

Direct non-oxidative methane aromatization over gallium nitride catalyst in a continuous flow reactor

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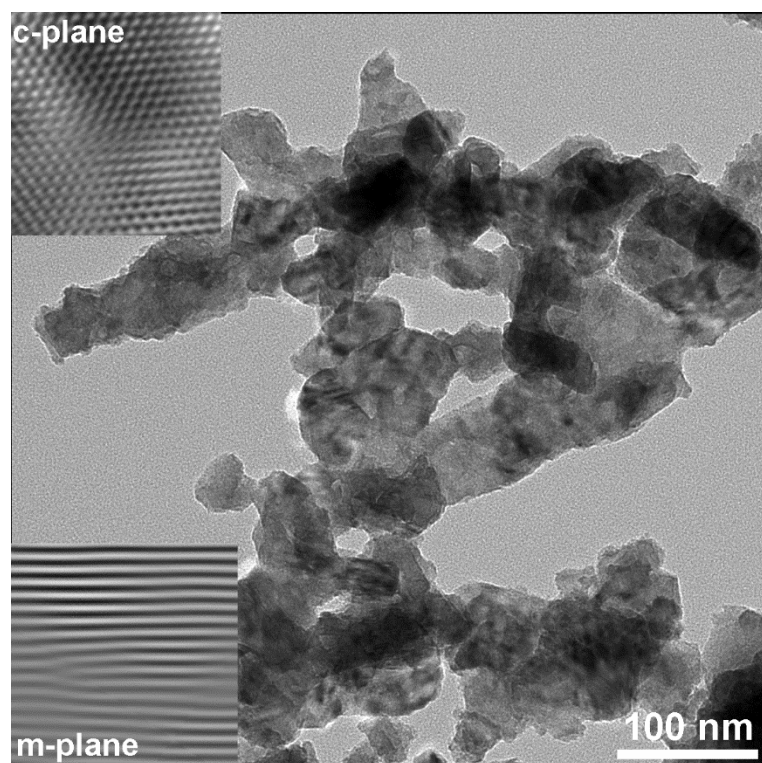
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Abstract

The direct non-oxidative methane aromatization over commercially available gallium nitride powder has been investigated for the first time in a fixed bed reactor under continuous operation. High reaction temperatures (650 – 710 °C) are needed to initiate benzene formation due to the small surface area ($8 \text{ m}^2 \text{ g}^{-1}$) of the gallium nitride material, thermodynamic constraints and the low residence time (1 – 4 s). Besides benzene and toluene, C_2 species



and coke were formed.

Keywords: Methane aromatization; gallium nitride; benzene formation; coke formation

1 Introduction

Aromatic compounds such as benzene and xylenes are important building blocks for the production of chemicals, which are usually derived by from petroleum feedstocks. Due to uncertainties in the

oil-price and geopolitical issues, much effort has been made to replace petroleum feedstock with natural gas and unconventional gas-resources. Vast amounts of shale gas and gas hydrates have been discovered, which will undoubtedly change the landscape of the chemical industry. In this context, methane is a feedstock of special interest. Processes that convert methane into chemicals are (1) indirect oxidative, (2) direct oxidative and (3) direct non-oxidative dehydrogenation [1]. Partial oxidation or reforming to syngas followed by coupling reactions are typical indirect processes. Direct oxidative coupling of methane to methanol and non-oxidative aromatization are examples for the other two processes. Despite the recent advances in the field, the syngas route with its low efficiency, high capital cost and CO₂ emissions is the dominant industrial practice. Direct non-oxidative methane aromatization is an efficient route, where methane is directly converted to aromatic compounds with hydrogen as a valuable by-product [2]. However, this route is very challenging due to thermodynamic and kinetic constraints. Methane is very difficult to convert directly into aromatics such as benzene due to its stable C–H bond ($6 \text{ CH}_4 \rightarrow \text{C}_6\text{H}_6 + 9 \text{ H}_2$, $\Delta G_R^0 = +434 \text{ kJ mol}^{-1}$, $\Delta H_R^0 = +531 \text{ kJ mol}^{-1}$), small electron affinity and large ionization energy [3]. The activation of the strong C–H bond requires high temperature (700-1100 °C) and an efficient catalyst, of which various metal-modified zeolites [2,4,5] embedded in silica have been investigated. The basic reaction mechanism involves C–H bond cleavage to a reactive $-\text{CH}_x$ that dimerizes to C_2H_y and subsequently oligomerizes and cyclizes to C_6H_6 with the formation of hydrogen. For the metal-modified zeolites, the oligomerization and cyclization are assumed to occur on the Brønsted acid site of the zeolites. The $-\text{CH}_x$ and C_2H_y complexes, however, lead to coke deposition, which is inevitable for most catalysts (e.g., zeolites) in a methane-rich atmosphere at high temperature and in the absence of oxygen [2,6]. The review articles from Ma et al. [2], Spivey and Hutchings [6] and Karakaya and Kee [7] summarize the research work that has been conducted with emphasis on metal-modified zeolites. Metals such as Mo,

