



## New synthesis strategies for Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1 core-shell catalysts for steam reforming of methane



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### ABSTRACT

The catalytic performance of Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1 core-shell catalysts was investigated for the steam reforming of methane (SRM). The core-shell catalysts consisting of Ni/Al<sub>2</sub>O<sub>3</sub> core catalyst and silicalite-1 (Sil-1) zeolite shell were prepared by different synthesis routes. Catalyst characterization indicates that repeated calcination at elevated temperatures during the catalyst preparation should be avoided to prevent the formation of the inactive NiAl<sub>2</sub>O<sub>4</sub> spinel phase. Thus, the new preparation procedure for the core-shell catalyst involves first growing a Sil-1 shell on the alumina beads to obtain Al<sub>2</sub>O<sub>3</sub>-Sil-1 core-shell beads, followed by an incipient wetness impregnation to obtain a Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1 catalyst. The catalytic activity of the catalyst for the SRM reaction displayed ca. 10% improvement over core-shell catalysts prepared by traditional method. The prepared catalysts maintained high reactivity even when exposed to alkali vapor during reaction.

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## 1. Introduction

Core-shell catalysts have enormous potential [1–7], particularly for catalysts with zeolite shell that acts as a selective barrier against impurities, poisons and byproducts resulting in enhanced catalyst activity, selectivity and life [8–11]. Tsubaki et al. [12,13] employed core-shell catalysts with a thin ZSM-5 shell to improve product yield and distribution in the Fischer–Tropsch synthesis reaction. Prior work by the authors used Fe/SiO<sub>2</sub>-Sil-1 core-shell catalyst for the direct synthesis of light alkenes from syngas via Fischer–Tropsch synthesis (FTS) reaction [14]. The zeolite shell suppresses the formation of undesired long-chain hydrocarbons while promoting the production of light alkenes. Kapteijn et al. [15,16] uses Sil-1 membrane as a selective barrier against branched hydrocarbons to obtain selective hydrogenation of linear 1-hexene in a mixture containing 3,3-dimethylbut-1-ene (3,3-DMB).

The core-shell catalysts with zeolite shell were used to avoid catalyst deactivation under the harsh operating conditions found in the direct internal reforming molten carbonate fuel cell (DIR-MCFC). The Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1 core-shell catalyst for the SRM reaction was designed to operate at high temperature (i.e., 923 K) and to

tolerate the high alkali vapor (i.e., Li<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>) in DIR-MCFC. The thin zeolite Sil-1 membrane shell acted as diffusion barrier against the alkali poisons [17,18]. The core-shell catalysts had lower conversion compared to Ni/Al<sub>2</sub>O<sub>3</sub> catalyst as a result of the transport resistance across the microporous Sil-1 shell. However, it is also possible that the traditional core-shell catalyst preparation procedure [19–21] could also affect the reactivity of the final catalyst. Generally, the core-shell catalysts were prepared by depositing a thin layer of zeolite shell on the surface of the core catalyst as illustrated in Fig. 1a. During the preparation, it was necessary to expose the catalysts to high temperature treatments that could cause sintering and phase transformation resulting in poorer catalyst activity. This work investigates the possible effects of core-shell catalyst preparation on the Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1 core-shell catalysts and their performance for SRM reaction in the presence of alkali poison. The purpose is to develop an optimum preparation procedure for the alkali-tolerant core-shell catalyst with target application in DIR-MCFC.

## 2. Experimental

### 2.1. Preparation of core-shell catalysts

The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> beads (0.8–2.2 mm diameter, pore volume of 0.40 cm<sup>3</sup> g<sup>-1</sup> and BET surface area of ca. 280 m<sup>2</sup> g<sup>-1</sup>) from Dalian

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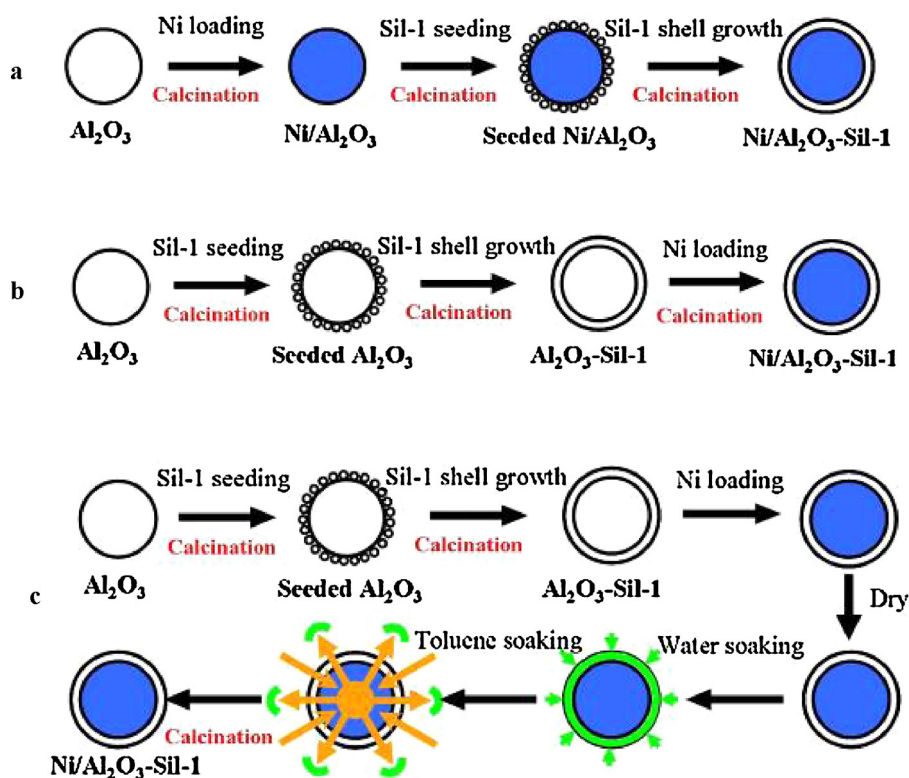


