



Effect of polyaromatic tars on the activity for methane steam reforming of nickel particles embedded in silicalite-1



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ABSTRACT

The steam reforming of methane was studied over Rh and Ni-based catalysts exposed to naphthalene, which was used as a representative of polyaromatic tars found in biomass-derived biogas. In particular, two Ni-based samples in which part of the metal was encapsulated within silicalite-1 nanoboxes were tested. The reforming reaction was carried at 700, 800 and 900 °C using a model feed and high space velocities to limit methane full conversion and better evidence any deactivation. A strong decrease of methane conversion was observed in the presence of 1400 ppm of naphthalene, stressing the marked deleterious effect of this molecule in the present conditions. The effect of naphthalene was partly reversible, especially at higher temperatures. The silicalite-1 membrane could not prevent the deactivation of embedded nickel particles, probably because naphthalene (kinetic diameter = 0.62 nm) could diffuse throughout the MFI-type (pore diameter ca. 0.56 nm) porous layer at the high reaction temperatures used. The effect of 5 ppm of the bulkier pyrene (kinetic diameter = 0.74 nm) was investigated at 700 °C and also led to a rapid deactivation of the Ni@silicalite-1, likely because pyrene was cracked into naphthalene, which could then enter the silicalite-1 nanoboxes. The poisoning effect of toluene on the Ni-based catalysts was minor in comparison to that induced by the polyaromatics. A marked sintering of the embedded Ni was also observed.

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1. Introduction

Syngas, a mixture of carbon oxides and dihydrogen, can be obtained from the steam reforming of fossil fuels [1–5] and the gasification of biomasses or carbon-containing wastes [6,7]. The gas obtained from biomass gasification contains significant concentrations of light hydrocarbons and tars that should be preferably reformed to increase syngas yield [8,9].

Tars, a mixture of condensable organic compounds such as mono- and polyaromatics, are well known coke precursors that can lead to the deactivation of reforming catalysts. The propensity for coke formation from tars will depend on the catalyst formulation and reaction conditions such as reaction temperature and steam/carbon (S/C) ratio. Di Carlo et al. reported no deactivation at 800 °C of Ni/Ca₁₂Al₂₄O₃₃ used for the steam reforming of tars derived from hazelnut shells gasification [10]. Sato and Fujimoto also reported stable naphthalene conversions at 825 °C over a WO₃-promoted Ni/MgO–CaO catalyst, even in the presence of H₂S [11].

The impact of tars on the reforming of methane is less documented. Dagle et al. recently showed that the presence of benzene and naphthalene led to marked deactivations of methane conversion due to coking over Ni, Rh and Ir-based catalysts [12]. The coking was alleviated by using higher reaction temperatures and by the presence of a noble metal.

The support has no direct role on the methane reforming, except for the dispersion and stabilization of metal particles [13]. High metal dispersion is important to achieve high specific activities. The reaction is thought to be structure-sensitive, low coordination metal sites exhibiting somewhat higher turn-over frequencies [14–16]. Ni is intrinsically less active than noble metals [13,16], but has a lower cost. The use of MgAl₂O₄ spinel as a support is often favored over that of alumina, especially because Ni can form a spinel phase with the latter that is difficult to reduce to metallic Ni [17].

Extensive carbon deposition can yet occur on Ni-based catalysts that can be of several types, i.e. pyrolytic, encapsulating and whiskers [18,19]. Encapsulating carbon (also referred to as “gum”) is formed during reforming of feeds containing aromatic compounds. The formation of whiskers, which have high mechanical strength, can lead to catalyst particle breaking up and a large pressure drop increase in the reactor. The deposition of carbon is overall

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a complex interplay between methane/hydrocarbon decomposition and carbon gasification [20].

In the present work, two commercial catalysts based on Rh and Ni were studied, as well as two Ni-based samples in which part of the metal was encapsulated in silicalite-1 (MFI structure) nanoboxes. The effect of naphthalene on methane conversion was investigated at 700, 800 and 900 °C and, importantly, high space velocities to limit the full conversion of methane and better assess deactivation. Additional experiments were also performed using toluene and pyrene to unravel the main origin of the deactivation.

Our investigation focused on naphthalene because this molecule is one of the most difficult tar representatives to steam reform [21,22] and one of the most abundant among the polyaromatics formed during low-temperature gasification [23] and fast-pyrolysis [24] of woody biomasses. Naphthalene is also the smallest polyaromatic available and thus any catalyst that would display a size-selective resistance with respect to this molecule should also do so for the other larger compounds.

Naphthalene has a kinetic diameter of 0.62 nm, which is larger than the pore diameter of MFI zeolites (ca. 0.56 nm). Millini et al. reported that diffusion of naphthalene in the medium pore-size zeolite of the MFI-type was difficult, with energy barriers of around 114 kJ/mol [25]. In contrast, the transport of H₂O, CO₂, CO, H₂ and CH₄ (and many other small hydrocarbons) through the MFI zeolite layer is markedly faster. It is therefore possible that the slow transport of naphthalene through MFI-type pores could protect the metal particles encapsulated therein from coking, through the interplay of coke formation and gasification/reforming. These materials would thus exhibit size selective properties, being able to steam reform small hydrocarbons, while being resistant against coking due to large polyaromatics.