Zn, W, Re, Cu, Mn, Ni, and Cr have been investigated [2]. Molybdenum-containing zeolites exhibited the highest activity in terms of methane conversion (3-16%) and benzene selectivity (50-75%) [3]. In addition to metals, different zeolite materials have been analyzed, of which HZSM and HMCM achieved the highest benzene selectivity. The main drawback of this reaction is the rapid and severe catalyst deactivation due to coking, which is the primary obstacle to commercialization. Catalyst performance can be improved by optimizing the support to suppress coking [3,7]. Mostly dealumination of the zeolite support or silanation methods are used to influence and reduce the amount of acid sites that facilitate coking. Adding promoters is another way; here, transition metals in Period 4 (Fe, Co, Ni, Cr) and metals in Group 13 (Ga and Al) show the best improvement in terms of methane conversion, benzene selectivity, and catalyst stability [2,8–11].

Li et al. showed for the first time the thermal catalytic activity of commercially available gallium nitride (GaN) powders towards non-oxidative alkane aromatization [12]. Small batch experiments confirmed that methane, propane and butane can be converted to benzene with high selectivity (89.8%) at a rather low temperature range of 450-550 °C without significant coke formation, but with a very high residence time (> 4 h). Considering the promising results, the objective of this work has been to investigate the applicability of GaN powders for direct methane aromatization under flow conditions with much shorter residence time (~ 2 s).

2 Experimental

Commercial GaN powder (99.99 %, Sigma Aldrich) was used in this study and analyzed with nitrogen adsorption/desorption, X-Ray Diffraction (XRD), transmission electron microscopy (TEM), temperature programmed surface reaction coupled with mass spectrometry (TPSR-MS) and temperature programmed oxidation (TPO). Catalytic activity towards methane aromatization was investigated in a fixed bed reactor system in a temperature range of 650 – 710 °C with gas hourly

space velocities (GHSV) ranging from 114 – 720 ml_N g_{cat}⁻¹ h⁻¹ at atmospheric pressure. Details about the catalyst characterization and experimental procedure are provided in the supplementary section.

3 Results and Discussion

3.1 Equilibrium calculation

Minimization of Gibbs free energy approach was used to calculate the equilibrium composition as a function of temperature. The calculations were performed for 1 mol of methane feed at 1 bar from 450-1000 °C. The components assumed to be present in the products were hydrogen, cyclohexane (C₆H₁₂), benzene (C₆H₆) and toluene (C₇H₈). Methane conversion was noticeable only at temperatures above 600 °C and benzene was favored thermodynamically over cyclohexane and toluene (Figure S1 A). The product profile completely changed when carbon was added in the calculations (Figure S1 B); the methane conversion was much higher with negligible amount of benzene, toluene and cyclohexane. Carbon as the main product can either be formed by methane pyrolysis or from polynuclear aromatic compounds. From the thermodynamic stand point, carbon deposition is favored over benzene and other hydrocarbons.

3.2 Catalyst Characterization

3.2.1 Nitrogen adsorption/desorption analysis

Nitrogen adsorption/desorption measurement of the GaN catalyst showed type-II isotherm according to the IUPAC classification, indicating non-porous or macroporous particles (Figure S1 C). The determined BET surface area was around 8 m² g⁻¹, which was considerably smaller than surface areas reported for the catalysts used in aromatization studies (i.e., $S_{\text{BET}} = 300 - 400 \text{ m}^2 \text{ g}^{-1}$ for Mo-ZSM-5 [11]).

