

Nanomaterials in Catalysis Applications

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1. Overview

The interconnected rapid development of nanomaterials science and advanced analysis and imaging techniques at the nano-level scale (some “operando”) fostered the parallel growth of heterogeneous catalysis and its evolution into “nano-catalysis” [1–6]. As a result, efficient approaches and advanced methods for designing nano-structured composite materials subjected to specific nanomorphologies is now routine for heterogeneous catalyst designers. These provide nanocatalysts with the desired metal–metal and metal–support interactions, multifunctionalities, and sizes and shapes of nanoparticles morphology. Moreover, such features and properties may play a critical role in determining and improving catalytic activity, selectivity, and stability [7–18].

Therefore, nano-catalysis enables fine-tuning of significant physicochemical properties of the materials, such as work function, oxidation state, and nanoparticle morphology, allowing catalyst optimization for reactions related to various applications with energy, environmental, industrial, and sustainability impacts.

Modern applications that are on the cutting edge include CO₂ capture and utilization (e.g., Sabatier reaction), natural gas and biogas reforming for H₂, added-value chemicals and liquid fuels production, deNO_x, deN₂O, and VOCs emissions control systems, wastewater and water treatment, electrochemical water splitting, photocatalytic, biorefinery processes, and fuel cells [8].

In this context, this SI compiled eight (8) high-quality contributions [19–26], covering recent research progress in various above-mentioned catalytic applications of nanomaterials, which are briefly discussed below.

2. Special Issue's Contribution and Highlights

Yentekakis et al. [19] focus on an important and unavoidable problem faced by industrial catalysis: the deactivation of supported catalysts due to thermal aging. Also known as the aggregation (sintering) of the catalyst nanoparticles, this phenomenon occurs when the catalyst is inevitably dead [26–28]. In response to this problem, the authors introduced a new approach for obtaining sintering resistant or even in situ redispersed catalysts using supports with high labile oxygen ions capacity and surface oxygen vacancies. Working with Rh nanoparticles dispersed on CeO₂-based supports (ACZ and CZ), which possess the above properties, the authors recorded high resistance to sintering and even redispersion. In other words, the higher the oxygen storage capacity (OSC) of the support, the greater the extent of particle redispersion, which increased with increasing sintering temperature. Yentekakis et al. propose a model that rationalizes the observed phenomena considering the synergistic action of two factors. The first factor is the spontaneous creation of an [O^{δ−}, δ⁺] double layer on the metal particles resulting from thermally driven oxygen back-spillover from high OSC supports. This factor quenches large particle migration and coalescence (PMC) from the resulting interparticle electrostatic repulsion. The second



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factor is the trapping of Rh atoms detached from large Rh crystallites by oxygen vacancies in the support surface. This factor suppresses the diffusion of rhodium species on the support and their subsequent attachment to larger particles, i.e., the Ostwald ripening (OR) mechanism of particle sintering. The higher the population of surface oxygen vacancies on the support, the greater the redispersion of Rh, which increased with temperature. The authors argue that these findings provide a new methodology for the in situ (on-stream)-controlled redispersion of metal catalysts, with highly beneficial implications for industrial heterogeneous catalysis [19].

In a subsequent article [20], Yentekakis et al. propose a model that rationalizes the observed phenomena. Their model accounts for the synergistic action of two factors that investigated the effects of the support OSC and Rh particle size on the performance of the Sabatier reaction under both integral and differential conditions to elucidate the combined role of these crucial catalyst design parameters on CO₂ methanation efficiency. A series of supported Rh catalysts on supports with different oxygen storage capacity characteristics, namely γ -Al₂O₃ (OSC = 0 $\mu\text{mol O}_2/\text{g}$), 80 wt%Al₂O₃–20 wt%Ce_{0.5}Zr_{0.5}O_{2– δ} (ACZ, with OSC = 101 $\mu\text{mol O}_2/\text{g}$), and Ce_{0.5}Zr_{0.5}O_{2– δ} (CZ with OSC = 557 $\mu\text{mol O}_2/\text{g}$), and different mean Rh particle sizes, varying between 1.2 nm to 5 nm, were involved in the study. The authors found a volcano-type variation of methanation turnover frequency concerning support OSC. The catalyst with the intermediate OSC value (Rh/ACZ) was optimal. On the other hand, the reaction was structure sensitive, i.e., its TOF was strongly dependent on Rh particle size. This structure sensitivity was found to be a combined function of support OSC and Rh particle size: for Rh/ γ -Al₂O₃ (lack of OSC), CO₂ methanation was strongly favored on small particles, while the opposite was true for Rh/CZ with high OSC. As the authors claim, these findings are promising for the rational design and optimization of CO₂ methanation catalysts by tailoring OSC and particle size characteristics.

