Producing catalyst such as Methanol Synthesis Catalyst, Ziegler Natta catalyst, ammonia catalyst

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1.Theme Description

Catalysts are substances used to speed-up chemical reactions or to selectively drive the desired reaction to promote maximum efficiency. They can be homogeneous or heterogeneous, that is they can be in the same aggregation state of one or more reagents or not. Focusing the attention on heterogeneous solid state catalysts, which are largely the most applied, they are generally shaped bodies of various forms, as rings (being Rashig rings the most diffused, refer to Figure 1), spheres, tablets and pellets and their performance is measured according to indices as:

- **activity** (rate with which a chemical reaction proceeds towards equilibrium in the presence of the catalyst);
- **selectivity** (the ratio between the rate of the desired reaction to the rate of the secondary undesired reactions);
- **Specific surface area** per cubic meter or kilogram;
- **Diffusivity,** which the ability to diffuse reagents and products within the catalyst structure.

Fig. 1 - Rashig rings

Catalysts are involved in 85-90% of the products in the chemical industry and the market is valued at $28,567 million, expected to reach $40,000 million by 2022[1] driven by emission control and environmental protection segments[2]. Catalyst materials can be zeolites, metals, synthetic chemical compounds, enzymes and organometallic materials (refer to Figure 2), being the first two the most used in the industrial processes.

The most significant catalyst sector drivers for the next years are[3]:

- Revamping of refining plants due to new environmental regulations;
- New technology to improve the use of innovative feedstocks (such as shale gas);
- Thermoplastics industries are increasing the investments on polyester and niche value-added product synthesis;
- CO_2 valorization technologies for the production of new products in biochemical/biopolymers sectors.

In the following, the main innovations in the catalysts sector are described and some case studies (catalysts for methanol synthesis, Ziegler-Natta processes and ammonia industry) are illustrated.

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[1] https://www.alliedmarketresearch.com/catalysts-market
[2] http://feeco.com/rd-around-catalyst-production-sees-growth/
[3] www.catalystgrp.com/wp-content/uploads/2017/05/pres-intelligence-report-2015-2021may-2016.pdf

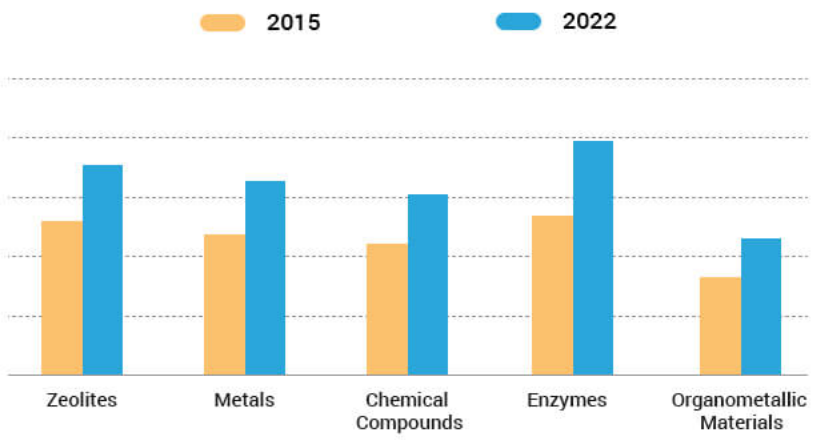

Fig. 2 - Global Catalyst Market by Type[1].

2. Innovations in the industrial catalysts production

Basically, a catalyst is composed by an **active principle**, which has the catalytic activities and the ability to speed-up the reactions by adsorbing the reactants and desorbing the products from its active surface, and a **support** needed to assure a proper shape, porosity to increase the specific surface and mechanical/thermal resistance.

The main aspects for an effective catalyst production are:

- the uniform deposition or impregnation of the catalytic substance on the support;
- the increase of the active surface.

Figure 2 reports the SEM images of a Zr-Al_2O_3 support and of the Co/Zr-Al_2O_3 catalyst, in which the active principle (Cobalt) is deposited with different methodologies as microemulsion (ME) and impregnation (IM) and used for CO hydrogenation reaction[4]: it is a matter of fact that the final catalyst morphology, and consequently its performance, strongly depends on the production process.

