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Beyond Avelino's scientific achievements: The building process of a community in catalysis

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1. Introduction

The scientific career of Avelino has recently been reviewed in some detail [1] and the contributions included in this special issue provide additional valuable and extensive insights into several aspects of his activities from a variety of perspectives, written with the purpose of completing the picture of Avelino as the author of outstanding breakthroughs in zeolite science and catalysis. But, it is precisely his excellence in science that motivates some key questions that have never been properly addressed, not at least in printing form: how all these achievements came into being? What is the nature of the process that has made such wide range of innovations possible? How the material and human resources required for that successful process were gathered and organized? These questions are usually not of primary concern for scientific journals, as this one is, and are in general best regarded as more suitable for historically oriented publications, and even for social and philosophical aspects of the scientific research. However, we think that these questions are relevant to those scientists who are actively contributing to the fields that Avelino has explored so successfully over the years, as well as to all those who wish to understand through the study of Avelino's career how science is practiced and organized as a human activity.

The authors of this contribution do not intend to provide full answers to these questions, but to offer their personal view, a first-hand account on how Avelino's scientific endeavours and environment evolved, a process in which they have been deeply involved from the very beginning. Indeed, J. Pérez-Pariente (JPP) arrived in 1980 in Avelino's modest lab then located in Madrid (Spain), at the premises of the Institute of Catalysis and Petroleum Chemistry (ICP), to become the first PhD student of Avelino. He was since then and until June 1993 member of his research team, and one of the founding members in the late 1980s

of the Instituto de Tecnología Química (ITQ) in Valencia (Spain). F. Rey joined as a young postgraduate Avelino's group in 1988, who at that time was occupying a small laboratory at the ICP, and moved along with other fellows and senior members of the research group to the recently created ITQ, where he has developed most of his scientific career. By the time this account is written he has been the director of the ITQ for eight years. Therefore, the involvement of these two scientists in Avelino's research overlaps in time. Hence, their experience, taken together, covers most of the scientific career of Avelino, providing a perspective that, however incomplete, may hopefully be useful for all those who in the future may wish to approach him and his achievements from a more professional historical perspective.

It is worth to include here a final warning to the readers. In providing this personal account, we by no mean intend to offer a "recipe" on how to build a successful and world-wide recognized research group for its excellence in science. There is nothing like "do this and in 30 years you will have an h-index over 80". Simply, there are no such recipes, no such eventual mechanical translation of Avelino's experience to any other group regardless personal, social and historical circumstances. Please, also avoid here "copy-and-paste". Science is as complex, rich and varied (not to say amazing), even as unpredictable as any other manifestation of human creativity. But it does not mean that there are no lessons to be learned in anatomizing Avelino's career. The mindful reader will be able to identify some patterns that would be advisable to follow, and others that would be better to avoid.

2. The years at the instituto de catálisis y petroleoquímica

2.1. The beginning: a little lab in a historical building

JPP arrived in Avelino's lab in the fall of 1980. It was located in the

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historical building that harboured the Institute of Physical Chemistry "Antonio Gregorio Rocasolano" (IQFR) and also the Instituto de Catálisis y Petroleoquímica (ICP), which arose five years earlier when the Department of Catalysis of the "Rocasolano" was transformed into the ICP [2]. The laboratory had about 30 m²; two wide and long windows opposite to the door, Avelino's desk below the right window, the one given to me on the left. He had been given this lab shortly before. Avelino received his PhD degree in 1976 for a research work on the isomerization of xylenes on acid catalysts (silica-alumina), carried out under the supervision of Prof. A. Cortés at the ICP, belonging to the Spanish Research Council (CSIC). Then, he departed to Canada for a postdoc internship in the laboratory of Prof Bohdan W. Wojciechowski of the Chemical Engineering Department at Queen's University in Kingston (Ontario, Canada), where he started his studies on catalytic cracking. Two years later, returned to Spain, and in 1979 he obtained a permanent position of associated researcher at ICP. In the first two papers published in 1978 and 1979 as well as in a few others that followed soon after, Avelino reported on the isomerization mechanism of xylenes that he had studied in his PhD [3-5]. These early studies already evidenced the importance that Avelino has always given to the understanding of the catalytic phenomena from a fundamental point of view, stressing the necessity of knowing the basic aspects of the reaction mechanism as prerequisite for a rational design of catalysts for specific chemical reactions. This approach shows all his potential in his studies on catalytic cracking, a topic on which he published his first paper in 1979 [6]. This is a particularly challenging reaction for this approach, due to the fast deactivation of cracking catalysts, joined to the variety and chemical complexity of the reaction products. To overcome this problem, a systematic methodology was applied that allows to determine the initial selectivity of the different reaction products and hence to stablish the reaction pathways that best described the overall catalysts performance for different feedstocks, including vacuum gas oil and single molecules as model compounds (see the summary on Avelino's early studies of catalytic cracking mainly elaborated by A. Martínez, reported in Ref. [1].

It was clear to Avelino from the very beginning of his systematic exploration of cracking reactions by using different types of commercial acid catalysts, including ultrastable faujasite, that the reaction mechanism and hence the overall reaction should necessarily be connected with the nature of the active sites present in the catalysts, which can be broadly defined as Brønsted and Lewis acid sites. But the instrumentation and expertise required for the characterization of such sites was not available to him by that time. Fortunately, it was by then, at the very early 1980s, that he got acquainted with two scientists that were to play a determinant role in Avelino's scientific career and life. Vicente Fornes and Amparo Mifsud were born in Valencia, as Avelino, but were also working in Madrid at the Institute of Mineral Physical-Chemistry (the seed of the actual Institute of Materials Science of CSIC, located in Madrid), just on the opposite side of the courtyard where the ICP was located (Fig. 1).

They both had experience in the chemistry and physico-chemical characterization of clay minerals and had indeed complementary expertise in fields that were of outermost strategic importance for Avelino's research: A. Fornés in infrared spectroscopy, while A. Mifsud was more focused on transmission electron microscopy (TEM), and both in X-ray diffraction. A deep and enduring friendship arose since they first meet, which served as solid foundation of their continued and extremely fruitful scientific cooperation on the physico-chemical properties of clays and zeolites and their relationship with their catalytic behaviour, that lasted until Amparo and Vicente retirement. The first paper coauthored by Avelino and Vicente was published in 1983 [7], and the following year an article regarding the acidity of sepiolite, a clay mineral, was published with Amparo [8]. She examined by TEM the large number of nickel catalysts supported on this clay that JPP was preparing as part of his PhD work. It was with great sadness that all those who had the privilege of working with Amparo knew she passed away on



Fig. 1. Most of the members of Avelino's research group in a meeting of the Catalysis Group of the Spanish Royal Society of Chemistry held in Madrid in 1988, at the headquarters of CSIC. From bottom to top, and from left to right: first row, Amparo Mifsud, Vicente Fornés, Avelino Corma and Francisco Melo; second row, José Prieto, Joaquín Pérez, Miguel Camblor, Consuelo Goberna and Teresa Blasco; third row, Gloria Garralón, Enrique Sastre, Juana Frontela and Agustín Martínez.

November 13, 2021. She was already retired, but had played an essential role in the foundation of ITQ, and for many years until her retirement, she was the manager of the institute. In addition, she served the whole UPV scientific community as responsible of the Electron Microscopy Unit of the university, transforming it into a modern and competitive laboratory. With this paragraph, we intend to pay a well-deserved tribute to Amparo Mifsud.

Avelino's early studies on catalytic cracking were published mainly in cooperation with Prof. Wojciechowski and his group. They published together in 1986 Catalytic Cracking, a book that was written with the purpose of serving as a guide for the rational exploration of this important process [9]. However, at the beginning of 1980s, a fruitful cooperation with researchers of the Universidad de Valencia (F. Tomás, J. B. Monton and A. V. Orchillés) started also on catalytic cracking involving theoretical studies on reaction mechanisms as well as experimental work. The first papers were published in 1983 and 1984 [10-12], which were followed by many others [13-22]. By that time, Avelino had been able to gather in a very short time a group involving researchers based on Madrid and Valencia, covering the essential aspects of catalytic cracking at laboratory scale: first, accurate experimental results based on a solid methodology; second, theoretical studies on reaction mechanisms and, finally, the physico-chemical characterization of the catalysts and in particular the study of the acidity and the nature of the active sites by IR spectroscopy. It is important to realize that what Avelino did in catalytic cracking in the 1980s from the perspective of research strategy was the forerunner of what he was going to do at much larger scale with the foundation of the ITQ only few years later, in 1990. The main ingredients of this unique successful cocktail were already there, and it was soon proved to be extremely powerful.

By mid 1980s, the many kinetic and mechanistic studies carried out on catalytic cracking evidenced that the activity and selectivity of the different types of faujasite zeolite used as catalysts was somehow related to their Brønsted acidity [12,14,20]. Following this idea, in 1984 researchers at Exxon proposed a single model that simply correlates the cracking behaviour of ultrastable equilibrated faujasites with their unit cell size (a_0) , which is directly related to the amount of aluminium present in the framework and hence to the density of framework Brønsted acid sites [23]. The simplicity of this model was certainly appealing, owing to the fact that the unit cell size of faujasite can be easily determined by routine X-ray diffraction. However, the experience accumulated by Avelino and co-workers on this reaction prompted them

to challenge this simply model by showing that it could not account for the cracking behaviour of HY zeolites dealuminated by different methods, steaming and silicon tetrachloride treatment [24]. Their work clearly evidenced the importance of two aspects that had so far been neglected in that a_0 –based model: the acidity associated to extra-framework aluminium species (EFAL) and the role of the mesopores present in the steamed zeolites in facilitating the accessibility of the bulky gas oil molecules to the active sites. The study of accessibility and, in general, the phenomena related to diffusion in zeolite chemistry plays an important role in Avelino's research in the coming years. Avelino disseminated his main results on cracking in several international meetings organized in USA, particularly by the American Chemical Society, and also in the 8th International Congress on Catalysis organized in Germany in 1984.

3. The beginning of zeolite synthesis at Prof Corma's laboratory

JPP arrived to Avelino's lab to work on an industrial project, what he did for some months before he was granted with a scholarship to research on the catalytic applications of sepiolite (a magnesium silicate clay mineral). This way, he became Avelino's first PhD student. By those years, Avelino recognized the need of having expertise in the synthesis of high-silica zeolite materials to boost his nascent group on catalysis. To materialize this idea, he proposed to JPP a postdoc internship in the laboratory of Prof. P. Jacobs at Katholieke Universiteit Leuven (KUL), Belgium, to learn on the fundamentals of the subject. Nobody at ICP had ever before synthesized zeolites, so we used what we had at hand for that purpose, which turned to be an old high-pressure autoclave lined with a home-made glass liner (not Teflon). JPP did his best, and from the few experiments he carried out in summer of 1984, we got beautiful crystals of analcime and also zeolite P. It has been a long-way from these highframework density zeolites to the extra-large pore synthetic materials recently invented by Avelino and co-workers ...

