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## Preface: GIC2022

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► **To cite this version:**

Stefania Albonetti, Pierdomenico Biasi, Francesco Di Renzo, Francesco Mauriello, Federica Menegazzo. Preface: GIC2022. *Catalysis Today*, 2024, 429, pp.114491. 10.1016/j.cattod.2023.114491 . hal-04591573

**HAL Id: hal-04591573**

**<https://hal.science/hal-04591573>**

Submitted on 28 May 2024

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This Special Issue of Catalysis Today is a compilation of 21 original research papers presented at the GIC2022, the 22nd conference of the Gruppo Interdivisionale di Catalisi (GIC) of the Società Chimica Italiana (SCI), held in Riccione on 11-14 september 2022. The Gruppo Interdivisionale di Catalisi is the exchange forum of all catalysis-related components of the Italian Chemical Society. It especially promotes the interdisciplinary aspects of catalysis and the interactions between technology and fundamental research. The 22nd conference of GIC had a special relevance for the youngest researchers. As the first meeting after the three years interruption due to the covid pandemics, it was the first opportunity of public speech for many PhD students. The GIC, the INSTM and several branches of the SCI promoted the participation of students and young researchers by awarding 37 bursaries covering accommodation and attendance. In the three days of the single-session conference, the 130 participants shared discussions based on 59 oral presentations and 21 poster communications. 29 of the speeches were given by PhD students and 15 by postdocs or junior researchers. The themes of the conference were introduced by 6 plenary and keynote lectures given by international representatives of academy and industry. The conference was also the ideal see for the awarding of prizes dedicated to the memory of honoured scientists, like Giacomo Fauser, Adolfo Parmaliana, Robert Karl Grasselli and Mauro Graziani.

The organisation of the GIC2022 conference would not have been possible without the support of its academic and industrial sponsors. Among them a special mention has to be done of the Università Cà Foscari of Venezia, the Alma Mater Studiorum Università di Bologna, the Società Chimica Italiana, Novamont, Casale and Polynt. The preparation and the day-to-day run of the conference completely relied on the enthusiastic participation of young and less young colleagues from Bologna and Venezia. They are too many to be individually acknowledged here but thanks be given to their dedication. Acknowledgments are also due to the seminal role of the coordinator and past-coordinator of the GIC, Michela Signoretto and Fabrizio Cavani.

The 21 papers of this Special Issue of Catalysis Today are the result of the collaboration of authors from 25 Italian academic and research institutions and 15 institutions from other countries, witnessing the opening of the Italian catalysis community to international cooperation. The articles highlight the primary role of catalysis in answering the challenges of global warming and energy transition. Papers of the Special Issue deal with the chemical valorisation of CO<sub>2</sub>, alternative processes for grey or green hydrogen, the production of chemicals from renewable biomass resources, the role of catalysis in environmental remediation and the search for greener polymerisation catalysts.

The papers [1-4] of the Special Issue propose innovations in the chemical valorisation of CO<sub>2</sub>. The synthesis of fuels and chemicals by hydrogenation of CO<sub>2</sub> is a valuable outlet for green hydrogen from renewable energies and allows to reduce our dependency from fossil fuels. The group of Luca Lietti and the regretted Barbara Picutti, sadly passed away a short time after the conference, presents an engineering evaluation of competing methods for one-pot synthesis of olefins from CO<sub>2</sub> [1]. A modified Fischer-Tropsch process is compared with a methanol-mediated olefin synthesis, obtained by coupling In<sub>2</sub>O<sub>3</sub>-based catalysts for methanol synthesis with SAPO-34 methanol-to-olefins (MTO) zeolitic catalysts. The integration in a single reactor of catalysts that normally operate at different pressure and temperature is a technological challenge, requiring to take into account the bottlenecks of each of the two steps of the methanol-mediated process. The results indicate which modifications of the zeolitic catalysts are needed to decrease the formation of paraffins by consecutive hydrogenation of the olefins. The optimisation of the In<sub>2</sub>O<sub>3</sub>-based catalysts of methanol synthesis is the subject of the article of Samir