3.2.2 XRD analysis

X-ray diffraction analyses were performed on both fresh and spent catalysts. Both fresh and spent catalysts diffractograms matched with the reference gallium nitride XRD patterns (International Centre for Diffraction Data ICDD PDF # 04-013-1733). Although, visibly the spent catalyst looked black due to carbon deposition, XRD did not exhibit any structural change even at 710 °C (Figure S1 D). No peaks for carbon (coke) were observed, indicating that the carbon was probably amorphous.

3.2.3 TEM analysis

Transmission electron microscope (TEM) was used to identify the crystal structure of fresh and spent catalysts. Figure 1 illustrates the GaN nanoparticles of the fresh catalyst, with crystal planes in the insets (also refer Figures S2 A, B and C). Gallium nitride has a regular wurtzite structure (Figure S2 D) with both c- and m-planes (Figure S2 B and C). The m-plane is non-polar and made of alternating gallium and nitrogen ions, with 5.5 Å as the smallest width ($\sqrt{3}$ times the lattice constant a depicted in Figure S2 B and D) of the hexagonal lattice system of wurtzite structure. On the other hand, the polar c-plane consists of either Ga or N atoms, with bilayer thickness of 5.2 Å along c-axis (lattice constant c as depicted in Figure S2 C and D). Based on density functional theory (DFT) calculations [12], it has been suggested that m-planes are active for aromatization where the carbon atom of methane is oriented towards the Ga^{3+} , whilst one hydrogen atom towards the N^{3-} anion (alkyl adsorption model). No difference in lattice structure was observed between the fresh and spent catalysts (not shown). TEM analysis was also carried out on the spent catalyst for detecting carbon deposition on the surface (Figures S2 E and F). Spent catalyst used at 710 °C (Figure S2 F) has a thin layer of carbon deposited on the surface, which was not observed on the fresh catalyst (Figure S2 E).

3.3 Activity measurements

3.3.1 Effect of temperature

The effect of reaction temperature was studied with a GHSV of $360 \text{ ml}_N \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$. Theoretically, methane conversion exceeds 8% only above 600 °C with hydrogen, benzene and toluene as the assumed products (Figure 2 A). Experiments conducted between 250 °C and 600 °C did not show any benzene formation. Methane conversion was detectable above 500 °C with hydrogen as the only gaseous product (not shown). Benzene was formed at temperatures of 650 °C and higher with the results illustrated in Figure 2 A, B, and C, showing methane conversion, benzene and hydrogen product flow rates as a function of reaction time, respectively. Toluene product flow rates were approximately 10 times smaller compared to benzene (Figure S3). Besides benzene and toluene, TPSR-MS experiment confirmed the formation of C_2 species such as ethane and/or ethylene (Figure S4). No cyclohexane nor other hydrocarbons were detected.

The mean residence time based on the inlet flow rate, catalyst volume, porosity and temperature was around 2.1 s, which was 7200 times shorter than the residence time used in the batch experiments (4 h) reported in [12].

As expected, methane conversion increased with the increasing temperature, but declined faster with time. The initial methane conversion increased from 5% to 11.5% for 650°C to 710°C. At all temperatures, an induction time was observed (0.5 – 1.5 h), in which the product flow rates increased, reached a maximum and then declined (Figure 1 B, and C). This induction period is probably due to the formation of active species ($-\text{CH}_x$), and once formed they react with each other to produce benzene and toluene, but also lead to coke formation. In case of Mo-containing zeolites an induction period is also observed, but is associated with the reduction of Mo^{6+} to Mo_2C structures [2].

Under the current operating conditions, the commercial gallium nitride material deactivated rather fast; within 4 to 7 h benzene and toluene formation dropped to zero. Hydrogen on the other hand reached a constant flow rate and methane conversion approached a value of 2% indicating continuous coke formation. For comparison purposes, batch reactor experiments conducted at 450 °C resulted in a methane conversion of 0.56% after 4 h and no sign of carbon deposition [12]. However, due to the small catalyst surface area ($8 \text{ m}^2 \text{ g}^{-1}$) and short residence time (2.1 s) in the flow reactor, higher temperatures were needed, which favoured a fast coke formation and low product yields. The maximum methane conversion, benzene and hydrogen formation rates at 710 °C (methane GHSV of $360 \text{ ml}_N \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$) were 11.5%, $22.5 \text{ nmol min}^{-1} \text{ g}_{\text{cat}}^{-1}$ and $23.5 \mu\text{mol min}^{-1} \text{ g}_{\text{cat}}^{-1}$, respectively. Metal modified zeolites achieved similar methane conversions, but much higher benzene yields (e.g., $X_{\text{CH}_4} = 8 - 14 \%$, $\text{rate}_{\text{C}_6\text{H}_6} = 1800 - 2400 \text{ nmol min}^{-1} \text{ g}_{\text{cat}}^{-1}$ at 700 °C with a GHSV of $1500 \text{ ml}_N \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ [11]). However, the zeolite catalysts had BET surface areas of $> 300 \text{ m}^2 \text{ g}^{-1}$.