The choice of Jacobs' lab for the postdoc was not made by chance. JPP remember quite well that in those days Avelino expressed his admiration for the work carried out at the Leuven group, which had so far gained worldwide recognition for its contributions to the scientific understanding of zeolite chemistry and catalysis [25-30]. Avelino's appreciated particularly the interdisciplinary character of the research carried out in that group, the integration of expertise in catalysis, zeolite synthesis, advanced characterization and computational techniques that had made possible such achievements. Leuven lab served as source of inspiration for Avelino's further developments. On arriving in Leuven, JPP realized how right Avelino was. The choice of the laboratory could not have been better, because he found there all facilities and help to learn on the subject. This is the place for a public recognition of how much JPP owe to Prof. Jacobs and Prof. Johann Martens for those two wonderful years at KUL, that so much influenced his scientific career in the years to come, and also to the many people who in one way or another help him at that time. Although the initial project had the objective of synthesizing the ZSM-20 zeolite, a material identified as Beta zeolite was always obtained. It was soon discovered that the repeated fails in getting the target zeolite were due to the enormous amount of potassium salt present as impurity (!) in the commercial tetraethylammonium hydroxide solutions required for the synthesis $(7.5 \text{ g} \cdot \text{L}^{-1} \text{ of K}^+, \text{ crystals could be seen at naked eye at the bottom of the})$ container) [31,32]. The experience acquired by JPP during his postdoc at Leuven allowed to launch a new and stable line on zeolite synthesis at Avelino's group, first centred on zeolite Beta, whose catalytic properties, including its cracking behaviour, were explored in Avelino's group from 1987 onwards, partially in cooperation with the KUL group [20,33].

It was just the right moment to do so. At the early beginning of 1980s, the field of high-silica zeolites was still dominated by ZSM-5. However, things were rapidly changing as the decade deployed. This was clearly recognized by Prof. David Vaughan in 1987, then serving as President of the International Zeolite Association, who in September of that year

declared "zeolite science is now clearly in a post-ZSM-5 period" [34]. This statement was presented at the conclusions of the conference on "Innovation in Zeolite Material Science" organized by the group of Prof. Pierre Jacobs at Katholieke Universiteit Leuven in Belgium, which was attended by Avelino and some of his co-workers, including JPP. As mentioned before, Jacobs' was one of the most worldwide active research teams on zeolite synthesis and catalysis at that moment. P. Jacobs together with J. Martens authored the first reliable compilation of syntheses of high-silica zeolites carried out at Leuven's lab, also containing many other interesting and useful properties of these materials, which was published in coincidence with the conference [35].

4. New premises for new projects

When JPP returned to ICP in October 1986, already as associate researcher, found that Avelino and co-workers had moved to a larger laboratory of 60 m² and, in addition, had an office shared with another researcher of his group, Dr Francisco Melo, and a secretary, to whom JPP joined from then on. It was located outside, but few meters away from the main ICP building, in the premises which had formerly housed a carpentry workshop belonging to CSIC. The place was overcrowded. Avelino's activity boosted in these two years and new predoctoral students, chemists and engineers working for industrial projects and technicians (and several new reactors as well) managed to do their best in such little space. It was there that zeolite synthesis hardware (ovens and on-purpose made autoclaves built following Leuven design) had to be accommodated while new PhD students arrived to work on zeolite synthesis and other topics (FR was one of them). The famous stateroom scene of the Marx Brother's comedy film A Night at the Opera represents quite nicely the physical environment prevailing in those years. But, most importantly, also illustrates everyone's commitment to carry out his or her own work, cooperating in the best possible way with the other fellows that shared the same reduced space. Because it was not just space what we shared, but the feeling of working in the same direction, of being actors of a play which necessarily required several actors for several roles, but in which all of them know that everyone's role is as unique as any other, but at the same time is meaningful only in connection with other actors' characters. Pushing ahead the comparison with the Marx Brother's film, was it a true brotherhood what we all contributed to build in those years? Where the friendship bonds, the subtle links we established along the years what keep all of us working for a common purpose? The organization of research groups is often compared to a pyramid: the boss at the top and the rest of people below him or her in descendant order of importance (usually associated to professional qualifications). We have always preferred the simile of a theatre play, or even a jazz band. Remove an a priori secondary character and the play gets meaningless. Which instrument is the best? Why not to introduce variations from play to play, if all agree? There is no doubt that Avelino is the one who has contributed the most to the script. However, he has not been the only one to do so.

New PhDs projects on m-xylene isomerization, synthesis of zeolites and cracking were at work in that little space full of activity. And it was also there that innovative projects for developing advanced instrumentation begun. Jose Prieto, a chemical engineer from Valencia, and Avelino started the project to develop a new semiautomatic reactor to carry out fixed-bed microactivity catalytic cracking tests (MAT) of zeolite materials. This reactor much improved the evaluation of FCC catalysts as compared with the commercial units then existing. The design was patented [36] and licensed to the company Vinci Technologies for commercialization. Marisol Grande, a chemical engineer who had recently moved to Spain from the Venezuelan Petroleum Institute (INTEVEP), started to work with the new reactor when she arrived in Avelino's lab on January 1988 and was in charge of it (including technical assistance to the licensed company abroad Spain) when she moved in August 1990 to the recently founded ITQ. As in other areas of activity mentioned along this work, this reactor also was the first example of the

contributions of the group to the several advanced reaction systems that were later developed. But beyond its scientific and technical significance, this example nicely illustrates the extraordinary commitment of Avelino's team members in carrying out their work well beyond what would have been reasonable to expect in other circumstances, an attitude essential for understanding the foundation of ITQ, as we will later

In addition to the increased number of scientific publications, the large expansion of the activities of the group that took place from mid 1980s also covered aspects and subjects that would to become from then on characteristic of Avelino's research. First to notice is the attention paid to applied research. As he always uses to say, there are no such things as applied and basic sciences, but the applications of science. This is something that may sound quite obvious nowadays, but it was not so in the Spanish scientific environment then existing. But, we have nevertheless to add that the catalysis research carried out first at the Department of Catalysis of the IQFR from the 1960s and later at ICP had a marked orientation toward applied projects, a characteristic that was shared with other CSIC institutes of the chemistry area.

An early example of this successful involvement of Avelino's group in applied research was the development of a zeolite-based catalyst for the isomerization of light paraffins in cooperation with the Spanish oil and petrochemistry company CEPSA. This project was started in 1987 on the initiative of the Director of the Research Centre of the company, Pedro Miró. The project run for several years and required a narrow cooperation between the CEPSA and ICP researchers to go from the lab to the pilot-plant scale and then the commercial unit. The catalyst was commercialized by Süd-Chemie under de name Hysopar [37–39]. World-wide, more than twenty industrial plants are currently using the CEPSA catalyst.

The other relevant aspect to underline is the ample international network of scientific cooperation that started to be established with different groups. In addition to what has been aforementioned, this cooperation concentrates at the beginning in several Iberoamerican countries, Argentina, Cuba and particularly Venezuela, and later on Brazil too. Several senior and predoctoral researchers came to Avelino's lab by that time. This networking process was stimulated by the participation of the group in a long-term program generously founded by the Spanish government that was launched in 1984, the CYTED program (Science and Technology for Development) with the participation of 21 countries of the area, including Spain and Portugal. The subprogram V named "Catalysts and Adsorbents" started in 1985 (ending 1992) with the aim of developing materials for refining, petrochemistry and fine chemicals industry. One of the projects was devoted to the development of competitive, commercial fluid catalytic cracking catalysts, and several groups were involved, Avelino's among them. The catalysts were evaluated at the MAT unit of our lab and in raiser pilot plants at CEPSA and INTEVEP. The results demonstrate the feasibility of the project, although the prototype catalyst was never marketed [40].

In addition to this project, a thematic network on molecular sieves was also launched within CYTED program. This network regularly organized workshops and schools that gathered postdoc and predoc students, and much contributed to establishing an Iberoamerican network on this subject. Avelino participated in several of them. An example is shown in Fig. 2, corresponding to the workshop organized in 1990 in Caracas, Venezuela.

5. From Madrid to Valencia. The foundation of the Institute of Chemical Technology (ITQ)

As we have above described, the research activity of Avelino's group was expanding rapidly from the second half of the 1980s. This is also reflected in his publications, which jumped from 5 to 6 per year in the early 1980s, to 12-14/year from 1985 to the end of that decade [41]. He and his team were, according to prof. Jacobs, "well-known in the



Fig. 2. Photography of the attendants to the workshop on molecular sieves organized in 1990 in Caracas by the CYTED program. Avelino is on the fourth row, the fourth starting from the left, close to the centre of the picture. JPP is just on the right of the third row.

scientific community of their area for their solid and good work in fluid catalytic cracking and the physico-chemical characterization of zeolite-based catalysts" (Translated to English from the Spanish version published in reference 41). A detailed account on the foundation of ITQ written in Spanish is given in reference 42. The international recognition of Avelino's achievements was evidenced when he was invited to give his first plenary lecture at the 8th International Zeolite Conference that took place in Amsterdam in 1989, where he summarized before the audience his view on the application of zeolites in fluid catalytic cracking [43]. It is interesting to reproduce the topics he enumerated as deserving particular attention in the closing remarks section entitled Present and Future Research on Molecular Sieves for Cracking Catalysts:

- Nature and role of the EFAL: Its control and/or elimination.
- Improvements in the synthesis of Y zeolite (higher Si/Al ratio, size, Al gradients).
- Improving the healing process of the dealuminated sites.
- Big pore (12 and 18 MR) hydrothermally stable (high-silica) zeolites.
- Zeolitic materials containing atoms other than Si and Al (SAPO, MeAPO).
- Hydrothermally stable Pillared Clays (PILCS).
- Submicrocrystalline silica-alumina.
- Improving the knowledge of the chemistry of the process involved in branching, hydrogen transfer coke and aromatic formation, etc, on molecular sieves.

As we have seen, he had already been contributing to many of these topics, other already were under way in his research group, which was to work with renovated intensity along these lines in the years to come. But by the time Avelino delivered this lecture, July 1989, he already knew that this work would not be carried out at ICP. In May of that year, Avelino and Prof. Jaime Primo, who hold a chair in organic chemistry at the Department of Chemistry of the School of Industrial Engineers at Universidad Politécnica de Valencia (UPV), located in the city of the same name, on the Mediterranean coast, started the first official contacts with the authorities of their respective institutions with the purpose of funding a new institute located in the UPV campus. Jaime and Avelino enjoyed a solid and long friendship. They had been fellow students at the Universidad de Valencia and they both came to Madrid to carry out their PhD work at CSIC institutes, Jaime Primo at the Institute of Organic Chemistry, although he went back to Valencia after earning his

doctorate. They knew each other and their corresponding research capabilities well, and started to think on the possibility of joining efforts together with the other members of their respective teams for the foundation of a new institute that would allow to boosting their research

It has been argued [42] that the interest of Avelino in establishing the new institute was determined by the scarce perspectives of expanding his research group due to the lack of available space at ICP. But, it has to be taken into account that the need of additional space was also a problem for other ICP research groups. The growing of this institute had since its creation in 1975 been constrained by the reduced space available in the historical premises erected in 1932, located just downtown Madrid, a place completely unsuitable to work with the chemical reactions (and reactors as well) required in catalysis research. Due to these facts, there was an urgent need of moving the institute outside the city to new premises. ICP authorities started by late 1980s the arrangements required to accomplish this objective, nearly overlapping in time with Avelino's similar actions toward the foundation of the new institute. JPP was one of the members of the commission established by the ICP to design the new building, which was located outside Madrid and besides the campus of Universidad Autónoma. Our research team could certainly have been given more space in the new ICP premises than the one available in the "carpentry" lab, maybe even twice its size, but from then one every additional space requirement would have started a competition with other research groups with similar needs. In addition, the new ICP was to be located far from the CSIC institute were his colleagues Fornés and Mifsud worked, which would have negatively affected their scientific cooperation. However, while these factors are certainly important, the main reason for the creation of ITQ was Avelino's approach to the organization of scientific research: he wished the new institute to operate just as a single large research group, just a big, very big expansion of the model that had so successful been working in the past years, whose main features have been above depicted. While preparing this paper, Prof Fornés handed down to us a brief summary he wrote on some key features of the creation of ITQ. He expressed in this way the main characteristics and functioning of the new institute:

- Full cooperation between researchers.
- Joined development of basic and applied science.
- Reinvestment of the funding coming from industries and patents in enlarging the human and technical resources of ITQ.