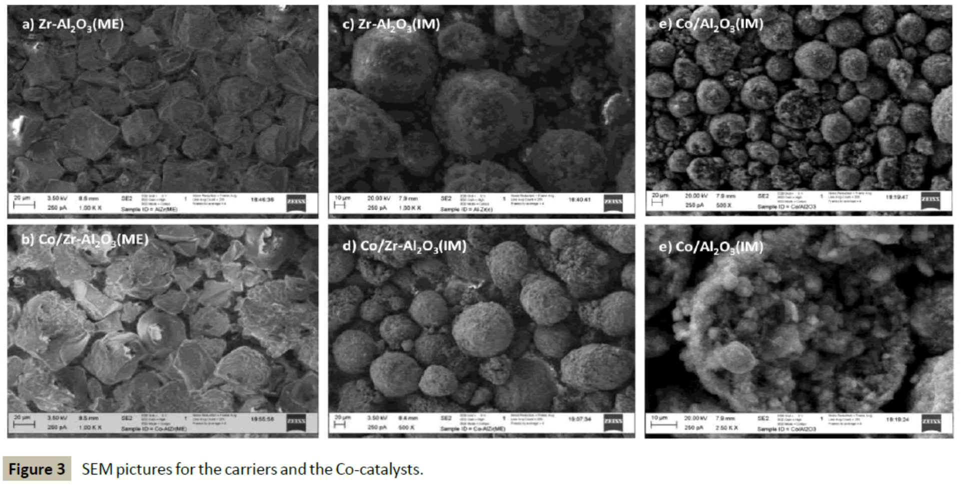

Figure 3 SEM pictures for the carriers and the Co-catalysts.

Fig. 3 - SEM images of a Co/Zr-Al2O3 catalyst manufactured by water-in-oil microemulsion (ME) or by impregnation (IM).

[4] Fatima Pardo-Tarifa, Saúl Cabrera, Margarita Sanchez- Dominguez, Robert Andersson and Magali Boutonnet, Synthesis and Characterization of Novel Zr-Al2O3 Nanoparticles Prepared by Microemulsion Method and Its Use as Cobalt Catalyst Support for the CO Hydrogenation Reaction, Synthesis and Catalysis: Open Access.

The innovations in the catalyst sector are mainly focused on:

- the increase of reactions rates at reduced temperature and pressure (leading to a reduction of the production plants operating costs);
- the reduction of secondary reactions rate, and therefore of the by-products generation;
- the increase of the process efficiency and the reduction of catalyst production costs.

Some innovative and effective catalyst production processes of industrially relevant catalyst are:

- **Homogeneous coprecipitation**, by which two or more components are precipitated from a solution at the same time, allowing a homogeneous distribution of the components. Examples are preparation of Al_2O_3 supported nickel catalysts for reactions as steam reforming and catalytic partial oxidation (CPO), supported platinum group (Pt and Pd) metals catalysts and TiO_2-supported rhodium, supported-ruthenium ($Ru/ZnO-Al_2O_3$) Fischer-Tropsch catalyst[5].
- Deposition on preformed supports of **metal precursors**, able to influence the final distribution of metals on the support. An example is the addition of viscosity-increasing agent such as hydroxyethyl cellulose to the iron-containing impregnating solution.
- **New extrusion processes for the preparation of optimized supports**. The rheological properties of the starting paste have a strong influence on the extrudate properties such as porosity and strength, and consequently on the catalytic performance of the final product[6]. Therefore, some technologies are applied to improve the properties of the support material paste, as the preliminary treatment with acids to support peptisation.

Moreover, interesting innovations are proposed in the following two sectors:

- Application of **ceramic or metal foams for structured catalysts**, able to strongly reduce the pressure drops along the reactors and to increase the active surface for the catalyst activity. Examples are ceramic foam supports as α-Al_2O_3 and ZrO_2 stabilized with Mg, Ca, and La_2O_3[7], or open-celled metal foams coated with a thin layer of palladium−alumina for the catalytic oxidation of CO[8].

