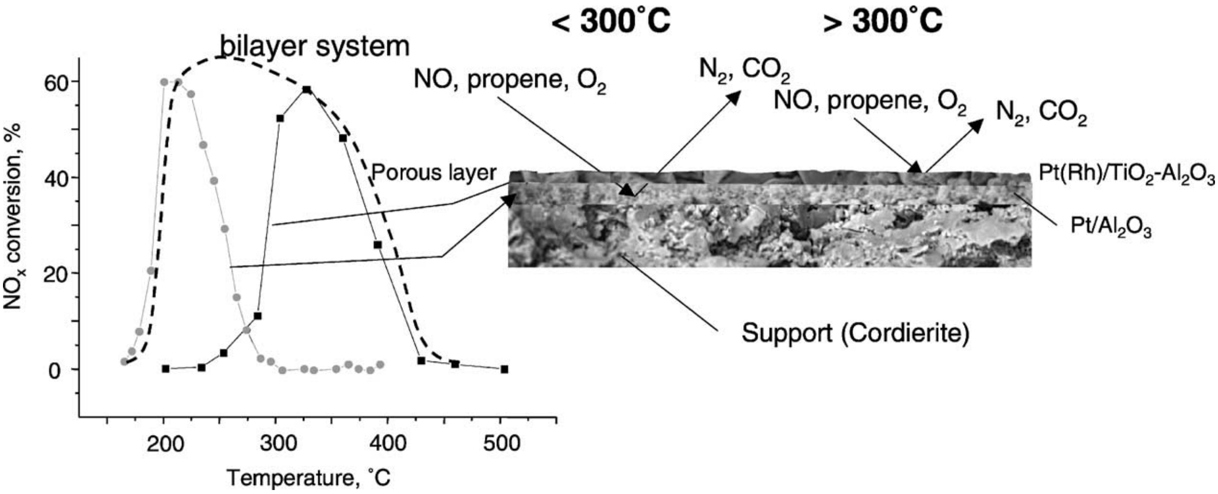

Fig. 4. Schematic drawing of the concept of multilayer catalysts for wider temperature window selective reduction of NO by propene in the presence of O_2.

Ilinitch et al. [25] showed that by incorporating nanosized Pd particles into a polyamide-6 membrane catalyst for the hydrogenation of sunflower oil (an important reaction of edible vegetable oils) can be prepared. These catalysts show a significant improvement in selectivity to the cis product (the trans product causes risks of coronary disease) when compared to performances possible in a conventional slurry reactor using carbon-supported Pd catalysts.

There are different possibilities of catalyst design at a microscale level in multiphase reactions. The examples reported above show some of the possibilities and indicate that these novel solutions offer good prospects of application.

4. Catalyst design at a macroscale level

An efficient multi-phase contact and the minimization of the influence on the reaction rate and selectivity of the reagents diffusion and products back-diffusion are two of the main aspects which have stimulated several researchers to develop novel designs in catalyst configuration (macrostructured catalysts), but there are several other advantages which sometimes can become the critical factors for the selection of these technologies: (a) catalyst separation and handling, (b) minimization of contamination of the solution by the catalyst, (c) safer operation, (d) improved heat supply and removal, and (e) easier scale-up and technology manageability.

Four main types of macrostructured catalysts have been used in multiphase reactions: (i) monoliths, (ii) foams, (iii) cloths and (iv) membranes. These macrostructured catalysts have been developed for gas–solid type reactions, and one of the largest areas of application is for the treatment of car exhaust emissions. Monoliths are currently used in all car catalytic converters; foams and cloths-type catalysts are used in novel catalytic filters for particulates. The use of catalytic membranes is still limited, but wider future use is expected [26]. The application of macrostructured catalysts in three-phase reactions is also increasing in importance. Several aspects of the use of monoliths in three-phase reactions already have been discussed by Kapteijn and co-workers [5,6,27].

Monoliths can combine the advantages of the slurry and trickle bed reactors and eliminate their disadvantages. In particular, the catalyst can be coated as a thin layer on the channel walls, thereby mimicking a fixed catalyst with the properties of the small slurry catalysts, but eliminating attrition. A relatively high geometric surface area is possible, depending on the cell density of the monolith which is determined by the acceptable pressure drop which increases with increasing cell density. The monolith washcoat may be a porous oxide which supports the active phase, a carbonaceous layer created by controlled pyrolysis of a polymer layer (created, for example, from furfuryl alcohol) [28] or a layer of microporous material (zeolite) [29] thus making it possible to combine nano- and macro-scale catalyst design.

Monolithic catalysts show improved performances in different three-phase reactions, starting from the pioneristic work on H_2O_2 synthesis via the anthraquinone process [30] which recently was developed to a full-scale process (AKZO-Nobel process). The plug flow in monolithic channels (narrow residence time distribution) combined with the thin catalytic layer of the catalyst allows higher selectivities in the case of consecutive reactions (for example, oxidation or hydrogenation reactions in the liquid phase).