It is interesting to notice that in this brief note, Prof Fornés also states that Avelino always dreamed since his days at university of establishing someday a research institute in his native Valencia, asserting that this dream started to become real by the late 1980s thanks to his relationship with his fellows at Valencia. While this was a crucial factor in the process, of no less importance was the willingness of the members of the team working and living in Madrid to unreservedly embarking in the project. This decision was taken by four senior researchers, eight PhD students and three technicians hired to work in R&D projects founded by industries, most of the members of the team [42]. JPP and FR were among them. We have often talked to Avelino on the circumstances that propitiated the foundation of ITQ. He always says that he from the very beginning had the idea of building up a multidisciplinary team able to attack key scientific and technical problems of catalysis. While we agree on that view, we use to remark that to realize that idea something extremely unusual occurred, namely that such large number of persons agreed to start the journey following Avelino's dream, which by then was also theirs. However, this decision was not easy to take and for many of us was not free of stress, the one existing between the centripetal and centrifugal forces that originate in Avelino's leadership. It is well-known that the German writer Johann Wolfgang von Goethe (1749-1832) used chemical reactions to metaphorically describe human relationships in his novel Elective Affinities (best known as poet and novelist, Goethe also authored now forgotten works on chemistry and other sciences and was

a practicing alchemist in his youth). Though not willing to follow Goethe's chemical approach to human behaviour too far, many of us were able to reach a reasonable equilibrium, always unstable however, among these opposite forces, the one represented in chemical equilibrium by two reactions running in opposite directions. The equilibrium position is the result of internal but also of external factors, and this has also been reflected in the evolution of the ITQ. There is no way to escape from that fundamental law of human (chemical) behaviour.

Amparo Mifsud moved to Valencia in September 1989 to take care of the many administration and technical aspects of the project, in particular in the supervision of the building and equipment of the provisional laboratories given to the institute on the commitment of UPV to relocate the institute in a new building as soon as it was possible. Few months later, on May 1990 the ITQ opened its doors in provisional premises in a parking area of the UPV. These 250 m² were distributed in three different sections. The first and largest one devoted to accommodate the catalytic reactors, the second one to synthesis of solid catalysts, which in addition had some desks for the students and technicians, while the equipment for catalyst characterization (XRD, IR, TG and gas adsorption) was arranged in the third one. There were in addition four offices in the main building (Fig. 3).

The ability of Avelino for putting efforts together can be envisaged at this early point of the ITQ's history. Indeed, four researchers from ICP moved to Valencia for starting the ITQ from scratch. In addition, four full professors from the UPV joined to the seminal ITQ. The skills of these researchers came from very diverse chemistry fields. Scientists from Madrid had developed their careers mostly in heterogeneous catalysis, but those members of the ITQ coming from the University were trained in organic chemistry (Prof Primo), Photochemistry (Prof Miranda and Prof García) and environmental chemistry (Prof Asensi). Thus, the ITQ launched two new fruitful research lines that were added to those brought from Madrid. One, for applying heterogeneous catalysis in the synthesis of high added value products (such as synthetic pheromones, flavours, food additives, etc.), and the other on photochemical processes in confined spaces (such as the voids of zeolites).

The research was organized at the ITQ around commune projects, joining different skills depending on the necessities for reaching the objectives of the projects. Thus, naturally, different research areas started to merge. One of the most successful examples of this approach is the synergy between organic and inorganic chemists working at the ITQ in the synthesis of new zeolites having novel topologies. Chemists specialized in organic and inorganic chemistry have been working together since the origin of the ITQ. At the beginning, simple organic cations for their use as organic structure directing agents (OSDAs) of

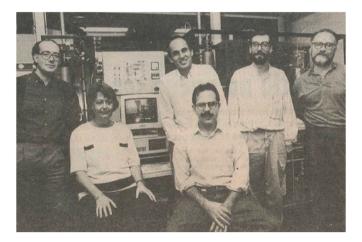


Fig. 3. Picture taken by 1990–1991 in the temporary premises of the ITQ. Avelino is at the centre and Amparo Mifsud on his right. Standing-up are from left to right: Miguel Ángel Miranda, Jaime Primo, José Manuel López Nieto and Vicente Fornés, some of the founders of the ITQ.

microporous zeolites. The complexity of such organic syntheses was gradually increased until today and now, there is a full research line at the ITQ of organic synthesis aiming to synthesize structure-directing agents especially designed by the final applications of the resulting zeolites and later, supported by computational chemistry, trying to predict the final properties of the microporous solids [44]. This approach has been extremely successful and ITQ has developed more than 70 different zeolites, many of them possessing new zeolite topologies. Also, many of these zeolites have found practical application in industrial processes, including catalytic and separation processes.

The collaboration between researchers specialized in organic chemistry with others specialized in catalytic processes, that were mostly focused on refining, allowed the same catalysis concepts to be applied to more complex organic reactions in which more than one functional group may be present. In these cases, the high selectivity of the catalyst is the main target to be achieved, since the active site must be able to 'recognize' one of the functional groups of the reactant, leaving the rest unchanged. The development of catalysts containing highly selective and active centers has made it possible to apply this knowledge to the development of new catalytic processes in fine chemicals, such as the production of an intermediate, diaminodiphenylmethane, used in the manufacture of polyurethanes, and even in the production of food additives.

As it has been said, most of Avelino's research team moved from the ICP to the recently inaugurated ITQ, but only minor equipment was available at that moment, since only a few reactors and some chromatographs were moved to Valencia and the Polytechnic University of Valencia did not have a general characterization service. Therefore, one of the first difficulties, added to the moving itself, was to provide the newly created ITQ with adequate scientific-technical equipment.

Unfortunately, the funding for Science in Spain has never been comparable to that of the European countries of our neighbourhood. Thus, the first characterization instruments, needed for starting the ITQ activities, were mostly purchased with own funds of the research group. These funds were generated through contracts with industries. Undoubtedly, this was a critical moment at the ITQ, since this was a nonreturn decision point. ITQ was an independent research institute within the umbrella of CSIC and UPV, the seed research group of the ITQ Institute assumed the risks that this decision entailed, but being aware of the enormous opportunities that were opened by participating in this common project.

As just mentioned, the support of the industry in the first steps of the ITQ was fundamental. In this sense, the fundamental support of CEPSA, which through its research department relied on the capabilities of the ITQ, and of Avelino Corma as principal investigator, should be highlighted. In these first steps of the ITQ, two relevant research projects were appointed with CEPSA. i) One project aiming to develop a shortchain alkane dehydrocyclization catalyst for the production of aromatics and, ii) A second project continuing with the development of the new isomerization catalysts for the paraffinic light straight run fraction (LSR).

The development of the new catalyst for the LSR naphthas fraction merits to be described in detail because represent a prime example of long and successful public/private collaboration, which was at the DNA of the Avelino's vision of applied science, and because was the first industrial process that reached real application of the long series of catalysts developed at the ITQ.

The improvement in LSR isomerization process was of high relevance early in the 90's because environmental regulations began to ban the use of lead in gasoline. Also, the new regulations fixed more restrictive specifications for olefins and aromatics in automotive fuels. The aforementioned ban on the use of lead as an octane booster in gasoline shifted the CEPSA focus towards the isomerization of light gasoline. Thus, isomerization of paraffinic LSR naphthas and C5/C6 natural gas condensates looked like cost effective process to replace lost octane value. The isomerization increases the octane value of LSR naphtha by

rearranging the low octane straight chain C5–C6 paraffins into their higher octane branched isomers. Isomerization reactions are controlled by thermodynamic equilibrium, with the isomer balance being a function of the temperature. Noble metal promoted catalysts are used to enhance the reaction rate; these catalysts have both a hydrogenation function (noble metal) and an acid component [45].

Essentially, when the project started, there were two types of catalysts depending on whether the noble metal was deposited on a chlorinated alumina or on a zeolite. In the former case, it was necessary to extensively hydrodesulfurize the naphtha feed since the catalyst was extremely sensitive to sulfur. Zeolitic catalysts, on the other hand, were typically more resistant to sulfur contaminants, but still the naphtha could not contain more than 100 ppm of sulfur if the catalyst was to operate effectively [45].

To address these limitations, Avelino Corma's team developed a bifunctional zeolitic catalyst, based on a mordenite, with a suitably adjusted acidity and its corresponding noble metal [37–39].

A transversal team made up of researchers from the Avelino's team and CEPSA Research Centre came together to tackle the project. Several catalysts were synthesized and tested at small scale. Longer and scaled up tests were done at CEPSA. The initial results at bench scale plant demonstrated the exceptional performance and robustness of the catalyst. Then, it was necessary to scale up the catalyst manufacturing process, which was achieved with the help of Süd-Chemie, a German catalyst manufacturer. Simultaneously, CEPSA's Engineering Department designed the new unit for the Algeciras Refinery, which was commissioned in 1991, being the first process being commercialized as consequence of the strong collaboration between a company, CEPSA, and the Avelino's team. Today, CEPSA, together with Süd-Chemie, has licensed up to 20 units in other refineries, with a total treatment capacity of more than 105 KBPSD, evidencing the superior quality of the CEPSA-ITQ catalyst, marketed under the Hysopar name [39].

With the input of the CEPSA projects and some public funding obtained through competitive calls, the ITQ was able to install some scientific equipment needed for its activity, such as X-Ray diffractometer, automatic adsorption analyzer for textural characterization of solids, IR spectrometer and others instruments for pursuing the proper physicalchemical characterization of the catalysts developed at the ITQ. Shortly, large instruments were installed at the ITQ, such as the solidstate NMR spectrometer or the X-ray photoelectron spectrometer, opening the possibility for deeper characterization of the catalysts developed at the ITQ. On top of this strategy, new scientists skilled in all these characterization techniques and technicians were hired at the ITQ for running the on-coming characterization facilities of the ITQ. All the instruments were installed as a characterization service unit of the ITQ and gave service to all researchers working at the ITQ, but prioritizing industrial projects since reporting periods for industry are usually much shorter than for public projects.

Of course, in parallel to this infrastructure for characterization of solid catalysts, several home-made fully automatized reactors were developed and installed at the ITQ, including atmospheric and high-pressure plug-flow reactors and batch reactors.

6. Attacking real industrial problems

The combination of strong staff motivation with a growing research infrastructure and clear scientific leadership boosted ITQ's research, leading to a sharp increase in scientific publications and patents, while the links with industry were strongly reinforced.