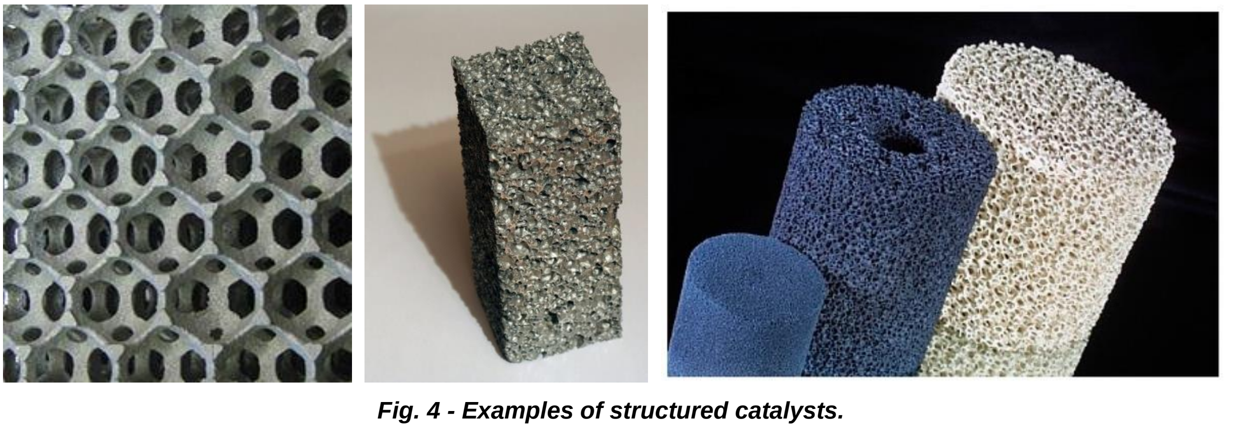

Fig. 4 - Examples of structured catalysts.

[5] Techniques for Catalyst Manufacture, REVIEW OF A ROYAL SOCIETY OF CHEMISTRY MEETING ON APPLIED CATALYSIS

[6] http://etheses.bham.ac.uk/5706/1/Winstone11EngD.pdf

[7] J.T. Richardson, Y. Peng, D. Remue, Properties of ceramic foam catalyst supports: pressure drop, Applied Catalysis A: General (2014) 204: 19-32.

[8] L. Giani, G. Groppi, E. Tronconi, Mass-Transfer Characterization of Metallic Foams as Supports for Structured Catalysts, Ind. Eng. Chem. Res. (2005) 44: 4993–5002.

- Nanocatalysts (Figure 5), mainly applied in water purification, fuel cell, energy storage, composite solid rocket propellants, bio-diesel production, in medicine, in dyes[9].