Bensaid and coworkers [2]. They highlight the critical role of other oxide components on the activity of the catalysts and show that  $\text{In}_2\text{O}_3\text{-ZrO}_2$  catalysts can be more selective than the classical Cu-ZnO catalysts even at high space velocity. The production of synthetic natural gas by methanation of  $\text{CO}_2$  is the subject of the article of Gabriella Garbarino and coworkers [3]. They address the problem of the low-temperature activity and stability of the Ni-based methanation catalysts and propose a comprehensive review of academic and industrial results on the positive effect of lanthanide addition on the field of application of the catalysts. The formation of CO by reverse water gas shift (RWGS) is a competitive reaction in  $\text{CO}_2$  methanation and can be a desired reaction when CO is the target product of the hydrogenation, in view of its use in successive carbonylation reactions. The factors driving the competition between methanation and RWGS are often not clearly defined in the literature. Guido Busca and coworkers have investigated how the conditions of preparation and activation affect the selectivity of  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  catalysts [4]. They show that RWGS is favoured by an incomplete reduction of cobalt, corresponding to the formation of spinel species by interaction with the alumina support.

The production of hydrogen is the subject of the articles [5-9] of the Special Issue. Among the processes for the production of grey hydrogen, the dry reforming of methane presents a special interest, as it implies both  $\text{CH}_4$  and  $\text{CO}_2$  in the formation of synthesis gas. The paper of Michela Signoretto and coworkers deals with the stability of the  $\text{Ni}/\text{Al}_2\text{O}_3$  dry reforming catalysts [5]. Doping the catalyst with vanadium, they achieved a significant decrease of the catalyst deactivation by carbon deposition. Additional introduction of calcium allowed a better dispersion of metal on the support, allowing a significant increase of activity. High endothermicity is a drawback of methane steam reforming, the most widely implemented method for the production of grey hydrogen. The energy requirement of steam reforming can be satisfied by coupling with exothermic oxy-reforming. The article of the group led by Gabriele Centi and Francesco Basile suggests improvements of the oxy-reforming process [6]. Coupling oxy-reforming and water gas-shift catalysts with hydrogen-selective Pd membranes allowed to shift the equilibrium of hydrogen formation beyond the closed-system equilibrium and provided a permeate flow of pure hydrogen. An alternative to the use of molecular oxygen in oxy-reforming is the reaction with a solid oxygen carrier. The reduced oxygen carrier can be reoxidized by steam, producing hydrogen by water splitting. If this chemical looping process is implemented on a biomass-derived molecule instead than methane, green hydrogen can be produced from renewable resources. Such a process is proposed in the article by the group of Francesco Di Renzo and Fabrizio Cavani [7], in which the mechanisms of reduction of different ferrites by ethanol are studied and related to the efficiency of the process and the purity of the hydrogen outlet. The purity of hydrogen from reforming is an essential requirement for its use in fuel cell anodes and demands preferential oxidation of CO traces left after water gas-shift. Nunzio Russo and coworkers have exploited several techniques of characterisation to elucidate the mechanisms of CO oxidation on Cu-doped  $\text{CeO}_2$  [8]. The extension of the use of hydrogen requires dealing with transport and storage problems. Possible solutions can be provided by the use of molecular hydrogen carriers. The article of Achilleas Constantinou and coworkers is a review of recent advances in the cycle of hydrogen storage in ammonia and hydrazine, with a special emphasis on the catalytic recovery of stored hydrogen [9].