In this period, some of the ITQ's most notable discoveries were patented and/or published. i) Synthesis of defect-free pure silica zeolites in fluoride-containing media and ii) Synthesis of Ti-Beta and Ti-MCM-41 catalysts for selective epoxidation reactions. These two major breakthrough discoveries were interlinked one to each other. Indeed, ENI (that stand for Ente Nazionale Idrocarburi) researchers reported the synthesis of Ti-silicalite [46] and later the TS-1 was found as an active

and selective epoxidation catalyst of linear olefins using hydrogen peroxide as oxidant [47-50]. Also, the high activity in epoxidation of short olefins of Ti-silicalite in methanol/water media was attributed to the high organophilic character of Ti-silicalite [48]. Therefore, the ITQ envisaged an opportunity in attempting the synthesis of Titanium containing large pore zeolites that may allow the oxidation of larger olefins than medium pore zeolite, such as Ti-Silicalite. Of course, the first option was zeolite Beta since it was a large accumulated knowledge in its synthesis. The first report of Ti-containing Beta zeolite appeared in 1992, but this Ti-Beta was also containing Aluminium and thus, showing Brønsted acidity [51,52]. The highest Ti content reported in that earlier paper was for a ratio Si/Ti = 30 and a Si/Al approx. 50. This Ti,Al-Beta catalyst was able to convert cycloalkanes in alcohols and ketones in much higher yields than Ti-Silicalite catalyst, especially for large cyclododecane, evidencing the larger accessibility of bulky reactants to the active Ti sites in Beta zeolites than in silicalite [52-55]. However, for olefin epoxidation by H₂O₂, the intrinsic activity of the Ti centers was found lower in Ti-Beta than in TS-1 and the selectivities towards the desired olefins were poor due to the presence of acid sites that catalyses the undesired oxirane ring opening reaction. Nevertheless, the large-pore Ti-Beta catalyst shows superior activity compared to the medium-pore TS-1 for the oxidation of bulkier molecules [54,55]. At this point, it was evident that Al-free Ti-Beta catalysts were required for achieving active and selective epoxidation catalysts. This was accomplished by seeding with zeolite Al-Beta resulting in an essentially free Al-Beta zeolite that provide a very high selectivity for 1-hexene [56].

As it has been said, ENI researchers proposed that the hydrophobic character of Ti-silicalite was responsible of its high performance as epoxidation catalysts because non-polar hydrocarbons are preferentially adsorbed than polar compounds, such as water or alcohols [48]. Thus, the epoxidation of bulky non-polar reactants, such as long chain carboxylates may be enhanced by an hydrophobic Ti-containing large pore zeolite, such as Ti-Beta zeolite.

Flanigen reported in 1977 that pure silica zeolites are highly hydrophobic and selectively adsorb organic compounds from water, either in liquid or vapour phase [57]. Also, she reported that zeolite synthesized in presence of fluoride anions yield to essentially silanol-free materials (i.e. defect free zeolites) with an exceptional degree of hydrophobicity [58]. Consequently, defect free Beta and Ti-Beta zeolites were obtained simultaneously in 1996 [59,60]. The defect-free Ti-Beta catalysts shown a much higher epoxide selectivity than the analogue acid zeolite synthesized in alkaline conditions. The hydrophobic character of Ti-defect free zeolite Beta and its influence on the epoxide selectivity were probed [60]. More important, Ti-Beta catalysts synthesized in fluoride media were able to epoxidase very bulky reactants, such as oleate derivatives, showing the benefit of the combination of the presence of large pore aperture in the zeolite structure and the hydrophobic character due to the absence of silanol groups [60-62]. A comprehensive comparison of the catalytic activity of Ti-silicalite and Ti-Beta has been reported by Saxton [63].

One of the major breakthroughs in material science and heterogeneous catalysis was the discovery of the MS family (MCM-41, MCM-48 and MCM-50) by Mobil researchers that were patented in 1991 and published in 1992 [64–66]. In these earlier communications, it was reported that structured mesoporous solids with very narrow pore aperture were obtained as pure silica and aluminosilicates. The first subsequent research publication on MCM-41 materials came from Corma's team in 1993 [67] and the Ti-substituted MCM-41 catalyst was patented in 1993 [68] and appeared published in January 1994 [69]. This evidenced the ability of Prof Avelino Corma for distinguishing groundbreaking ideas from recent published articles and patents, and his enormous capacity to launch research lines in very short time. This has been a continual in his career as scientific researcher.

The first catalytic results applying Ti-MCM-41 as epoxidation catalyst of very bluky olefins clearly indicates that Ti-MCM-41 overcome the activity of any Ti-zeolite when bulky reactants are involved. Indeed, Ti-

MCM-41 was able to oxidise norbornene and α -pinene to the corresponding epoxides and their derivatives using tertbutyl-hydroperoxide as oxidant. No catalytic activity was obtained on Ti-silicalite and much lower conversion on Ti-Beta than in Ti-MCM-41 [70,71]. This was taken a clear benefit of the large pore aperture of MCM-41 material than that of Ti-Beta. However, the intrinsic activity of Ti sites of MCM-41 was very low when compared to those of Ti-Beta and Ti-silicalite for short-chain olefins, like 1-hexene [71]. At this point and based on these very preliminary catalytic results, Sumitomo and ITQ signed an agreement for developing epoxidation catalysts of propylene using cumene-hydroperoxide as oxidant. ITQ was engaged in the synthesis and optimization of the catalyst based on model reactions, while Sumitomo was up-scaling and testing in lab and pilot plant scale the most promising catalysts developed along the project.

The main problem of this first reported Ti-MCM-41 was the low activity and selectivity towards the desired epoxide. The explanation of this low performance was again the high hydrophilic character of the catalyst due to the presence of a large concentration of silanol groups on their pore surfaces. Thus, ITQ's team successfully turned the MCM-41 into highly hydrophobic material by incorporating organic moieties on the MCM-41 surface. This was achieved through direct anchoring of organosilanes by reacting silanol groups with organosilanes reactants, such as hexamethyldisilazane among many others, or by introducing directly organosilanes in the synthesis media of MCM-41, yielding to hybrid organo-inorganic mesoporous MCM-41 solids or by combining both approaches [72–76]. The optimization of the Ti-MCM-41 catalyst and the understanding of the poisoning mechanisms of the active Ti sites of MCM-41 catalysts allowed developing an extremely active and selective catalyst based on mesoporous Ti-silica [77].

As consequence of this joined project, Sumitomo Chemical Ltd Co. industrially applied the optimised catalyst, quoting approximately by 6% of the worldwide propylene oxide production [78,79].

There are other examples of collaboration between industry and ITQ that have resulted in commercial applications of joint developments in addition to these two examples described above. Some of them are listed below:

- Development of a zeolite catalyst with improved activity for methanol to olefins in collaboration with Clariant Produkte Deutschland GMBH (Süd-Chemie AG). This collaboration was based on earlier research work done at the ITQ for FCC catalytic cracking on zeolites Faujasite and ZSM-5, showing that P-treated catalysts show better stability upon steaming at high temperatures and higher olefin yields than non-treated zeolites [80–82]. Along the R&D project with Clariant, the catalyst was optimised for MTO process, achieving a very long life time and selectivity under reaction conditions. The catalyst was up-scaling and tested in pilot plant at Clariant facilities. The first commercial plant started in 2014 [83,84].
- Development of a new absorbent for sulfur elimination in natural gas in collaboration with Johnson & Matthey PLC. The optimum absorbent composition was obtained by applying combinatorial synthesis, characterization and testing tools. These high-throughput techniques were not easily available at that time. Thus, ITQ developed the high-throughput reactors and characterization techniques as well as the analysis tools for analysing the huge amount of data collected by applying combinatorial techniques [85–87]. The use of high-throughput techniques strongly reduced the optimization process for developing an improved adsorbent able to remove Sulfur from gas streams (particularly natural gas), with very high efficiency and for very long time. JM up-scaling and tested the optimised absorbent in pilot plant and the first commercial plant started working in 2008 [88–90].

In all the examples that ITQ-industry collaborations become commercial, the ITQ role was creating the scientific grounds and optimization process at lab scale, but the companies took the responsibilities of

scaling up, pilot plant testing, catalyst manufacturing and commercialization. These catalyst developments exemplify how the collaboration between industry and academia may push societal progress, which has always been the first goal throughout Avelino's entire career. It is not possible to understand his contribution to the catalysis field without considering the fruitful collaborations with companies. These research projects do not result in many open scientific publications, but they contribute to the advancement of the chemical industry through patents and production plants in operation. Therefore, it is necessary to look at the more than 300 patents in which Avelino Corma appears as an inventor (many of them in operation) to understand the enormous impact that his research has had on the chemical industry and on catalysis in general.

In addition to the industrial projects in which the ITQ, led by Professor Corma, has achieved success. ITQ is been recognized as a prestigious research centre in heterogeneous catalysis and especially in the field of zeolites. Indeed, the ITQ has made relevant contributions into the synthesis of new zeolites and in their application as heterogeneous catalytic processes, including refinery, chemicals and commodities products.

7. Breakthroughs in zeolite science

Here, we will highlight some of the achievements that Corma's group has reached in zeolite synthesis that have opened new avenues for researchers working in the zeolite field. Also, we will emphasize the ability of Avelino of joining researchers of different disciplines for targeting common objectives.

7.1. Delaminated zeolites

Today, the application of 2D-materials is one of the hot topics in nanotechnology and catalysis [91-93]. The ITQ was a pioneer on this regard by proposing the benefits of applying 2D zeolitic materials into catalysis. In 1995, the first patent claiming the delamination of the lamellar precursor of the zeolite MCMC-22 (MWW) was filed [94] and later, published in the open literature in 1998 [95]. This seminal work shows the benefits of combining microporosity of zeolitic materials with a very large external surface area typical of mesoporous solids. In this earlier publication, it was proved that ITQ-2 (the name of the first delaminated zeolite) shows a very similar catalytic activity in hydrocarbon cracking for relatively small molecules, such as decane, than MCM-22, but its cracking activity is enhanced for bulkier molecules such as di-isopropyl-benzene or real vacuum-gasoil feeds [95,96]. The delamination of other zeolitic lamellar precursors was successfully applied to the layered precursors of ferrierite, NU-6 and ITQ-19. The corresponding delayered materials were named as ITQ-6, ITQ-18 and ITQ-20, respectively, showing that the delamination procedure can be applied to most of the layered precursor of zeolites [97–99].

The presence of micro and mesoporosity in zeolitic catalysts as well as the possibility of incorporating other active sites such as Ti [98,100] or even enzymes [101,102] opened new possibilities for catalytic transformation of bulkier reactants, such as those typically found in fine chemistry and/or biomass transformation. Thus, epoxidation of olefins, Beckman rearrangements of bulky ketone-oximes or acetalisation of alcohols were successfully carried out using delaminated zeolites [103-109].

However, we would like to end this section highlighting the project carried in collaboration with Huntsman BVBA consisting in the application of delayed zeolites as a successful heterogenous catalysts for the synthesis of diamino diphenyl methane (DADPM), a monomer used in the production of polyurethane, instead of stoichiometric HCl. The optimised delaminated ITQ-18 zeolite has been tested under similar industrial conditions resulting in a real option for substituting HCl in the DADPM production [110–113].

