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Foam/fiber-structured catalysts: non-dip-coating fabrication strategy and applications in heterogeneous catalysis

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Development and use of the structured catalysts and reactors (SCRs) is a promising strategy to overcome the major drawbacks encountered in the traditional packed-bed reactor due to improved hydrodynamics in the combination with enhanced heat/mass transfer, thus being a hot topic in the heterogeneous catalysis. One of the most typical SCRs is the ceramic honeycomb catalyst extensively applied in the control of automotive emissions and the reduction of nitrogen oxides from power stations. Such honeycomb catalyst consists of thousands of opening parallel channels in millimetric diameter (to offer high void fractions for low pressure drop at high flow rates through the catalyst bed) with catalytic washcoat in micrometric thickness on the channel walls (to improve mass transfer due to the short gas diffusion distance). Over the years, this type of SCRs has found other applications, such as catalytic combustion, partial oxidations and liquid-phase hydrogenations [1, 2]. However, using monolithic honeycomb still remains challenging because of their relatively lower heat transfer and the lack of radial mixing, which should be improved for the endo-/exo-thermic and/or high-throughput reactions [1].

Metal fiber/foam-based supports have attracted ever-increasing interest within the last decade [3]. Besides the high voidage and internal-diffusion as typically in ceramic honeycomb catalysts, their unique three-dimensional (3D) network and open structure as well as high thermal conductivity and mechanical strength allow low pressure drop, high mass/heat transfer and especially high contacting efficiency of reactants resulted from the radial mixing

(Fig. 1). Moreover, their metallic feature has unique form factors that provide a great flexibility in geometric appearance when filling up the structured reactors. These characteristics are particularly beneficial for very fast and heat/mass-transfer-controlled reactions (Fig. 1) [4, 5]. However, catalytic functionalization of the fiber/foam-based supports remains challenging because the conventional washcoating technique suffers from nonuniformity and exfoliation of coatings as well as binder contamination. Recently, a series of effective and efficient non-dip-coating methods has been developed for catalytic functionalization of the fiber/foam structures.

Based on the galvanic replacement reaction, several fiber/foam-structured catalysts engineered from nano- to macro-scales are fabricated successfully in one step. One example is the sinter-locked Ni-microfibers (8 μm in diameter) structured gold catalyst of Au/Ni-microfiber [6], which is facilely obtainable by dipping Ni-microfibers into an $HAuCl_4$ aqueous solution to galvanically deposit gold nanoparticles (NPs) on the Ni-microfibers, owing to the great potential difference between Ni^0/Ni^{2+} (−0.25 V) and Au^0/Au^{3+} (1.5 V). The Au/Ni-microfiber catalyst is applied in the gas-phase selective aerobic oxidation of benzyl alcohol, a strongly exothermic process, and 93 % conversion selectivity can be stably obtained with 99 % benzaldehyde within 700-h running. Additionally, Au and Pd can be galvanically co-deposited on Cu-microfibers by dipping Cu-microfibers into a mixed $HAuCl_4$ and $Pd(Ac)_2$ aqueous solution [7], and the as-prepared Au–Pd/Cu-microfiber catalyst is highly active, selective and stable for the dimethyl oxalate (DMO) hydrogenation to ethylene glycol (EG).

Catalytic combustion of methane is a promising technology for deoxygenation of coalbed methane (CBM), energy production and environment protection. The strong

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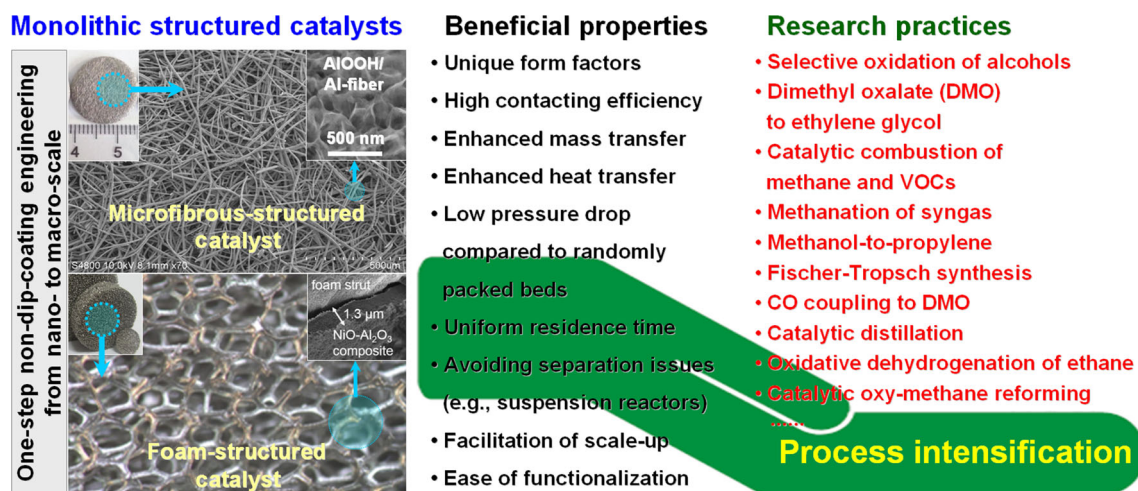e-mail: ylu@chem.ecnu.edu.cn