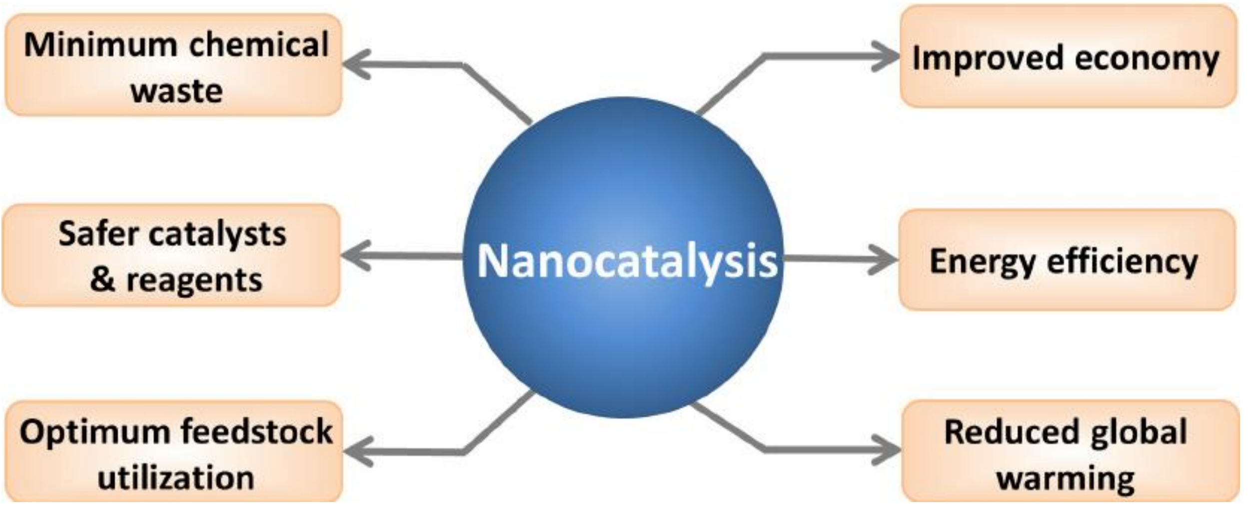

Fig. 5 - Expected benefits of nanocatalyst application10

3. Case studies

3.1 Methanol Synthesis

Methanol synthesis process attracts great interests because of its importance in chemical industries and its potential as an environmentally friendly energy carrier. Methanol is produced by the hydrogenation reaction of syngas with small amounts of CO_2 and the highest research effort is focused on the discover of methodologies able to increase the CO_2 content in the feedstock (CO_2 valorization technologies[11]). Many research groups are engaged in catalyst preparation using different catalyst compositions and preparation methods, being the Copper the main active principle used[12].

The most interesting innovations are summarized as follow:

- a ultrafine $Cu/ZnO/Al_2O_3$ ultrafine ternary catalyst was prepared by means of an oxalate gel coprecipitation by the research group of Deng[13]. The activity of the catalyst in presence of high content of CO_2 in much higher than the activity of conventional Cu-based catalyst.
- Ultrafine Cu-based catalysts produced by a reduction method and doped by Cr, Zr and Th for the increasing of dispersion and stability of Cu was studied by Liaw and Chen, showing a performance enhancement[14].

[9] Shalini Chaturvedi, Pragnesh N.Dave, N.K.Shah, Applications of nano-catalyst in new era, Journal of Saudi Chemical Society (2021) 16: 207-325.

[10] https://www.researchgate.net/figure/The-expected-benefits-of-nanocatalysis-Reprinted-from-2-with-permission-from-Wiley-VCH_fig1_264798243

[11] M. De Falco, M. Capocelli, Direct Synthesis of Methanol and Dimethyl Ether From a CO2-Rich Feedstock: Thermodynamic Analysis and Selective Membrane Application, Methanol Science and Engineering (2018), pages 113-128.

[12] Xin-Mei Liu, G. Q. Lu, Zi-Feng Yan, Jorge Beltramini, Recent Advances in Catalysts for Methanol Synthesis via Hydrogenation of CO and CO2, Ind. Eng. Chem. Res. (2003) 42: 6518-6530.

[13] Deng, J. F.; Sun, Q.; Zhang, Y. L.; Chen, S. Y.; Wu, D. A, Novel Process for Preparation of a Cu/ZnO/Al2O3 Ultrafine Catalyst for Methanol Synthesis from CO2 + H2: Comparison of Various Preparation Methods, Appl. Catal. A 1996, 139, 75.

[14] Liaw, B. J.; Chen, Y. Z. Liquid-Phase Synthesis of Methanol from CO2/H2 over Ultrafine CuB Catalyst. Appl. Catal. A (2001) 206: 245.

- Proper addition of ZnO to a Cu/ZrO_2 catalyst showed a significant increase of catalytic activity as reported by[15].
- A Cu/ZnO binary catalyst (copper to zinc ration = 1) using ethylene glycol as the solvent is prepared by Tanaka research group[16], thus increasing the methanol selectivity.

3.2 Ziegler-Natta catalyst

Ziegler-Natta catalysts are used to polymerize α-olefins with high linearity and stereoselectivity[17].

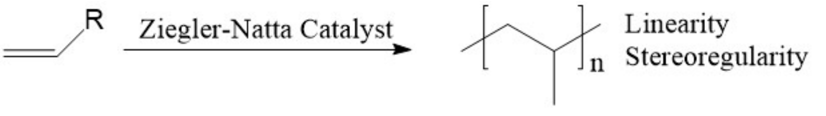

Fig. 6 - Ziegler-Natta reaction

Generally, a Ziegler-Natta catalyst is a combination of a transition metal compound of an element from groups IV to VIII and an organometallic compound with the metal from group I to III of the periodic table.