7.2. Ge-containing zeolites

In 1997, Prof Corma and Dr Camblor reported the first synthesis of a new Ge-containing zeolite, called ITQ-5, at the ITQ [114]. Also, Ge-containing MFI and FAU zeolites were reported previously [115–118], as well as some pure-Germania zeolites. Notoriously, some of these pure-GeO₂ zeolites contained 3-Ring and 4-Ring secondary building units in their structures [119–123]. The presence of strained units was attributed to the longer Ge–O distance (0.172 nm), which is substantially longer than Si–O distance, that produces the narrowing of the Ge-O-Ge angle with respect to Si–O–Si. Indeed, Ge-O-Ge in quartz and in zeolites were found to be around 130°, much smaller than Si–O–Si (approx. 145°) [124]. Thus, it was proposed that Ge might stabilise strained rings in zeolites given rise to low density zeolites as postulated by Meier [125].

This moved to Avelino to launch an ambitious internal research project in 1999 focussed in proving the inorganic directing effect of Ge during the synthesis of zeolites. Very soon, it was confirmed that the presence of Ge favours the crystallization zeolites containing double-4ring (D4R) units in their structures. The zeolite ITQ-17, which was isostructural to the polymorph C of zeolite Beta and to the pure Germania material reported in reference 123, was synthesized in presence a large number of different organic structure agents when Ge was incorporated into the synthesis gel. It was observed that Ge was preferentially located at the crystallographic sites corresponding to the D4R units, supporting the hypothesis of the stabilization effect of strained rings in zeolites by the presence of Ge. The stabilization effect of D4R units was further supported by theoretical calculations, that clearly indicates that D4R units were stabilized by Ge incorporation [126,127]. This approach was expanded to many other D4R-containing zeolites, such as ITQ-7 or ITQ-13 among many others [128,129].

However, this approach turned out to be extremely useful to obtain new large and ultra-large pore zeolitic materials. Thus, the zeolites ITQ-15, ITQ-21, ITQ-22, ITQ-24, ITQ-26, ITQ-34, ITQ-37, ITQ-38, ITQ-49, ITQ-53, ITQ-54, ITQ-62, etc. were obtained as silicogermanates, all of them containing D4R units in their structures [130–141]. But even, more strained 3R and D3R containing zeolites, such as ITQ-53, ITQ-40, ITQ-33 and ITQ-44, were synthesized by pursuing this strategy [139,142–144]. Meier's rule was mostly obeyed in these zeolites resulting most of them in large or ultralarge pore zeolites with some of the lowest framework densities reported in literature at that moment.

It should be pointed out that, some zeolites that were first reported as germanosilicates were later obtained as pure silica by modifying synthesis conditions, such as ITQ-17, ITQ-24 and ITQ-29 [145–147].

Today, the directing effect of Ge has been used by many research groups for obtaining new zeolites. Somehow related, the ADOR approach has extended the possibilities of Ge-containing zeolites for obtaining new zeotypes. Indeed, the ADOR approach consists in the direct chemical degermanation and subsequent condensation of the deassembled layers resulting in pore shrinkage with respect to the parent zeolite. Additionally, chemical degermanation followed by pillaring with silica species has produced new zeotypes with equal or even larger pore apertures than the starting zeolite, but always with different topologies [148–150].

Other relevant contribution of the ITQ in the field of zeolite synthesis is the use of phosphorous containing OSDAs that have given rise to the crystallization of new zeolite structures, such as ITQ-58, ITQ-52, ITQ-49, ITQ-34, ITQ-26 and ITQ-27 [134,135,138,139,151–153]. The presence of P in the occluded OSDA yields to the presence of extraframework P species upon calcination that may modulate the acid strength of the zeolite and also increase the stability of the acid catalysts during high temperature steaming as observed by post-synthesis treatments in medium pore zeolite. However, these post-treatments are useless for softening the acidity and stabilizing small pore zeolites due to diffusional restrictions of phosphate anions through 8R windows. The incorporation of P-OSDA in small pore zeolites allows the formation of extraframework

P species and therefore to achieve these beneficial effects on these family of zeolitic catalysts.

7.3. Recent achievements in zeolite science

More recently, Prof Corma has reported the employ of OSDA that mimics the transition states of relevant reactions. This methodology fixes not only the appropriated confinement space for the transition state stabilization of the desired reaction, but also drives the active site towards the right location within the space where the transition state will be formed. Thus, there is a double stabilization effect. On one side, due to large number of van der Waals interaction that stabilizes the transition state due to its close fitting inside the zeolite cavities. On the other hand, the favourable coulombic interaction between the positively charged transition state and the negatively charged zeolite framework due to the right location of the active site [154]. It is important to emphasize that by this approach, the same zeolite may result for different reactions just being different in the active site location. At present, this catalyst optimization methodology has been successfuly applied by a number of different processes of industrial interest, such as the translakylation reaction of ethylbenzene and benzene and the Methanol-to-Olefin reactions [155,156].

Finally, a recent area of research that has been started at the ITQ in collaboration with the Department of Materials Science and Engineering of the MIT, is trying to apply advanced data-mining and artificial intelligence for the synthesis of zeolites. Up to now, theoretical calculations are very successful in understanding the crystallization of one particular zeolite in presence of one particular OSDA attending to the interactions stablished between the occluded organic moieties and the void spaces of the zeolites, as well as the charge compensation of the organic-inorganic as-made zeolite. Thus, calculation may predict the formation of one zeolite due to the templating effect of one particular OSDA. However, computational chemistry fails in predicting the competition between different phases that may crystallize in presence of one OSDA as very often occurs. This research line has started by analysing the whole information contained in more than half-million references automatically found in literature by applying data mining methods, machine learning and generative neural network models. This approach has allowed to examine the links between OSDAs, gel composition and resulting zeolite structures. Importantly, this methodology has been experimentally validated and several zeolite intergrowths have been synthesized by this approach with good agreement to the predicted results. Finally, a parameter of 'chemical feasibility' has been introduced in the system and automatic retrosynthesis analysis of the proposed OSDA is carried out. Those results that involves a large number of synthesis steps are discarded and only the OSDA syntheses that involves commercially available reactants and a few number of synthesis steps are given as positive output of the calculation. This is a still under development project, but preliminary results have been highly promising and it seems that this approach can be a useful tool for predicting the right OSDA for a given zeolite by taking advantage of the huge accumulated knowledge in the field [157-160].

This work does not attempt to exhaustively review the scientific production Avelino Corma, but it pretends to highlight his enormous capacity to propose new projects capable of exciting a very large number of researchers of different disciplines and making them work in a coordinated manner and sharing common objectives.

This has turned the ITQ and many of its researchers a reference in their respective fields of research. Without a doubt, the ITQ would not have reached the level of excellence without the foundations that Prof Corma has fostered throughout his research career.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- [1] M. Boronat, M.J. Climent, P. Concepción, U. Díaz, H. García, S. Iborra, A. Leyva-Pérez, L. Liu, A. Martínez, C. Martínez, M. Moliner, J. Pérez-Pariente, F. Rey, E. Sastre, P. Serna, S. Valencia, A career in catalysis: Avelino Corma, ACS Catal. 12 (2022) 7054–7123.
- [2] J. Pérez-Pariente, J. Soria Ruiz, J.F. García de la Banda, The origin of the Instituto de Catálisis y Petroleoquímica (ICP, institute of catalysis and Petroleum chemistry) of the Spanish national research Council and its relationship with the development of catalysis in Spain, Catal. Today 259 (2015) 3–8.
- [3] A. Cortes, A. Corma, The mechanism of catalytic isomerization of xylenes: kinetic and isotopic studies, J. Catal. 51 (1978) 338–344.
- [4] A. Corma, A. Cortes, I. Nebot, F. Tomas, On the mechanism of catalytic isomerization of xylenes. Molecular orbital studies, J. Catal. 57 (1979) 444–449.
- [5] A. Corma, A. Cortes, Kinetics of the gas-phase catalytic isomerization of xylenes, Ind. Eng. Chem. Process Des. Dev. 19 (1980) 263–267.
- [6] A. Corma, B.W. Wojciechowski, J. Catal. 60 (1979) 77-82.
- [7] A. Corma, A.L. Agudo, V. Fornés, Infrared spectroscopic evidence for the presence of H⁺(H₂O)_n ions in a decationated Y-type zeolite, JCS, Chem. Commun. (1983) 942–944.
- [8] A. Corma, J. Perez-Pariente, V. Fornes, A. Mifsud, Surface acidity and catalytic activity of a modified sepiolite, Clay Miner. 19 (1984) 673–676.
- [9] B.W. Wojciechowski, A. Corma, Catalytic Cracking, Marcel Dekker, Inc., New York, 1986.
- [10] A. Corma, A.L. Agudo, I. Nebot, F. Tomás, A kinetic study of the cracking, isomerization, and disproportionation of n-heptane on a chromium-exchanged Y zeolite, J. Catal. 77 (1982) 159–168.
- [11] A. Corma, J.B. Monton, A.V. Orchilles, Influence of acid strength distribution on the cracking selectivity of zeolite Y catalysts, Ind. Eng. Chem. Process Des. Dev. 23 (1984) 404–409.
- [12] A. Corma, V. Fornés, J.B. Monton, A.V. Orchilles, Comparison of the activity, selectivity and decay properties of LaY and HY ultrastable zeolites during the cracking of alkanes, Appl. Catal. 12 (1984) 105–116.
- [13] J. Planelles, J. Sánchez-Marín, F. Tomás, A. Corma, A molecular orbital approach to a comprehensive cracking mechanism for linear long chain alkanes in heterogeneous acid catalytic conditions through carbenium ion β-cleavage, JCS, Perkin Trans. 2 (1985) 333–340.
- [14] A. Corma, J. Planelles, F. Tomás, The role of different types of acid site in the cracking of alkanes on zeolite catalysts, J. Catal. 94 (1985) 445–454.
- [15] A. Corma, J.B. Monton, A.V. Orchilles, Cracking of n-heptane on a HZSM-5 zeolite. The influence of acidity and pore structure, Appl. Catal. 16 (1985) 161–168.
- [16] J. Planelles, F. Tomás, A. Corma, The influence of branching isomerization on the product distribution obtained during cracking of n-heptane on acidic zeolites, J. Catal. 93 (1985) 30–37.
- [17] J. Planelles, J. Sánchez-Marín, F. Tomás, A. Corma, On the formation of methane and hydrogen during cracking of alkanes, J. Mol. Catal. 32 (1985) 365–375.
- [18] A. Corma, V. Fornés, J.B. Monton, A.V. Orchilles, Structural and cracking properties of REHY zeolites. Activity, selectivity, and catalyst-decay optimization for n-heptane cracking, Ind. Eng. Chem. Process Des. Dev. 25 (1986) 231–238.
- [19] A. Corma, J.B. Monton, A.V. Orchilles, Influence of the process variables on the product distribution and catalyst decay during cracking of paraffins, Appl. Catal. 23 (1986) 255–269.
- [20] A. Corma, V. Fornés, J.B. Monton, A.V. Orchilles, Catalytic activity of large-pore high Si/Al zeolites: cracking of heptane on H-Beta and dealuminated HY zeolites, J. Catal. 107 (1987) 288–295.
- [21] A. Corma, V. Fornés, J.B. Monton, A.V. Orchilles, Catalytic cracking of alkanes on large pore, high SiO₂/Al₂O₃ zeolites in the presence of basic nitrogen compounds. Influence of catalyst structure and composition in the activity and selectivity, Ind. Eng. Chem. Process Des. Dev. 26 (1987) 882–886.

