



How to improve stability in excess-methane dry reforming over Ni/KIT-6 catalysts? Reduction behavior of thermally stable Ni phyllosilicates (Si/Ni=1:1) monitored by *in situ/operando* XAS-XRD and IR spectroscopy

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Significance and Relevance

Synthesis gas is one of the most important intermediates to produce chemicals and fuels. For the first time, excess-methane dry reforming was studied over a Ni/KIT-6 catalyst synthesized by one-pot method. This method allowed Ni phyllosilicate to form *in situ* within the silica framework. As monitored by *operando* XAS-XRD, Ni phyllosilicate (Ni/Si=1:1) was found to be thermally stable after reduction at 750°C for 90 min (4% H₂/He) and during the catalytic test (CH₄/CO₂/Ar=5.3/3.0/1.7, 700°C). The catalyst showed remarkably stable catalytic behavior compared to an impregnated sample. More dispersed Ni species contributed to improved stability with less coke formation.

Preferred and 2nd choice for the topic: CO₂ utilization and recycling, Sustainable and clean energy production and transport

Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) Oral only

Introduction and Motivations

Dry (CO₂) reforming of methane (DRM) has emerged as the most widely studied reaction to convert CH₄ and CO₂ into synthesis gas¹. The synthesis gas is a versatile feedstock used for production of methanol and synthetic fuels. Excess-methane dry reforming poses an alternative to the conventional DRM as it can offer a future choice for upgrading low-quality natural gas to synthesis gas.

DRM has been widely investigated over nickel-based catalysts due to their high activity and relatively low cost compared to noble metals, yet, their performance may be limited due to sintering of nickel and carbon build-up¹. KIT-6 mesoporous silica has a unique 3D channel network, allowing easy access of host species without blocking the pores. Ni/KIT-6 silica catalysts are commonly prepared through post-synthesis impregnation of the silica support with an aqueous Ni solution, however, even at low loading (ca. 5 wt.%) nickel particles can be deposited on the outer surface of silica, reducing the strength of their interaction with support². A pH adjustment strategy appears as one of the most efficient solutions, allowing Ni species to be introduced during one-pot synthesis method.

Metal phyllosilicates have attracted attention in catalysis research due to their unique lamellar structure offering strong metal-support interaction (MSI), and small metal domain size having high dispersion³. In the existing literature, Ni phyllosilicate (Ni-PS) formation is not addressed in the context of KIT-6. The pH value can significantly affect the formation of 1:1 Ni-PS by polycondensation between Ni²⁺(OH)₂ and silicic acid Si-OH on the SiO₂ framework. Moreover, as far as we surveyed, the nature of Ni-PS 1:1 as well as their role in excess-methane dry reforming were not previously studied. Herein, we aim at understanding the behavior of Ni-PS supported on KIT-6-like silica using *in situ* or *operando* techniques: X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), and IR spectroscopy.

Materials and Methods

KIT-6/Ni onepot, KIT-6/Ni imp catalysts and parent supports (KIT-6 pH9, KIT-6) were studied. The one-pot synthesis assumed preparation steps typical for KIT-6 synthesis protocol⁴ with some modifications. After addition of Pluronic P123 (4g), HCl (7.47g), Ni(NO₃)₂·6H₂O (0.061 mol), TEOS (8.6g) and aging for 20h, the pH of the solution was adjusted to 9 by dropwise addition of ammonia solution (25%). The hydrothermal synthesis was carried out at 100°C for 24h. The sample was dried and calcined at 600°C for 6h. KIT-6 support was also synthesized at pH of 9, excluding the addition of nickel precursor. For the sake of comparison, KIT-6/Ni imp was synthesized by wet impregnation as described elsewhere⁴. By combining a variety of characterization methods (ICP-OES, N₂ physisorption, SAXS, TPR-H₂, HRTEM, H₂ chemisorption), we examined the role of Ni phyllosilicates in KIT-6-like mesoporous

silica. The catalytic tests were carried in $\text{CH}_4/\text{CO}_2/\text{Ar} = 53/30/17$ and $\text{WHSV} = 120,000 \text{ ml} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$. *In situ/operando* XAS-XRD were performed at the SNBL (BM31) at ESRF, France. XAS scans were collected during reduction in 4% H_2/He (*in situ*) and excess-methane dry reforming (*operando*) at the Ni K-edge, while collecting XRD patterns. The reaction flow was monitored by MS. *In situ* IR spectroscopy of CO adsorption was performed at room temperature to characterize the Ni sites.