Kondarides et al. [21] provide a detailed kinetic and mechanistic study of CO₂ hydrogenation reaction to methanol over La₂O₃-promoted CuO/ZnO/Al₂O₃ (CZA) catalysts. They found that the progressive substitution (0, 25, 50, 75, or 100%) of the Al₂O₃ by La₂O₃ resulted in a systematic decrease of CO₂ conversion, though accompanied by an increase in methanol selectivity. Therefore, the study obtained optimal results for the CZA-La50 catalyst, which exhibited a 30% higher yield of methanol compared to the unpromoted CZA sample. The relatively high specific surface area and porosity of CZA-La50, and the creation of basic sites of moderate strength, which enhance the adsorption of CO₂ and intermediates that favor hydrogenation steps and the ability of CZA-La50 to maintain a large part of the copper in its metallic form under reaction conditions, were the key factors contributing to its superiority. Using in situ infrared spectroscopy (DRIFTS), the authors found that the reaction proceeded with the intermediate formation of surface formate and methoxy species and that both methanol and CO were mainly produced via a common formate intermediate species. Furthermore, Kondarides et al. provide a kinetic model that well fits the measured reaction rates.

Panagiotopoulou et al. [22] investigate the effect of operating conditions on the Liquefied Petroleum Gas (LPG) steam reforming performance of a Rh/TiO₂ catalyst. Operating parameters examined were reaction temperature, H₂O/C ratio, Gas Hourly Space Velocity (GHSV), absence and presence of butane in the feed, and time-on-stream. Performance-improving parameters were found to be increasing reaction temperature, steam content in the feed, and decreasing GHSV. Propane conversion decreased by adding butane to the feed, indicating that the presence of butane delays propane steam reforming. The Rh/TiO₂ catalyst performance were insensitive to abrupt changes of the steam/C ratio between 2 and 7 and exhibited excellent time-on-stream stability at 500 and 650 °C. Macro-constructed Rh/TiO₂ catalysts in the form of large-sized pellets also showed good activity, selectivity, and time-on-stream stability, thus they look promising for practical LPG steam reforming applications.

Neagu et al. [23] continued their outstanding works on metal nanoparticles exsolution from perovskite structures [12,13] by obtaining catalysts with excellent performances in

various applications, e.g., for partial oxidation of CH₄ to syngas production in chemical looping redox processes (CLPO) [14]. They attempt to further lower the temperature for CLPO of methane conversion by complementing exsolution with infiltration. An exsolution of the non-noble metal endo/exo-particle system was prepared, with exsolved Ni particles on the surface and throughout the bulk, which was subsequently infiltrated with a minimal amount of Rh (0.1 wt%) to functionalize the surface and induce low-temperature activity. Through this combined approach, the authors successfully lowered the methane activation temperature by almost 220 °C and increased the conversion by up to 40%. However, at the same time, changes in the surface morphology of the materials due to infiltration were observed, with a negative impact on their long-term durability. The authors conclude that their results demonstrate that microstructure tuning and surface functionalization are important aspects to consider when designing materials for redox cycling applications.

Hang et al. [24] used an electrospinning method for the preparation and in situ doping with Si of the β -Ga₂O₃ photocatalyst (highly promising alternative of conventional TiO₂) to enhance its photocatalytic performance under ultraviolet irradiation. To this end, β -Ga₂O₃ nanofibers formed via the electrospinning method, and Si atoms subsequently doped. The authors demonstrated that the optical bandgap of the β -Ga₂O₃ nanofibers systematically decreases, from 4.5 eV for the un-doped to 4.0 eV for the 2.4 at.% Si-doped β -Ga₂O₃ nanofibers, as the Si concentration in the β -Ga₂O₃ nanofiber increases, thus resulting in an enhancement in the photocatalytic activity of the doped material. This promoting effect of Si doping was attributed to the increased doping-induced carriers in the conduction band edges. Moreover, the Si-dopant effect on the photocatalytic performance of the β -Ga₂O₃ nanofibers was more significant compared to those of TiO₂ and ZnO with other dopants. The authors argue that the observed promotion differs from the traditional mechanism in which the doping-induced defect sites in the bandgap enhance separation and inhibit the recombination of photon-generated carriers.

Liu et al. [25] synthesized solar-light-driven N-doped 3C-SiC powder via a simple one-step combustion route. They found that SiC-N₂ photocatalysts exhibited 205.3 μ L/g·h hydrogen evolution rate, nearly two times higher than that of SiC-Ar (120.1 μ L/g·h), and much higher than that of SiC nanowires (83.9 μ L/g·h), SiC nanoparticles (82.8 μ L/g·h) as well as the boron-doped SiC photocatalysts (166 μ L/g·h). Moreover, in cyclic tests, N-doped SiC offered excellent photocatalytic durability and good structural stability. The authors concluded that N-doping introduced defects into the SiC photocatalyst by occupation and mixed phase structure, transformed the band structure into the direct band gap, and formed a shallow donor level for trapping holes. Thus, the study achieved higher photocatalytic activities and lower recombination. Furthermore, the carbon on the photocatalyst yielded from the substitution of N or remained after combustion could play the role of an efficient interfacial contact with SiC accelerating the light-driven electron transfer to the surface and simultaneously strengthening the adsorption capacity and light-harvesting potential. They argue that this work provides a simple method to meet the requirements for cost-effective, non-toxic, and durable photocatalysts.

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