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Fig. 1 (Color online) The fiber/foam-structured catalysts engineered from nano- to macro-scale: non-dip-coating preparation, beneficial properties and research practices in heterogeneous catalysis

exothermicity (ΔH_{298} of -802.7 kJ mol^{-1}) and high throughput operation in these processes require the catalyst not only to be active, selective and stable, but also to be highly thermally-conductive and highly permeable. Towards this end, Precision Combustion Inc. has developed short channel length, high channel density supports and high surface area ceramic coatings for them [1]. These supports avoid substantial buildup of boundary layer and greatly enhance heat/mass transfer, but the catalytic functionalization via conventional dip-coating still suffers from inhomogeneous coatings. Seeing the beneficial features of metal foams to the design of structured catalysts, a foam-structured catalyst is fabricated also via galvanic deposition of Pd NPs on Ni-foam [8], which exhibits as-expected low pressure drop and high heat/mass transfer. More interestingly, Ni atoms from Ni-foam can alloy into Pd NPs to form PdNi during the reaction process, which contributes to high low-temperature activity/selectivity and oscillation-free feature. It is anticipated that this type of catalyst might stimulate commercial exploitation of the new-generation structured catalyst technology towards CBM efficient utilization and environmental protection.

Even though galvanic deposition of precious metals is effective and efficient for catalytically functionalizing typical metal fiber/foams, this strategy is invalid for the metals with lower potentials. Interestingly, the metal fibers/foams can be directly activated, for example by wet chemical etching method, to serve as catalysts in applications such as methanation of syngas (a mixture of H_2, CO and CO_2) to produce synthetic nature gas (SNG). The strong exothermicity and high throughput operation of this process require the catalyst to have excellent mass/heat transfer and porosity. Microchannel plate heat-exchanger technology offers the potential for solving temperature

management problems by integrated reactor cooling [9]. However, the parallel and unconnected microchannels prohibit the mass mixing in radial direction. By directly immersing the Ni-foam substrate into a chemical etching solution followed by calcination in air, fortunately, uniform $NiO–CeO_2–Al_2O_3$ composite layer in 3 µm thickness is efficiently formed and firmly anchored onto the Ni-foam struts [10]. Such a catalyst, with significantly enhanced heat transfer, is highly active, highly selective, and very stable for syngas methanation. Computational fluid dynamics calculations and experimental measurements consistently show a large reduction in the "hotspot" temperature in the Ni-foam-structured catalyst bed owing to high thermal conductivity.

In recent years, ZSM-5 zeolite-based catalysts for methanol-to-olefin (MTO) have been extensively studied to orient product selectivity toward light olefins and especially propylene and to further improve the catalyst stability, although Lurgi's methanol-to-propylene (MTP) process based on a packed bed with a ZSM-5 catalyst has been industrially demonstrated. Most efforts have been focused on ZSM-5 modification such as tuning the acidity, size- and/or morphology-controllable synthesis and hierarchical design of the pore structure. However, their practical use in millimetric pellet form still remains problematic when packed in fixed-bed reactor [1]. In view of the beneficial features of SCRs for process intensification, ZSM-5 is firstly structured on SiC-foam with visible lifetime improvement. However, the product distribution remains almost unchanged in comparison to the particulate ZSM-5; in addition, the uniform growth of ZSM-5 on SiC-foam are greatly challenging due to the cellular geometry of SiC-foam [1]. Encouraged by the simulation calculation [11], a sinter-locked microfiber structured HZSM-5

catalyst of SS-fiber@HZSM-5 is fabricated by direct growth of HZSM-5 on a 3D microfibrous structure using 20-μm stainless steal fiber (SS-fiber) [12]. Such microfibrous-structured design exhibits dramatic selectivity and stability improvements for MTP process compared with the particulate microporous zeolite. Moreover, the kinetic and modeling study also displays the higher diffusion efficiency and narrower residence time distribution of such design, not only promoting the propylene formation but also improving the utilization efficiency of HZSM-5 [13].

