Reforming Catalysts

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Steam and dry reforming of hydrocarbons (e.g., methane, ethane or propane), alcohols (e.g., methanol, ethanol or glycerol) or bio-compounds is one of the most promising and effective routes to enhanced hydrogen production and for the production of synthesis gas likewise. For steam reforming, the most crucial step of this reaction is efficient water activation, which is a necessary prerequisite for both a high CO_2 selectivity and a high associated hydrogen yield. The reactions have been studied on a variety of different catalytic surfaces, encompassing oxides, supported metal-oxide systems or (supported) intermetallic compounds. The controllable steering of product selectivity is thereby an obvious key criterion for technical usage. For methanol steam reforming, the key targets—apart from pronounced CO_2 selectivity—are, thus, a maximum hydrogen yield and a low CO content in the reformate to realize the efficient on-board production of clean hydrogen in, e.g., automotive applications. Given the structural and chemical complexity and diversity of the materials used, the question about the common elementary reaction steps of the steam reforming reaction is imperative. For structurally more complex materials, such as the recently put-forward oxide-supported Pd-based intermetallic phases, a bifunctional synergism is usually assumed, where the participating catalytic entities (or the in situ created interface) synergistically act in the catalytic reaction. In this special issue, we show the complexity of the interplay between the synthesis and performance of novel materials in a variety of technologically important reforming reactions. To do the complexity justice, the materials discussed particularly reflect the importance of accurate synthesis procedures to prospective catalytic materials.

Two review reports by Debek et al. [1] and Du et al. [2] deal with the reforming properties of hydrotalcite-derived materials in methane dry reforming and methane and ethanol steam reforming, respectively. The effects of catalyst preparation and regeneration, thermal treatment processes, composite design, catalyst deactivation and the addition of dopants are addressed in both reviews for Ni-based hydrotalcite materials.

The role of metal-oxide and oxide-oxide composite materials as well as intermetallic and alloy catalysts in reforming of hydrocarbons, alcohols and bio-compounds (acetone, furfural and glucose) forms the core of the eight regular articles that are part of this special issue. Ethanol steam reforming over Sc_2O_3-doped Co-ZnO catalysts is adressed by Liang et al. Sc_2O_3 doping is shown to enhance catalytic performance, exceeding that of Sc_2O_3-free Co-ZnO considerably [3]. The improved catalytic activity is ascribed to an increased electronic interaction between Co and ZnO, leading to elevating the reduction temperature of Co oxides, increasing the disperison of ionic Co species and improved sintering behavior of active Co species. Cheng et al. focus on the role of auto-reduced Ni-Al_2O_3 catalysts in steam reforming of four feature classes of bio-molecules: ethanol, acetone, furfural and glucose [4]. Type-specific effects of temperature and steam-to-carbon-ratios, as well as carbon deactivation features are addressed. While ethanol steam reforming leads to a large amount of methane in the product feed, considerable carbon deposition is found for steam reforming of acetone. Glucose coking in turn caused severe agglomeration of catalyst particles, while the high thermal stability of furfural generally restricts the latter use in steam reforming. Finally, Wang et al. [5] provide data on the steam reforming of acetic acid using an Ni/attapulgite clay catalyst. Different preparation

routines are assessed, whereby catalyst synthesis by precipitation features the highest hydrogen yields. In addition, catalyst deactivation is shown to mainly stem from agglomeration and sintering of Ni particles, but less so from direct carbon deposition.

Two oxide composite materials are adressed by Karuppiah et al. [6] and Akbari-Emadabadi et al. [7]. In the former, the dry reforming performance of propane over alumina-supported NiO-CeO$_2$ is assessed. It is shown that the presence of Ce efficiently suppresses Ni particle sintering, and thereby improves the reducibility of NiO. A temperature range between 480–580 °C is shown to be particularly effective. Akbar-Emadabadi et al., in turn, focus on the performance of an yttrium-promoted bifunctional Ca-Co catalyst in methane steam reforming. It is shown that the effect of yttrium doping effectively influences the structure and regeneration of the entire catalyst system by improving the morphology and textural properties of the catalyst. A specific ratio of CaO, Co$_3$O$_4$ and Y$_2$O$_3$ (mass ratios Ca/Co = 9 and Ca/Y = 4.5), as evidenced by X-ray diffraction, is shown to exhibit superior performance and stability in terms of methane conversion, hydrogen yield and resistance against catalyst deactivation.

The role of intermetallic compound and alloy formation in enhancing the performance of metal catalysts in reforming reactions are subsequently addressed by Carrero et al. [8] and Köpfle et al. [9]. Glycerol steam reforming and the associated hydrogen production are studied by the former on a variety of bimetallic Ni-M/silica (M = Co, Cu, Cr) catalysts. Cr addition is shown to be most promising in terms of glycerol conversion, reduction of coke formation and hydrogen formation, which is ascribed to enhanced metal-support interaction [8]. In situ decomposition of a Cu$_{51}$Zr$_{14}$ intermetallic compound during methanol steam reforming is shown to enhance the CO$_2$ selectivity by in situ activation and corrosion of both catalyst bulk and surface to form dispersed Cu particles in synergistic contact with tetragonal ZrO$_2$. The latter interface is then particularly active and selective for water activation and subsequent CO$_2$ formation. Despite general inferior catalytic performance in terms of CO$_2$ selectivity, addition of Zr to Pd catalysts similarly opens water activation channels to increase the CO$_2$ selectivity.

The theoretical aspect of steam reforming is finally addressed by Cifuentes et al. [10]. The integration of the theoretical model of Response Surface Methodology enabled the assessment of energy balances in hydrogen-fed fuel cells. Hydrogen was generated by ethanol steam reforming over RhPt/CeO$_2$ catalysts. A delicate balance of operating temperature and Rh:Pt ratio (0.4:0.4) is shown to result in a maximum net energy of hydrogen production at 700 °C.

Summarizing, the present special issue encompasses state-of-the-art approaches to dealing with pending questions in reforming catalysis from various viewpoints, including experimental and theoretical work. The guest editor would like to express his gratitude to both the editorial team for professional assistance and all the authors for their valuable scientific contributions.

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