Fig. 1. Synthesis procedures of Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1 core-shell catalysts by different methods: (a) LM; (b) ML and (c) IML.

Haixin Chemical Ltd. were used for catalyst support. The beads were washed with deionized distilled water and rinsed in ethanol before calcination in air for 5 h at 823 K. Three preparation procedures described in Fig. 1 were used to prepare the Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1 core-shell catalysts.

**Method 1—LM method** follows the conventional approach in preparing core-shell catalysts. The Ni/Al<sub>2</sub>O<sub>3</sub> catalysts (12.5 wt.% NiO) were prepared by incipient wetness impregnation of a nickel nitrate solution (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%, Kermel) at room temperature followed by drying at 373 K for 12 h, before calcining in air at 823 K for 4 h to convert the nickel salts to oxides. A thin Sil-1 zeolite shell was deposited on the catalyst beads by following the seeding and regrowth method commonly used for preparing zeolite membranes [22–25]. The catalyst beads were seeded with 160 nm Sil-1 seeds using 3-aminopropyltrimethoxysilane (APTMS, Aldrich) as an organic linker. The zeolite was then deposited and grown on

the bead surface under hydrothermal conditions. Calcination in air at 823 K for 4 h was needed to remove organic structure directing agent (SDA) from the zeolite pores. The obtained core-shell catalyst was designated as Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1-LM. It should be noted that the catalyst was exposed to high temperature (i.e., 823 K) three times during the preparation.

**Method 2—ML method** proceeds by first growing the Sil-1 shell on the Al<sub>2</sub>O<sub>3</sub> beads before impregnating with the nickel nitrate solution as illustrated in Fig. 1b. The resulting core-shell catalyst was calcined once at 823 K for 4 h and is designated as Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1-ML.

**Method 3—IML method** is similar to ML method but with additional steps taken to remove residual nickel from Sil-1 shell as shown in Fig. 1c. A gram uncalcined Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1-ML was immersed rinsed with deionized distilled water and then placed in toluene kept at 313 K for 24 h (Fig. 2). This treatment was repeated

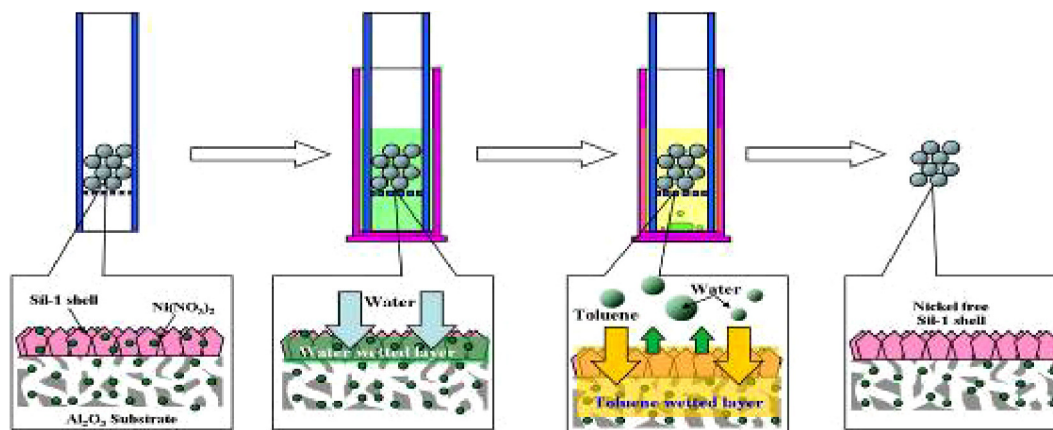


Fig. 2. Operation process of Ni/Al<sub>2</sub>O<sub>3</sub>-Sil-1 catalysts by IML method.

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