The articles [10-16] of the Special Issue present an overview of the progress in catalytic processes for the replacement of oil-derived products by sustainable biomass-derived molecules. A one-pot method to produce biofuel from cellulose is proposed in the paper by Anna Maria Raspolli Galletti *et al.* [10]. They developed a one-step acid catalysis method for the solvolysis of paper paste by butanol to form butyl

levulinate, a solvent itself and a biofuel blend component. In many cases, the formation of useful products has to cope with the high oxygen content of biomass and hydrogenation processes are required. Michela Signoretto and coworkers studied the preparation of biochar supports for Pd hydrogenation catalysts by pyrolysis and steam activation of different kinds of waste biomasses [11]. Cu-based hydrogenation catalysts are an interesting alternative to the use of noble metal catalysts. They have been used by Nicoletta Ravasio and coworkers in the reductive amination of gamma-valerolactone to N-butyl pyrrolidinone, a solvent designed to replace mutagenic solvents for the pharmaceutical industry [12]. Maela Manzoli and coworkers have managed to perform in a single solventless step the dehydrogenation of glucose to sorbitol and the dehydration of sorbitol to isosorbide, an important platform molecule [13]. Their bifunctional catalytic system, based on supported Ru and zeolite beta and assisted by microwave activation, was versatile enough to form isosorbide directly from cellulose. In this last case, formic acid was used as a solvent and as a source of hydrogen in replacement of molecular hydrogen. Catalytic hydrogen transfer was also used by Stefania Albonetti and coworkers in the hydrogenation of furfural with methanol to obtain furfurylic alcohol on CaO, an especially cheap and eco-friendly catalyst [14]. The valorisation of bioalcohols into chemicals has been the subject of several papers. The group of Fabrizio Cavani and José Manuel López Nieto has shown that simple catalysts as alkali-doped sepiolites are effective in the Guerbet condensation of ethanol to n-butanol [15]. Homogeneous catalysts have been proposed for the homologation of alcohols in milder reaction conditions. Rita Mazzoni and coworkers have reviewed the performances of homogeneous catalysts for bioethanol condensation with a special attention to the process variables and the recyclability of catalysts [16].

The introduction of noble metal-free catalysts for the degradation of pollutants is an important contribution to the protection of the environment and is the subject of the papers [17-19] of the Special Issue. The oxidation of organic sulfides, beyond its wide-scale application in refinery desulfurisation and in the synthesis of valuable sulfones, present a special interest in the detoxification of chemical warfare agents. The article of Marcello Crucianelli and coworkers presents the synthesis and characterization of several vanadyl complexes, that show high effectiveness in the oxidation of a variety of S-bearing substrates [17]. Francesco Basile and coworkers have studied the reduction of nitrophenol, a water pollution agent impervious to biological degradation. They have tested the reduction by NaBH<sub>4</sub> at room temperature on a variety of oxides obtained by calcination of layered double hydroxides [18]. The best results were obtained on mixed nickel-copper oxide catalysts on alumina. The article of Alberto Vomiero and coworkers deals with the elaboration of new materials for the photodegradation of water pollutants [19]. The formation of vacancy-doped homojunctions between titania nanorods and a layer of reduced TiO<sub>2-x</sub> allowed to enhance the electron transfer and improve the photodegradation of methylene blue.

The development of new polymerisation catalysts, a field in full development with the aim of reducing the environmental impact of plastic production, has been examined in the articles [20-21] of the Special Issue. The article of Alvisè Perosa and coworkers deals with the use of N-doped carbon dots as metal-free sensitizers in the photopolymerisation of methacrylates [20]. In olefin polymerisation, the adjunction of electron-donor diethers in the preparation of catalysts has led to the introduction in industrial practice of a new generation of catalysts. Elena Groppo and coworkers have investigated the preparation of these catalysts and shown that the conditions of precipitation of the precursors are critical for the kinetics of propylene polymerisation in mild conditions [21].

The Guest Editors express their sincere acknowledgments to Dr. Miguel A. Bañares (Editor-in-Chief of Catalysis Today), Dr. Elena Groppo (Editor of this special issue) and Mr. Samuel C. Palaniswamy (Senior Journal Manager) for their continued advice and support in the making this Special Issue a success. The Guest Editors also thank all the authors and reviewers without whose contributions this Special Issue could not have been completed.

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