- [22] A. Corma, A.V. Orchilles, Formation of products responsible for motor and research octane of gasolines produced by cracking. The implication of framework Si Al ratio and operation variables, J. Catal. 115 (1989) 551–566.
- [23] L. Pine, P.J. Maher, W.A. Wachter, Prediction of cracking catalyst behavior by a zeolite unit cell size model, J. Catal. 85 (1984) 466–476.
- [24] A. Corma, V. Fornés, A. Martínez, A.V. Orchillés, Parameters in addition to the unit cell that determine the cracking activity and selectivity of dealuminated HY zeolites, ACS Symp. Ser. 368 (1988) 542–554 (Chapter 35).
- [25] J.A. Martens, P.A. Jacobs, J. Weitkamp, Attempts to rationalize the distribution of hydrocracked products. I qualitative description of the primary hydrocracking modes of long chain paraffins in open zeolites, Appl. Catal. 20 (1986) 239–281.
- [26] J.A. Martens, P.A. Jacobs, J. Weitkamp, Attempts to rationalize the distribution of hydrocracked products. II qualitative description of the primary hydrocracking modes of long chain paraffins in open zeolites, Appl. Catal. 20 (1986) 283–303.
- [27] J.A. Martens, M. Tielen, P.A. Jacobs, J. Weitkamp, Estimation of the void structure and pore dimensions of molecular sieve zeolites using the hydroconversion of n-decane, Zeolites 4 (1984) 98–107.
- [28] J.A. Martens, P.A. Jacobs, J. Weitkamp, H.K. Beyer, Shape-selectivity changes in high-silica zeolites, Faraday Discuss. Chem. Soc. 72 (1981) 353–369.
- [29] P.A. Jacobs, M. Tielen, J.A. Martens, H.K. Beyer, Comparison of acid- to metalcatalysed conversion of n-decane and cyclodecane on ZSM-5 and faujasite-type zeolites, J. Mol. Catal. 27 (1984) 11–23.
- [30] P.A. Jacobs, J.A. Martens, Exploration of the void size and structure of zeolites and molecular sieves using chemical reactions, Pure Appl. Chem. 58 (1986) 1329–1338.
- [31] J. Pérez-Pariente, J.A. Martens, P.A. Jacobs, Crystallization mechanism of zeolite Beta from (TEA)2O, Na2O and K2O containing aluminosilicate gels, Appl. Catal. 31 (1987) 35–64.
- [32] J. Pérez-Pariente, J.A. Martens, P.A. Jacobs, Factors affecting the synthesis efficiency of zeolite BETA from aluminosilicate gels containing alkali and tetraethylammonium ions, Zeolites 8 (1988) 46–53.
- [33] J.A. Martens, J. Pérez Pariente, E. Sastre, A. Corma, P.A. Jacobs, Isomerization and disproportionation of metaxylene. Selectivities induced by the void structure of the zeolite framework, Appl. Catal. 45 (1988) 85–101.
- [34] D.E.W. Vaughan, Preface, Stud. Surf. Sci. Catal. 37 (1988) XI-XII.
- [35] Peter A. Jacobs, Johan A. Martens (Eds.), Synthesis of High-Silica Aluminosilicate Zeolites (Book Series: Studies in Surface Science and Catalysis, Elsevier B.V., Amsterdam), 1987 vol. 33.
- [36] A. Corma, F. Melo, J. Prieto, Computerized unit for the study and evaluation of FCC catalysts, WO 90 (1990), 12317.
- [37] J. Lázaro Múñoz, A. Corma Canos, J.M. Frontela Delgado, Preparation of an isomerization catalyst for light hydrocarbons, US Patent, SP Patent ES 5 (1990), 2014811, 057,471 (1991).
- [38] A. Corma, J. Frontela, J. Lázaro, M. Pérez, Design of Pt-mordenite catalysts for the isomerization of C5 and C6 n-alkanes in light straight run, Preprint Paper Am. Chem. Soc. Div. Petrol. Chem. 36 (1991) 833–840.
- [39] M.F. Gilbert, C.O. Mora, Anshumali, F.M. Floyd, M. Pérez-Pasqual, E. Köhler, Coping with Sulphur and Water in Naphtha Isomerisation Feeds, PTQ Q2, 1999, pp. 1–7 (accessed, www.digitalrefining.com/article/1000685, 21/11/2022.
- [40] P. Andreu, Development of catalysts for the fluid catalytic cracking process: an example of CYTED-D program, Catal. Lett. 22 (1993) 135–146.
- [41] A. Alexaindre, Análisis de la actividad científica de Avelino Corma a través de indicadores bibliométricos, M.Sc., Universidad Católica de Valencia, 2014.
- [42] E. Castro, I. Fernández de Lucio, Iniciativas institucionales e individuales en la creación de estructuras científicas, vol. 183, El Instituto de Tecnología Química, Arbor. 2007. pp. 803–819.
- [43] A. Corma, Application of zeolites in fluid catalytic cracking and related processes, Stud. Surf. Sci. Catal. 49A (1989) 49–67.
- [44] M.J. Sabater, G. Sastre, A computational study on the templating ability of the trispyrrolidinium cation in the synthesis of ZSM-18 zeolite, Chem. Mater. 13 (2001) 4520–4526
- [45] M.A. Romero, J. Lázaro, J. Frontela, in: V. Blay, L.F. Bobadilla, A. Cabrera García (Eds.), Oil Refining and Petrochemistry: Use of Zeolites and Opportunities for MOFs in 'Zeolites And Metal-Organic Frameworks', Amsterdam University Press, Amsterdam, 2018, pp. 89–116.
- [46] M. Taramassi, G. Perego, B. Notari, Preparation of Porous Crytsalline Synthetic Material Comprised of Silicon and Titanium Oxides, 1983, p. US4410501.
- [47] G. Bellussi, M.G. Clerici, F. Buonomo, A. Esposito, B. Notari, Catalyst on the Basis of Silicon and Titanium Having High Mechanical Strength, 1986, EP0200260.
- [48] G. Perego, G. Bellussi, C. Corno, M. Taramasso, F. Buonomo, A. Esposito, Titanium-silicalite: a novel derivative in the pentasil family, Stud. Surf. Sci. Catal. 28 (1988) 129–136.
- [49] M.G. Clerici, G. Bellussi, U. Romano, Synthesis of propylene oxide from propylene and hydrogen peroxide catalyzed by titanium silicalite, J. Catal. 129 (1991) 159–167.
- [50] G. Bellussi, A. Carati, M.G. Clereci, G. Maddinelli, R. Millini, Reactions of titanium silicalite with protic molecules and hydrogen peroxide, J. Catal. 133 (1992) 220–230.
- [51] M.A. Camblor Fernández, A. Corma Canós, J. Pérez Pariente, Síntesis de un silicoaluminatotitanato isomorfo a la zeolita Beta, activo para la oxidación selectiva de compuestos orgánicos, ES2037596, 1993.
- [52] M.A. Camblor, A. Corma, A. Martínez, J. Pérez-Pariente, Synthesis of a titaniumsilicoaluminate Isomorphous to zeolite beta and its application as a catalyst for the selective oxidation of large organic molecules, J.C.S., Chem Commun. (1992) 589–590.

- [53] M.A. Camblor, A. Corma, J. Pérez-Pariente, Synthesis of titanoaluminosilicates isomorphous to zeolite Beta, active as oxidation catalysts, Zeolites 13 (1993) 82–87.
- [54] M.A. Camblor, A. Corma, A. Martínez, J. Pérez-Pariente, S. Valencia, Influence of the synthesis procedure and chemical composition on the activity of titanium in Ti-beta catalysts, Stud. Surf. Sci. Catal. 82 (1994) 531–540.
- [55] A. Corma, M.A. Camblor, P. Esteve, A. Martínez, J. Pérez-Pariente, Activity of Ti-Beta catalyst for the selective oxidation of alkenes and alkanes, J. Catal. 145 (1994) 151–158.
- [56] M.A. Camblor, M. Constantini, A. Corma, L. Gilbert, P. Esteve, A. Martínez, S. Valencia, Synthesis and catalytic activity of aluminium-free zeolite Ti- β oxidation catalysts, Chem. Commun. (1996) 1339–1340.
- [57] R.W. Grose, E.M. Flanigen, Crystalline Silica, 1977, p. US4061724.
- [58] E.M. Flanigen, R.L. Patton, Silica Polymorph and Process for Preparing Same, 1978, p. US4073865.
- [59] M.A. Camblor, A. Corma, S. Valencia, Spontaneous nucleation and growth of pure silica zeolite-β free of connectivity defects, Chem. Commun. (1996) 2365–2366.
- [60] T. Blasco, M.A. Camblor, A. Corma, P. Esteve, A. Martínez, C. Prieto, S. Valencia, Unseeded synthesis of Al-free Ti- β zeolite in fluoride medium: a hydrophobic selective oxidation catalyst, Chem. Commun. (1996) 2367–2368.
- [61] T. Blasco, M.A. Camblor, A. Corma, P. Esteve, J.M. Guil, A. Martínez, J. A. Perdigón-Melón, S. Valencia, J. Phys. Chem. B 102 (1998) 75–88.
- [62] M.A. Camblor, A. Corma, P. Esteve, A. Martínez, S. Valencia, Epoxidation of unsaturated fatty esters over large-pore Ti-containing molecular sieves as catalysts: important role of the hydrophobic-hydrophilic properties of the molecular sieve, Chem. Commun. (1997) 795–796.
- [63] R.J. Saxton, Crystalline microporous titanium silicates, Top. Catal. 9 (1999) 43–57.
- [64] J.C. Beck, C. Chu, L.D. Johnson, C.T. Kresge, M.E. Leonowicz, W.J. Roth, J. C. Vartuli, Synthesis of Mesoporous Crystalline Material, 1992, p. US5108725.
- [65] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.C. Beck, Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, Nature 259 (1992) 710–712.
- [66] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T. W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, A new family of mesoporous molecular sieves prepared with liquid crystal templates, J. Am. Chem. Soc. 114 (1992) 10834–10843.
- [67] W. Kolodziejski, A. Corma, M.T. Navarro, J. Perez-Pariente, Solid-state NMR study of ordered mesoporous aluminosilicate MCM-41 synthesized on a liquidcrystal template, Solid State Nucl. Magn. Reson. 2 (1993) 253–259.
- [68] A. Corma Canós, M.T. Navarro Villaba, J. Perez Pariente, Material de estructura tipo zeolita de poros ultragrandes con un red constituida por óxidos de silicio y titanio; su síntesis y utilización para la oxidación selectiva de productos orgánicos, 1996, p. ES2092428.
- [69] A. Corma, M.T. Navarro, J. Perez-Pariente, Synthesis of an ultralarge pore titanium silicate Isomorphous to MCM-41 and its application as a catalyst for selective oxidation of hydrocarbons, J.C.S., Chem. Commun. (1994) 147–148.
- [70] A. Corma, M.T. Navarro, J. Perez-Pariente, F. Sánchez, Preparation and properties of Ti-containing MCM-41, Stud. Surf. Sci. Catal. 84 (1994) 69–75.
- [71] T. Blasco, A. Corma, M.T. Navarro, J. Perez-Pariente, Synthesis, characterization, and catalytic activity of Ti-MCM-41 structures, J. Catal. 156 (1995) 65–74.
- [72] J. Tsuji, J. Yamamoto, A. Corma Canos, F. Rey García, M.T. Navarro, Catalizador de óxido de silicio que contiene titanio, 2002, p. ES2165771.
- [73] J. Tsuji, J. Yamamoto, A. Corma Canos, F. Rey García, Method for Producing Propylene Oxide, 2001, p. US6211388.
- [74] A. Corma, M. Domine, J.A. Gaona, J.L. Jordá, M.T. Navarro, F. Rey, J. Pérez-Pariente, J. Tsuji, B. McCulloch, L.T. Nemeth, Strategies to improve the epoxidation activity and selectivity of Ti-MCM-41, Chem. Commun. (1998) 2211–2212.
- [75] A. Corma, J.L. Jordá, M.T. Navarro, F. Rey, One step synthesis of highly active and selective epoxidation catalysts formed by organic-inorganic Ti containing mesoporous composites, Chem. Commun. (1998) 1899–1900.
- [76] M.L. Peña, V. Dellarocca, F. Rey, A. Corma, S. Coluccia, L. Marchese, Elucidating the local environment of Ti(IV) active sites in Ti-MCM-48: a comparison between silylated and calcined catalyst, Microporous Mesoporous Mater. 44–45 (2001) 345–356.
- [77] J. Silvestre-Alberó, M. Domine, J.L. Jordá, M.T. Navarro, F. Rey, F. Rodríguez-Reinoso, A. Corma, Spectroscopic, calorimetric, and catalytic evidences of hydrophobicity on Ti-MCM-41 silylated materials for olefin epoxidations, Appl. Catal. Gen. 507 (2015) 14–25.
- [78] J. Tsuji, J. Yamamoto, M. Ishino, N. Oku, Development of new propylene oxide process, Sumitomo Kagaku I (2006) 1–8. https://www.sumitomo-chem.co.jp/ english/rd/report/files/docs/20060100_ely.pdf, 20/11/2022.
- [79] T. Kawabata, J. Yamamoto, H. Koike, S. Yoshida, Trends and views in the development of technologies for propylene oxide production (English Edition), SUMITOMO KAGAKU (2019), 1-9, https://www.sumitomo-chem.co.jp/english/ rd/report/files/docs/2019E_1.pdf, 20/11/2022.
- [80] A. Corma, V. Fornés, W. Kolodziejski, J. Martínez-Triguero, Orthophosphoric acid interactions with ultrastable zeolite Y: infrared and NMR studies, J. Catal. 145 (1994) 27–36.
- [81] W. Kolodziejski, V. Fornés, A. Corma, Solid-state NMR study of ultrastable zeolite Y modified with orthophosphoric acid, Solid State Nucl. Magn. Reson. 2 (1993) 121–129.
- [82] T. Blasco, A. Corma, J. Martínez-Triguero, Hydrothermal stabilization of ZSM-5 catalytic-cracking additives by phosphorus addition, J. Catal. 237 (2006) 267–277.