Alumina (Al_2O_3) is a most widely used catalyst support for the heterogeneous catalysis due to its large surface area, excellent mechanical strength and brilliant hydrothermal stability [14]. Similar to ZSM-5 zeolite, Al_2O_3 is also anticipated to be used in a structured way to avoid the problems emerging in its particulate applications. The Al_2O_3 immediate manufacturing into honeycomb monoliths and open-cell foams is still under development due to the poor mechanical strength, while its deposition on ceramic and metallic materials by dip-coating techniques suffers from the nonuniformity and exfoliation of coatings [1]. Recently, a facile one-step route is developed to structure AlOOH (convertible into γ-Al_2O_3 and/or α-Al_2O_3) 2D-nanosheets on Al-substrates via steam-only oxidation (based on the reaction: $2Al + 4H_2O = 2AlOOH + 3H_2$) [15]. This in situ one-step route achieves the structuring of AlOOH/γ-Al_2O_3 homogeneously on various monolithic Al substrates such as microfiber, foam, tube and foil. One application of Al_2O_3/Al-fiber is the utilization as structured support to fabricate FeMnK catalyst for Fischer–Tropsch to olefins process [16], which requires enhanced heat/mass transfer and high permeability (permitting high throughput operation) to significantly improve regular-flow and in-turn conversion and selectivity patterns. Additionally, AlOOH/Al-fiber is used to support highly dispersed Pd NPs for CO coupling to DMO. As an example, the catalyst with a very low Pd-loading of only 0.25 wt% delivers $\sim$66 % CO conversion and $\sim$94 % DMO selectivity for a feed of CH_3ONO/CO/N_2 (10/14/76, vol%) at 150 °C with a gas hourly space velocity of 3000 L kg^{-1} h^{-1}, and particularly, is stable for at least 200 h without deactivation. Moreover, the Al-structured AlOOH/γ-Al_2O_3 monoliths are also qualified for the other mass/heat transfer limited reactions at high throughput with low pressure drop, such as Pd-catalyzed CH_4 and vapor organic compounds (VOCs) combustion and Ni-catalyzed syngas methanation [15].

Hydrogen production via the water-splitting reaction is a sustainable way in catalysis and renewable energy. Noble-metal-based catalysts are still the best known catalysts for the two half-reactions in water-splitting: the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). However, these catalysts suffer from the high cost and low Earth abundance of noble metals. While some alternative, non-noble metal-based electrocatalysts have been investigated, the catalytic efficiency of many of them (e.g., MoS_2) is greatly limited by their low electrical conductivity [17]. Recently, a monolithic bifunctional electrocatalyst of Ni_3S_2/Ni-foam is fabricated via in situ growth of highly-active Ni_3S_2 nanosheets on highly-conductive metallic Ni-foam [18], offering $\sim$100 % Faradaic yield toward both HER and OER and remarkable catalytic stability (for >200 h).

The up-to-date progress of SCRs has been proven to be superior to conventional packed-bed reactor in the field of heterogeneous catalysis. However, there still is room for improvement in practical applications. Firstly, the high temperature stability of SCRs and their coke-resistance properties at this temperature need to be greatly improved for the high temperature reactions such as oxy-methane reforming that usually proceeds at 700–800 °C. To achieve this goal, the supports should be modified with the aim to high temperature stability and coke-resistance properties and further be combined with the opening of high-performance catalyst compositions. Therefore, new strategies should be developed to more effectively functionalize the supports via in situ growth of other catalytic materials such as hydrotalcite on them. Also, the novel SCRs will find their place in other applications such as catalytic distillation for some chemicals production. What to be noted is that, unfortunately, most often there are no correlations for pressure drop and mass transfer between different structures for reactor designs, and there should be a more intense focus on the description of hydrodynamics and transport properties. Anyhow, a close collaboration between chemical engineering and materials science is highly required to develop the more advanced SCRs, which could lead to such improved or new advantageous structures attractive for applications in industrial catalysis.

Conflict of interest The authors declare that they have no conflict of interest.

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