Although, the use of monolithic catalysts offers several good prospects of application in three-phase reactions, there are several aspects which need to be further explored, especially in relation to the question of how to optimize the specific catalyst composition in relation to its use in monoliths. For example, catalyst composition can be gradually changed along the axial monolith direction, similarly to what has been done in the recent generation of reactors for oxidation reactions, in order to achieve a much more uniform reaction rate profile along the reactor (the less active catalyst at the beginning of the catalyst bed, where the concentration of the reactants is higher, and the most active catalysts at the end where the concentration of the reactants is lower) [31].

Also the question of how catalyst wetting properties (related to the hydrophilic character of the catalyst) should be tuned as a function of the specific flow characteristics in monoliths has not been analyzed in detail. For a co-current gas–liquid flow in monoliths, the flow pattern is often the so-called Taylor or slug flow [5]. The gas bubbles and liquid slugs flow consecutively through the small monolith channels. This flow regime is advantageous for reactor performances in catalytic reactions, but the catalyst surface becomes alternatively exposed to gas and liquid phases, differently from what occurs in other three phase reactors. Lavelle and McMonagle [32] recently demonstrated that the presence of a gas envelope at the surface of a highly hydrophobic solid catalyst significantly increases the reaction rates in the oxidation of aqueous organic compounds with respect to the case of wetted (hydrophilic) solid catalysts. The presence of alternating gas and liquid zones at the contact with the catalyst in the monolith (differently from other three-phase reactors) suggests that the catalyst wetting properties must be different in a monolith or when the same catalyst is suspended in solution (slurry reactor).

Štepánek et al. [33], using mesoscale modelling in multiphase catalysts, showed that new operating regimes might be obtained in a highly wettable support with relatively large mean macropore diameter, in which spreading of a liquid film instead of pore clogging by the bulk liquid would occur upon external wetting. Such an operation regime is a pore-scale analogue of Taylor flow of a gas bubble in a monolith channel. This result indicates how a better understanding of the effects at a nano-, micro- and macro-scale is necessary in multiphase catalyst design.

When a higher geometrical area is required together with the complete absence of porosity, fiber-type catalysts (which can be macrostructured in the form of woven cloth) can be used. The fibers can be made of carbon, glass or ceramic, depending on the characteristics required for adhesion of the catalytically active phase, mechanical strength, stability in the reaction conditions and cost. The structured catalysts made from fiber materials as catalyst supports combine an open macro-structure with mechanical elasticity and flexibility to adapt to space constraints not possible for monoliths, for example. They are also preferable to monoliths when rapid fluctuations in the flow regime occur, as often encountered in applications for environmental protection [34].

Being virtually absent intraphase diffusional limitations, fiber-type catalysts show interesting reactivity properties. In the three-phase nitrobenzene hydrogenation using Pd and Pt supported on woven glass fibers, Holler et al. [35] observed a two-fold increase in the catalyst activity with respect to conventional catalysts for liquid-phase hydrogenation. Glass fibers in the form of woven cloth on which Pd/Cu bimetallic catalysts have been deposited also show high performances in the reduction of nitrate in water [36].

A particular case of multiphase systems is that of photocatalytic reactions for water treatment (oxidation of harmful compounds), where an optimal contact between the solution, O_2 and light must be realized. Reactor configurations should optimize the light distribution inside the reactor, and provide high surface areas of illuminated catalyst at the contact with the liquid solution. A new generation of photocatalytic reactors has recently been proposed to meet these requirements [37]. The solution proposed is analogous to that of fiber-type catalysts. The new reactor design is based on several hollow tubes employed as a means of light delivery to the catalyst present on the outside surface of the tubes. Experiments carried out on the degradation of a textile dye showed promising results [37], although further improvements require a better understanding of how to optimize the relationship between the characteristics of hollow tubes (macroscale design), wall thickness and surface roughness of the catalyst (microscale design) and specific photocatalyst properties (nanoscale design).

Catalytic membranes [38–42] also represent a very interesting possibility for improving performances in three-phase reactions by proper catalyst design at the macroscale level. In comparison with monoliths and cloth-type catalysts, catalytic membranes offer the advantage of allowing a distributed addition of reactants or removal of products.