We reported earlier on the total size exclusion of mesitylene (kinetic diameter = 0.87 nm) from MFI-type silicalite-1 hollow nanocrystals [26,27]. In addition, we also have reported that these nanoboxes act as nanoreactors [28,29] in which the nanoparticles are encapsulated and protected from sintering by coalescence [30]. The activity and durability of Ni particles embedded in similar silicalite-1 nanoboxes during steam methane reforming catalyst will be of particular interest here, since the effect of operating at temperatures as high as 900 °C has not yet been reported. The synthesis and characterization of the Ni@silicalite-1 samples used here are described in details elsewhere [31] and are only briefly recalled here.

2. Experimental section

2.1. Catalyst synthesis

Silicalite-1 was prepared using tetraethylorthosilicate (TEOS, Aldrich, 98%) and 1 M TPAOH solutions obtained from aqueous TPABr by exchange with Ag₂O. The gel of composition SiO₂-0.4TPAOH-35H₂O was stirred at room temperature overnight to fully hydrolyze the TEOS, then transferred into a Teflon-lined autoclave and heated at 170 °C under static conditions for 3 days. The autoclave was then cooled to room temperature and the solid was centrifuged, washed with water until pH = 7 and dried overnight at 90 °C. Finally, the resulting solid was calcined for 12 h at 525 °C in air yielding silicalite-1 crystals of approximately 200 × 150 × 140 nm in size.

Ni@silicalite-1 materials were synthesized following the previously described generic method for the encapsulation of transition metal nanoparticles in hollow silicalite-1 single crystals [26,27,30,32,33–35]. In brief, 5 wt.%Ni@silicalite-1 catalyst was prepared by incipient wetness impregnation: 2 mL of Ni(NO₃)₂·6(H₂O) (99.99%, Sigma-Aldrich) aqueous solution with a

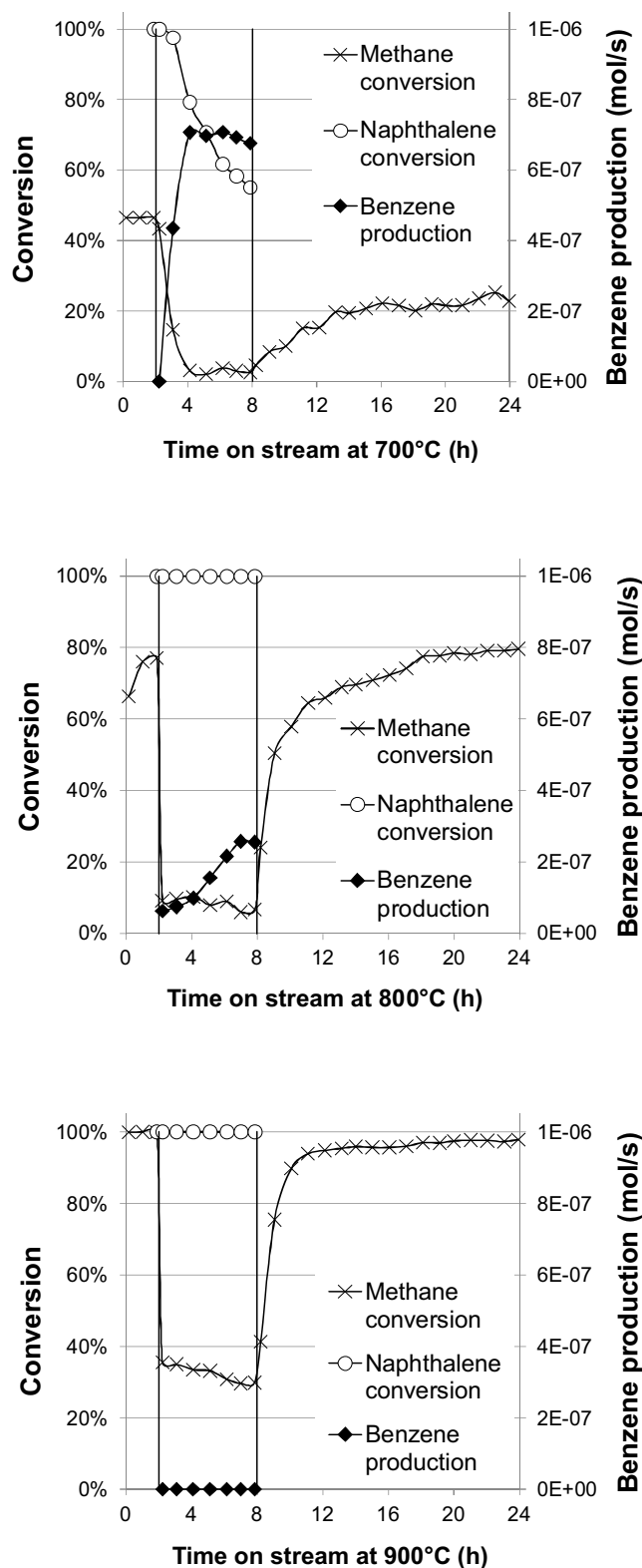


Fig. 1. Methane and naphthalene conversions and benzene production measured over time on stream at 700, 800 and 900 °C over the Rh-based commercial catalyst. 1400 ppm of naphthalene were introduced in the feed between 2 h and up to 8 h.

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