Results and Discussion

ICP-OES analysis showed that both catalysts had similar content of Ni: 6.0 wt.% (KIT-6/Ni onepot), 6.2 wt.% (KIT-6/Ni imp). *In situ* XAS-XRD revealed that KIT-6/Ni imp showed typical transformation of NiO to Ni^0 , whereas diffraction peaks of $\text{Ni}_3\text{Si}_2\text{O}_5(\text{OH})_4$, posing a structure of nepouite (Ni/Si 1:1) were observed for KIT-6/Ni onepot. As illustrated in Fig. 1a,b, nickel phyllosilicate (Ni-PS) partially reduced to metallic phase, while a certain content of Ni species retained their initial cationic state. According to TPR- H_2 , the degree of reduction was 75.9% for onepot sample, while the impregnated material was reduced close to 100%. Excess-methane dry reforming was conducted over the reduced catalysts. The KIT-6/Ni onepot showed remarkably stable CO_2 and CH_4 conversions, as well as H_2/CO molar ratio, whereas KIT-6/Ni imp exhibited a declining trend (Fig. 1c,d). *Operando* XAS-XRD experiments revealed that Ni oxidation state did not change for both catalysts which indicates that the catalyst deactivation is due to carbon formation instead of a rapid oxidation (Fig. 1e-h). *Operando* XRD showed that the mixture of Ni phyllosilicate and Ni^0 was stable under reaction conditions (Fig. 1g). No increase in crystallite size was registered for Ni^0 retaining $6.5 \pm 0.2 \text{ nm}$ for KIT-6/Ni onepot, and $10.3 \pm 0.1 \text{ nm}$ for KIT-6/Ni imp. For the latter, the intensity of the graphite peak increased over time.

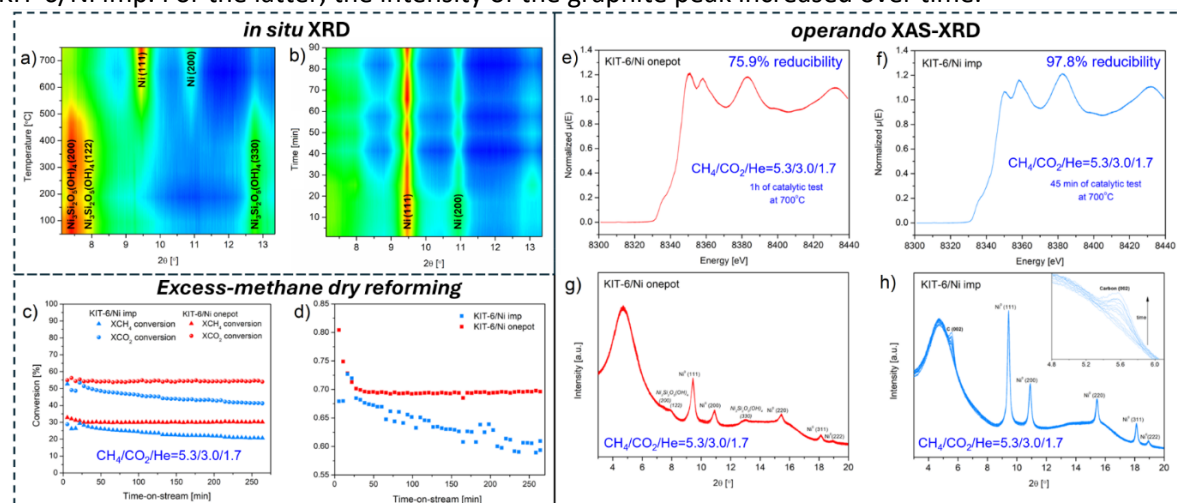


Figure 1 Contour plots of the acquired *in situ* XRD ($\lambda = 0.0338 \text{ nm}$): (a) KIT-6/Ni onepot during reduction as a function of temperature and time, (b) followed by isothermal reduction for 90 min. Catalytic tests in excess-methane dry reforming over KIT-6/Ni onepot and KIT-6/Ni imp, (c) CH_4 and CO_2 conversions, (d) H_2/CO molar ratio as a function of time-on-stream. *Operando* XAS-XRD changes registered during catalytic tests (e, f, g, h).

Our work provides insight into the impact of synthesis protocols on KIT-6-supported Ni sites and how stability can be tuned to improve DRM. Further optimization of our synthesis promises to push the boundaries of catalyst stability for excess-methane dry reforming.

References

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