Over the years, the catalysts have developed from simple $TiCl_3$ crystals into $MgCl_2/TiCl_4$/donor systems, increasing the activity and selectivity.

In the last years, the most important innovation was the development of $MgCl_2$ supported catalysts prepared by co-milling $TiCl_3$ and $TiCl_4$ with $MgCl_2$[18].

The next generations of Ziegler-Natta catalysts differ for internal-external donor couple typology. Giannini and coworkers found that the incorporation of electron donors into the $MgCl_2$ supported catalyst system allows a crucial selectivity improvement[19].The selection of internal-external donor pair has a strong influence on the catalyst performance.

Despite all this progress, producing high molecular weight polyolefins with a controlled incorporation of functional groups remains a significant and unsolved challenge[20]. Other crucial aspects to be tackled in the next years are twofold:

- improving the catalytic activity to reduce the polyolefins production costs;
- increasing the molecular weight of the copolymers to improve their functionalities and application range (the current industrial catalysts are not capable of polymerizing functional olefins to high molecular weights);

3.3 Ammonia catalyst

For ammonia synthesis, the most relevant innovations concern:

- the development of fused iron catalyst, prepared by melting iron oxides with structural promoters, such as Al_2O_3 and/or CaO, and an activating promoter (K_2O)[21];

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[15] Nitta, Y.; Suwata, O.; Okamoto, Y. Copper-Zirconia Catalysts for Methanol Synthesis from Carbon Dioxide: Effect of ZnO Addition to Cu-ZrO2 Catalysts. Catal. Lett. (1994) 26: 345.

[16] Tanaka, Y.; Kawamura, C.; Ueno, A.; Kotera, Y.; Takeuchi, K.; Sugi, Y, A Novel Catalyst for Methanol Synthesis. Appl. Catal. (1983) 8: 325.

[17]https://chem.libretexts.org/Core/Inorganic_Chemistry/Catalysis/Catalyst_Examples/Olefin_Polymerization_with_Ziegler-Natta_Catalyst

[18] https://pure.tue.nl/ws/files/3950534/761023.pdf

[19] Giannini, U.; Cassata, A.; Longi, P.; Mazzochi, R., US 4336360, Montedison, 1982.

[20] Samir H Chikkali, Ziegler–Natta Polymerization and the Remaining Challenges.

- ruthenium based catalysts, which demonstrated optimal efficiency and high reaction rates[22];
- Topsoe introduced SK-501 Flex™, a high temperature shift catalyst able to operate at any steam-to-carbon ratio and allowing to achieve unparalleled plant efficiency in ammonia, hydrogen and syngas production[23]: the catalyst is iron-free and based on zinc oxide and zinc aluminum spinels;
- molten-sodium catalyst, developed by Fumio Kawamura and Takashi Taniguchi and able to strongly reduce the operating temperature and pressure of ammonia synthesis reactor (H_2-N_2 mixed gas passes through the Na-melt at 500–590 °C under atmospheric pressure, achieving high reaction rates and high conversions to ammonia)[24].

Moreover, the use of ammonia as a carbon-free fuel has attracted a booming interest in the energy sector, and a number of works are focused on the formulation and development on catalyst to promote the NH_3 combustion and its conversion in N_2 and water. Among these studies, Kumamoto University has developed a CuOx/3A_2S catalyst[25], highly active in the selective production of N_2 and avoiding the NOx formation, also at high operating temperatures.

[21] Bartłomiej Wilk, Rafał Pelka, Walerian Arabczyk. Study of the Iron Catalyst for Ammonia Synthesis by Chemical Potential Programmed Reaction Method. Journal of Physical Chemistry (2017), 121: 8548-8556.
[22] https://books.google.it/books/about/Ammonia_Synthesis_Catalysts_Innovation_A.html?id=nze7CgAAQBAJ&redir_esc=y
[23] http://www.catalystgrp.com/wp-content/uploads/2017/05/prop-ammonia-production-catalyst-and-process-technology-advances-july-2016.pdf
[24] www.nature.com/articles/s41598-017-12036-9.pdf
[25] https://www.sciencedaily.com/releases/2018/04/180427100256.htm