- [83] M. Frauenrath, S. Klingelhöfer, G. Burgfels, A. Corma Canós, J. Martínez Triguero, E. Corresa Mateu, Improved Process for Manufacture of a Zeolite Based Catalysy for the Conversion of Methanol to Olefins, 2018, p. US10005073.
- [84] M. Frauenrath, S. Klingelhöfer, G. Burgfels, A. Corma Canós, J. Martínez Triguero, E. Corresa Mateu, Process for Manufacture of a Zeolite Based Catalyst for the Conversion of Methanol to Olefins, 2018, p. US10112188.
- [85] J.M. Serra, A. Corma, A. Chica, E. Argente, V. Botti, Can artificial neural networks help the experimentation in catalysis? Catal. Today 81 (2003) 393–403.
- [86] J.M. Serra, A. Corma, E. Argente, S. Valero, V. Botti, Neural networks for modelling of kinetic reaction data applicable to catalyst scale up and process control and optimisation in the frame of combinatorial catalysis, Appl. Catal. Gen. 254 (2003) 133–145.
- [87] L.A. Baumes, J.M. Serra, P. Serna, A. Corma, Support vector machines for predictive modeling in heterogeneous catalysis: a comprehensive introduction and overfitting investigation based on two real applications, J. Combin. Chem. 8 (2006) 583–596.
- [88] G.E. Wilson, N. MacLeod, E.M. Vass, A. Chica Lara, A. Corma Canós, Y. Saavedra López, Desulphurisation Process, 2014, p. US8702974.
- [89] G. Potter, G.E. Wilson, N. MacLeod, A. Chica Lara, A. Corma Canós, Y. Saavedra López, Desulphurisation Materials, 2012, p. US8236262.
- [90] N. MacLeod, A. Chica Lara, A. Corma Canós, Y. Saavedra López, Preparation of Desulphurisation Materials, 2012, p. US8314047.
- [91] E. Schulman, W. Wu, D. Liu, Two-dimensional zeolite materials: structural and acidity properties, Materials 13 (2020) art. no. 1822.
- [92] J. Přech, P. Pizarro, D.P. Serrano, J. Áejka, From 3D to 2D zeolite catalytic materials, Chem. Soc. Rev. 47 (2018) 8263–8306.
- [93] M.V. Opanasenko, W.J. Roth, J. Čejka, Two-dimensional zeolites in catalysis: current status and perspectives, Catal. Sci. Technol. 6 (2016) 2467–2484.
- [94] A. Corma Canós, V. Fornés Seguí, S.B.C. Pergher, Oxide Materials, Process for Their Preparation and Catalyst Composition Containing These Materials, 2003, FP0859742
- [95] A. Corma, V. Fornés, S.B. Pergher, Th.L.M. Maesen, J.G. Buglass, Delaminated zeolite precursors as selective acidic catalysts, Nature 396 (1998) 353–356.
- [96] A. Corma, V. Fornés, J. Martínez-Triguero, S.B. Pergher, Delaminated zeolites: combining the benefits of zeolites and mesoporous materials for catalytic uses, J. Catal. 186 (1999) 57–63.
- [97] A. Corma, V. Fornés, U. Díaz, ITQ-18 a new delaminated stable zeolite, Chem. Commun. (2001) 2642–2643.
- [98] A. Corma, U. Díaz, M.E. Domine, V. Fornés, Al-ITQ-6 and Ti.ITQ-6: synthesis, characterization, and catalytic activity, Angew. Chem. Int. Ed. 39 (2000) 1499–1501.
- [99] A. Corma Canós, V. Fornés Seguí, U. Díaz Morales, Microporous Crystalline Zeolite Material (ITO-20) and Production Method Thereof, 2006, US7008611.
- [100] A. Corma, U. Diaz, V. Fornés, J.L. Jordá, M.E. Dómine, F. Rey, Ti/TTQ-2, a new material highly active and selective for the epoxidation of olefins with organic hydroperoxides, Chem. Commun. (1999) 779–780.
- [101] A. Corma, V. Fornés, J.L. Jorda, F. Rey, R. Fernández-Lafuente, J.M. Guisan, C. Mateo, Electrostatic and covalent immobilisation of enzymes on ITQ-6 delaminated zeolitic material, Chem. Commun. (2001) 419–420.
- [102] A. Corma, V. Fornés, F. Rey, Delaminated zeolites: an efficient support for enzymes, Adv. Mater. 14 (2002) 71–74.
- [103] A. Corma, O. de la Torre, M. Renz, Production of high quality diesel from cellulose and hemicellulose by the Sylvan process: catalysts and process variables, Energy Environ. Sci. 5 (2012) 6328–6344.
- [104] K.S. Arias, M.J. Climent, A. Corma, S. Iborra, Synthesis of high quality alkyl naphthenic kerosene by reacting an oil refinery with a biomass refinery stream, Energy Environ. Sci. 8 (2015) 317–331.
- [105] M. Moliner, A. Corma, Advances in the synthesis of titanosilicates: From the medium pore TS-1 zeolite to highly-accessible ordered materials, Micropor. Mesopor. Mater. 189 (2014) 31–40.
- [106] M.J. Climent, A. Corma, A. Velty, Synthesis of hyacinth, vanilla, and blossom orange fragrances: the benefit of using zeolites and delaminated zeolites as catalysts, Appl. Catal. Gen. 263 (2004) 155–161.
- [107] I. Rodríguez, M.J. Climent, S. Iborra, V. Fornés, A. Corma, Use of delaminated zeolites (ITQ-2) and mesoporous molecular sieves in the production of fine chemicals: preparation of dimethylacetals and tetrahydropyranylation of alcohols and phenols, J. Catal. 192 (2000) 441–447.
- [108] P. Botella, A. Corma, S. Iborra, R. Montón, I. Rodríguez, V. Costa, Nanosized and delayered zeolitic materials for the liquid-phase Beckmann rearrangement of cyclododecanone oxime, J. Catal. 250 (2007) 161–170.
- [109] A. Corma, U. Díaz, M.E. Domine, V. Fornés, New aluminosilicate and titanosilicate delaminated materials active for acid catalysis, and oxidation reactions using H₂O₂, J. Am. Chem. Soc. 122 (2000) 2804–2809.
- [110] P. Botella, J.K.P. Bosman, C. Mitchell, A. Corma, Process for the Production of Diaminodiphenylmethane and its Higher Homologues, 2008, p. EP1487777.
- [111] P. Botella, A. Corma, C. Mitchell, Synthesis of diamine diphenyl methane (DADPM) and its higher homologues on delaminated zeolites: A challenge for a non-polluting process, Stud. Surf. Scien. Catal. 158 (2005) 1263–1270.
- [112] A. Corma, P. Botella, C. Mitchell, Replacing HCl by solid acids in industrial processes: synthesis of diamino diphenyl methane (DADPM) for producing polyurethanes, Chem. Commun. (2004) 2008–2010.
- [113] P. Botella, A. Corma, R.H. Carr, C. Mitchell, Towards an industrial synthesis of diamino diphenyl methane (DADPM) using novel delaminated materials: a breakthrough step in the production of isocyanates for polyurethanes, Appl. Catal. Gen. 398 (2011) 143–149.