Often in consecutive catalytic reactions, it is necessary to realize a high ratio between two reactants (hydrocarbon and oxygen, for example) in order to maximize the selectivity. In a tubular porous membrane reactor this can be realized by adding O_2 continuously along the axial reactor direction (diffusing it through a membrane) instead of that introducing all the oxygen at the reactor inlet (as in fixed-bed reactors). However, there is still a change in the optimal hydrocarbon to oxygen concentration ratio between the beginning and end of the reactor, because the hydrocarbon is consumed, while the oxygen flux remains almost constant along the axial direction of the reactor. Using novel reducible membranes (for example, making a $V_2O_5/AlPO_4$ layer on a ceramic membrane) it is possible to change the oxygen flux along the axial direction of the reactor (membrane), because the flux of oxygen across this oxidized membrane is about

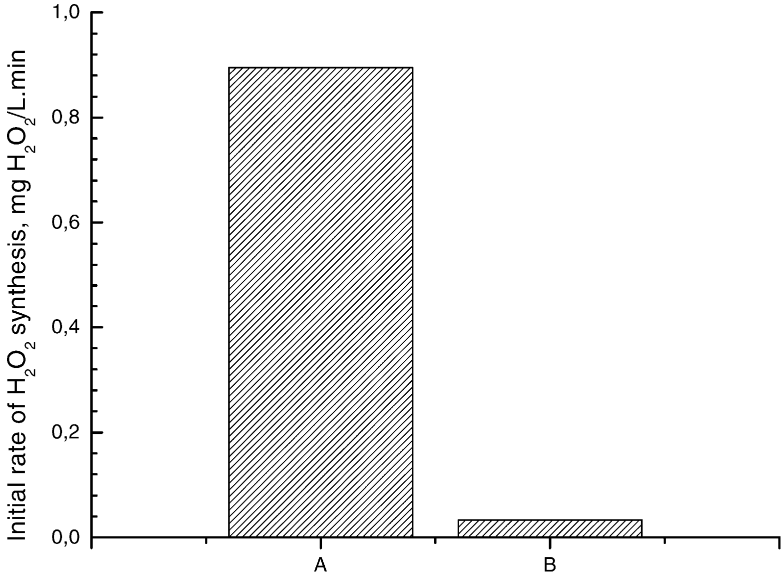

Fig. 5. Initial rate of reaction in the synthesis of H_2O_2 from $H_2 + O_2$ at room temperature over a Pd/carbon/alumina catalytic membrane [43]. (A) The solution is presaturated with oxygen at 5 bar and then, after stopping O_2 feed, H_2 only is fed through the catalytic membrane. (B) Both H_2 and O_2 (1:1) are cofed through the catalytic membrane (pressure 5 bar).

two orders of magnitude lower than across the same membrane, but reduced. When the hydrocarbon concentration is decreased from the inlet to outlet of the reactor, the reducing power of the gas phase also is changed with a consequent change in the oxygen diffusion flux across the membrane in the axial direction of the reactor. Therefore, the distribution profile of the reagents in the reactor can be optimized with an increase in the selectivity.

Not only at the macroscale level can the concentration ratio between reactants be optimized using membranes as in the former case, but also at the nano- and micro-scale levels. This is exemplified by the synthesis of H_2O_2 from H_2+O_2 in solution over a membrane catalyst (Pd/carbon/alumina) [43]. Due to the different solubilities of O_2 and H_2 in solution and the constraints given by the necessity of using $O_2 + H_2$ mixtures out of the explosion range, the effective oxygen concentration at the Pd surface is not optimal with a lowering of the rate of formation of H_2O_2 and/or increase in the rate of its decomposition. By diffusing H_2 through a catalytic membrane, while the solution saturated with O_2 is on the other side of the membrane where the Pd active phase is present, better control of the O_2/H_2 ratio at the Pd surface is possible with a significant improvement in the rate of H_2O_2 generation (Fig. 5) [43]. In addition, use of the catalytic membrane allows intrinsically safer operation because there is no formation of hydrogen and oxygen mixtures.

Very recently the concept of H_2O_2 synthesis from H_2/O_2 on a Pd-based membrane was extended to the one step synthesis of phenol from benzene [44]. A gaseous mixture of benzene and oxygen is fed into a porous alumina tube coated with a thin layer of palladium and hydrogen is fed into the shell. It is possible to obtain selectivities to phenol in the 80–97% range at a benzene conversion of 2–16% and temperatures in the 200–250 °C range.

5. Conclusions

Optimization of performances in multiphase reactions requires proper catalyst design integrated with reactor design. Three levels of catalyst design have been discussed. At the nanoscale level, two concepts were emphasized: the nano-environment around the active sites and its relationship with the hydrophilic character of the support, and limiting deactivation by constraints in the access to nano-cavities of deactivating molecules. Particularly important is the fact that the diffusion properties of chemicals in the liquid phase are different from those in the gas-phase and depend on the hydrophobic character of the nano-cavities. At the microscale level the concept of microstructuring catalyst composition (multilayers and microassembled catalyst bodies) was emphasized. At the macroscale level the question of macrostructured catalysts (monoliths, cloths and membranes) was discussed. For full optimization of the performances in multiphase reactions, the three levels of catalyst design should be considered in an integrated, and not separate view, together with the relationship between catalyst and reactor design.

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