- [114] M.A. Camblor Fernández, A. Corma Canóns, S. Valencia Valencia, Zeolita ITQ-5, 1999, p. ES2137885.
- [115] R.M. Barrer, J.W. Baynham, F.W. Bultitude, W.M. Meier, Hydrothermal chemistry of the silicates. Part VIII. Low-temperature crystal growth of aluminosilicates, and of some gallium and germanium analogues, J. Chem. Soc. (1959) 195–208.
- [116] L. Lerot, G. Poncelet, J.J. Fripiat, Synthesis, structural characterization and stability of a germanic (A1-Ge) near Faujasite zeolite, Mater. Res. Bull. 9 (1974) 979–988.
- [117] Z. Gabelica, J.L. Guth, Silica/Germanium Oxide Zeolites, 1994, p. US5371307.
- [118] Z. Gabelica, J.L. Guth, A silicogermanate with a Si: Ge ratio ≥ 2 an MFI zeolite of novel composition, Angew. Chem., Int. Ed. 28 (1989) 81–83.
- [119] H. Li, O.M. Yaghi, Transformation of germanium dioxide to microporous germanate 4-connected nets, J. Am. Chem. Soc. 120 (1998) 10569–10570.
- [120] M. O'Keefe, O.M. Yaghi, Germanate zeolites: contrasting the behavior of germanate and silicate structures built from cubic T₈O₂₀ units (T=Ge or Si), Chem. Eur J. 5 (1999) 2796–2801.
- [121] J. Chen, R. Xu, G. Yang, Synthesis, structure and characterization of a novel germanium dioxide with occluded tetramethylammonium hydroxide, J. Chem. Soc. Dalton Trans. (1991) 1537–1540.
- [122] X. Bu, P. Feng, G.D. Stucky, Novel germanate zeolite structures with 3-rings, J. Am. Chem. Soc. 120 (1998) 11204–11205.
- [123] T. Conradsson, M.S. Dadachov, X.D. Zou, Synthesis and structure of (Me₃N)₆[Ge₃₂O₆₄]·(H₂O)_{4.5}, a thermally stable novel zeotype with 3D interconnected 12-ring channels, Micropor. Mesopor. 41 (2000) 183–191.
- [124] G.S. Smith, P.B. Isaacs, The crystal structure of quartz-like GeO₂, Acta Crystallogr. 17 (1964) 842–846.
- [125] G.O. Brunner, W.M. Meier, Framework density distribution of zeolite-type tetrahedral nets, Nature 337 (1989) 146–147.
- [126] A. Corma, M.T. Navarro, F. Rey, J. Rius, S. Valencia, Pure polymorph C of zeolite Beta synthesized by using framework isomorphous substitution as a structuredirecting mechanism, Angew. Chem. Int. Ed. 40 (2001) 2277–2280.
- [127] G. Sastre, J.A. Vidal-Moya, T. Blasco, J. Rius, J.L. Jordá, M.T. Navarro, F. Rey, A. Corma, Preferential location of Ge atoms in polymorph C of beta zeolite (ITQ-17) and their structure-directing effect: a computational, XRD, and NMR spectroscopic study, Angew. Chem. Int. Ed. 41 (2002) 4722–4726.
- [128] T. Blasco, A. Corma, M.J. Díaz-Cabañas, F. Rey, J.A. Vidal-Moya, C.M. Zicovich-Wilson, Preferential location of Ge in the double four-membered ring units of ITQ-7 zeolite, J. Phys. Chem. 106 (2002) 2634–2642.
- [129] J.A. Vidal-Moya, T. Blasco, F. Rey, A. Corma, M. Puche, Distribution of Fluorine and Germanium in a new zeolite structure ITQ-13 studied by ¹⁹F nuclear magnetic resonance, Chem. Mater. 15 (2003) 3961–3963.
- [130] A. Corma, M.J. Dîaz-Cabañas, F. Rey, S. Nicolopoulus, K. Boulahya, ITQ-15: the first ultralarge pore zeolite with a bi-directional pore system formed by intersecting 14- and 1-ring channels, and its catalytic implications, Chem. Commun. (2004) 1356–1357.
- [131] A. Corma, M.J. Díaz-Cabañas, J. Martínez-Triguero, F. Rey, J. Rius, A large-cavity zeolite with wide pore windows and potential as an oil refining catalyst, Nature 418 (2002) 514–517.
- [132] A. Corma, F. Rey, S. Valencia, J.L. Jordá, J. Rius, A zeolite with interconnected 8-, 10- and 12-ring pores and its unique catalytic selectivity, Nat. Mater. 2 (2003) 493–497.
- [133] R. Castañeda, A. Corma, V. Fornés, F. Rey, J. Rius, Synthesis of a new zeolite structure ITQ-24, with intersecting 10- and 12-membered ring pores, J. Am. Chem. Soc. 125 (2003) 7820–7821.
- [134] D.L. Dorset, K.G. Strohmaier, C.E. Kliewer, A. Corma, M.J. Díaz-Cabañas, F. Rey, C.J. Gilmore, Crystal structure of ITQ-26, a 3D framework with extra-large pores, Chem. Mater. 20 (2008) 5325–5331.
- [135] A. Corma, M.J. Díaz-Cabañas, J.L. Jordá, F. Rey, G. Sastre, K.G. Strohmaier, A zeolitic structure (ITQ-34) with connected 9- and 10-Ring channels obtained using phosphonium cations as structure directing agents, J. Am. Chem. Soc. 130 (2008) 16482–16483.
- [136] J. Sun, C. Bonneau, A. Cantin, A. Corma, M.J. Díaz-Cabañas, M. Moliner, D. Zhang, M. Li, X. Zou, The ITQ-37 mesoporous chiral zeolite, Nature 458 (2009) 1154–1157.
- [137] M. Moliner, T. Willhammar, W. Wan, J. González, F. Rey, J.L. Jorda, X. Zou, A. Corma, Synthesis design and structure of a new multipore zeolite with interconnected 12- and 10-MR channels, J. Am. Chem. Soc. 134 (2012) 6473–6478.
- [138] M. Hernandez-Rodriguez, J.L. Jordá, F. Rey, A. Corma, Synthesis and structure determination of a new microporous zeolite with large cavities connected by small pores, J. Am. Chem. Soc. 134 (2012) 13232–13235.
- [139] Y. Yun, M. Hernández, W. Wan, X. Zou, J. L. Jorda, A. Cantin, F. Rey, A. Corma, The first zeolite with a tridirectional extra-large 14-ring pore system derived using a phosphonium-based organic molecule, Chem. Commun. 51 (2015) 7602–7605.
- [140] J. Jiang, Y. Yun, X. Zou, J.L. Jordá, A. Corma, ITQ-54: a multi-dimensional extralarge pore zeolite with 20 x 14 x 12-ring channels, Chem. Sci. 6 (2015) 480–485.
- [141] L. Bieseki, R. Simancas, J.L. Jorda, P.J. Bereciartua, A. Cantin, J. Simancas, S. B. Pergher, S. Valencia, F. Rey, A. Corma, Synthesis and structure determination via ultra-fast electron diffraction of the new microporous zeolitic germanosilicate ITQ-62, Chem. Commun. (2018) 2122–2125.
- [142] A. Corma, M.J. Díaz-Cabañas, J. Jiang, M. Afeworki, D.L. Dorset, S.L. Soled, K. G. Strohmaier, A new extra-large pore zeolite (ITQ-40) with the lowest framework density containing double four and double three-rings, Proc. Natl. Acad. Sci. USA 107 (2010) 13997–14002.

- [143] A. Corma, M.J. Díaz-Cabañas, J.L. Jordá, J. Marínez, M. Moliner, Highthroughput synthesis and catalytic properties of a molecular sieve with 18- and 10-member rings, Nature 443 (2006) 842–845.
- [144] J. Jiang, J.L. Jorda, M.J. Díaz-Cabañas, J. Yu, A. Corma, The synthesis of an extralarge-pore zeolite with double three-ring building units and a low framework density, Angew. Chem. Int. Ed. 49 (2010) 4986–4988.
- [145] A. Cantín, A. Corma, M.J. Díaz-Cabañas, J.L. Jordá, M. Moliner, F. Rey, Synthesis and characterization of the all-silica pure polymorph C and an enriched polymorph B intergrowth of zeolite beta, Angew. Chem. Int. Ed. 45 (2006) 8013–8015.
- [146] A. Cantín, A. Corma, M.J. Diaz-Cabañas, J.L. Jordá, M. Moliner, Rational design and ht techniques allow the synthesis of new IWR zeolite polymorphs, J. Am. Chem. Soc. 128 (2006) 4216–4217.
- [147] A. Corma, F. Rey, J. Rius, M.J. Sabater, S. Valencia, Supramolecular selfassembled molecules as organic directing agent for synthesis of zeolites, Nature 431 (2004) 287–290.
- [148] P. Eliášová, M. Opanasenko, P.S. Wheatley, M. Shamzhy, M. Mazur, P. Nachtigall, W.J. Roth, R.E. Morris, J. Čejka, The ADOR mechanism for the synthesis of new zeolites, Chem. Soc. Rev. 44 (2015) 7177–7206.
- [149] M. Opanasenko, M. Shamzhy, Y. Wang, W. Yan, P. Nachtigall, J. Čejka, Synthesis and post-synthesis transformation of germanosilicate zeolites, Angew. Chem. Int. Ed. 59 (2020) 19380–19389.
- [150] S.E. Ashbrook, R. Morris, C.M. Rice, Understanding the synthesis and reactivity of ADORable zeolites using NMR spectroscopy, Curr. Opin. Colloid Interface Sci. 61 (2022), 101634 art. n°.
- [151] D.L. Dorset, G.J. Kennedy, K.G. Strohmaier, M.J. Díaz-Cabañas, F. Rey, A. Corma, P-derived organic cations as structure-directing agents: synthesis of a high-silica zeolite (ITQ-27) with a two-dimensional 12-ring channel system, J. Am. Chem. Soc. 128 (2006) 8862–8867.

- [152] R. Simancas, J.L. Jorda, F. Rey, A. Corma, A. Cantin, I. Peral, C. Popescu, A new microporous zeiolitic silicoborate (ITQ-52) with interconnected small and medium pores, J. Am. Chem. Soc. 136 (2014) 3342–3345.
- [153] J. Simancas, R. Simancas, P.J. Bereciartua, J.L. Jorda, F. Rey, A. Corma, S. Nicolopoulos, P.P. Das, M. Gemmi, E. Mugnaioli, Ultrafast electron diffraction tomography for structure determination of the new zeolite ITQ-58, J. Am. Chem. Soc. 138 (2016) 10116–10119.
- [154] E.M. Gallego, M.T. Portilla, C. Paris, A. León-Escamilla, M. Boronat, M. Moliner, A. Corma, "Ab initio" synthesis of zeolites for preestablished catalytic reactions, Science 355 (2017) 1051–1054.
- [155] C. Li, C. Paris, J. Martínez-triguero, M. Boronat, M. Moliner, A. Corma, Synthesis of reaction-adapted zeolites as methanol-to-olefins catalysts with mimics of reaction intermediates as organic structure-directing agents, Nat. Catal. 1 (2018) 547–554.
- [156] C. Li, P. Ferri, C. Paris, M. Moliner, M. Boronat, A. Corma, Design and synthesis of the active site environment in zeolite catalysts for selectively manipulating mechanistic pathways, J. Am. Chem. Soc. 143 (2021) 10718–10726.
- [157] Z. Jensen, E. Kim, S. Kwon, T.Z.H. Gani, Y. Román-Leshkov, M. Moliner, A. Corma, E. Olivetti, A machine learning approach to zeolite synthesis enabled by automatic literature data extraction, ACS Cent. Sci. 5 (2019) 892–899.
- [158] Z. Jensen, S. Kwon, D. Schwalbe-Koda, C. Paris, R. Gómez-Bombarelli, Y. Román-Leshkov, A. Corma, M. Moliner, E.A. Olivetti, Discovering relationships between osdas and zeolites through data mining and generative neural networks, ACS Cent. Sci. 7 (2021) 858–867.
- [159] M. Moliner, Y. Román-Leshkov, A. Corma, Machine learning applied to zeolite synthesis: the missing link for realizing high-throughput discovery, Acc. Chem. Res. 52 (2019) 2971–2980.
- [160] D. Schwalbe-Koda, S. Kwon, C. Paris, E. Bello-Jurado, Z. Jensen, E. Olivetti, T. Willhammar, A. Corma, Y. Román-Leshkov, M. Moliner, R. Gómez-Bombarelli, A priori control of zeolite phase competition and intergrowth with highthroughput simulations, Science 374 (2021) 308–315.