3.3.2 Influence of catalyst amount

Experiments with different amount of catalyst were conducted at 670 °C and methane GHSV of 180-360 $\text{ml}_N \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$. This not only changed the total surface area (2, 4 to 8 m^2) but also increased the residence time from 1.0, 2.1 to 4.3 s for 250, 500 and 1000 mg GaN, respectively. The product molar flow rates were almost proportional to the catalyst amount. The maximum benzene rates (Figure 3 B) were $13.0 \text{ nmol min}^{-1} \text{ g}_{\text{cat}}^{-1}$ for 1000 and 500 mg catalyst, respectively. In the same sequence, the maximum hydrogen flow rates were 6 to $7 \mu\text{mol min}^{-1} \text{ g}_{\text{cat}}^{-1}$ (Figure 3 C). For the run with 250 mg of catalyst, benzene was only formed during the first hour. Higher catalyst mass led to slower deactivation, which was evident from benzene and hydrogen flow rates at the end of run (Figure 3 B and C). Unlike the product flow rates, the conversion of methane was not directly proportional to the catalyst mass (Figure 3 A).

3.3.3 Influence of methane partial pressure

Effect of methane feed concentration is also an important parameter, as it is directly proportional to the amount of active species ($-\text{CH}_x$). Two different feed gas compositions were used: 40 vol% and 60 vol% methane with balance argon. The temperature was set at 670 °C with a methane GHSV of 228 and 360 $\text{ml}_\text{N} \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$. Methane conversion, benzene and hydrogen molar flow rates as a function of time are illustrated in Figure 3 A, B and C (note; curve labeled with 500 mg refers to 60 vol%) respectively. Methane conversion was about 3.5 times higher for the higher partial pressure (Figure 2 A, 500 mg vs 500 mg, 40 vol%). This was most likely due to an increased formation of reactive surface intermediates ($-\text{CH}_x$), which in turn results in a higher benzene and hydrogen formation rate. The maximum benzene and hydrogen rates were 2.3 times and 1.5 times higher for the experiment conducted with 60 vol% methane compared to experiment conducted with 40 vol% methane (Figure 2 B and C). Nevertheless, carbon deposition was still dominant given the black appearance of the spent catalyst and the TEM analysis (Figure S2 F).

3.4 Temperature Programmed Oxidation

Temperature programmed oxidation (TPO) was carried out for both fresh and spent catalyst (Figure S5). Prior to the oxidation with air, the catalysts were dried under nitrogen at 130 °C for 30 minutes, yielding a small weight decrease of 0.26 wt% for the fresh catalyst and no change in weight for the spent catalyst. This could be due to moisture sensitivity of gallium nitride powder. A further increase of the temperature to 400 °C resulted in an additional very small weight loss due to devolatilization of other species in the fresh catalyst. On the other hand, spent gallium nitride did not exhibit any weight loss until 440 °C. Thereafter, a 0.5 wt% drop in weight was observed until a temperature of 540 °C, indicating oxidation of the coke. The temperature range confirms that the coke deposition was amorphous in nature and not graphitic [13].

For the fresh catalyst, the weight increased at a temperature higher than 420 °C due to oxidation of gallium nitride (GaN) to gallium oxide (Ga₂O₃). Two moles of gallium nitride produce one mole of gallium oxide which increases weight by about 12% (assuming complete oxidation). No analysis was done for the fate of nitrogen during oxidation. Weight increase was also observed for the spent catalyst after 540 °C. The oxidation of the coke deposition and gallium nitride might be overlapping, which mask the weight loss due to carbon oxidation.

4 Conclusions

For the first time, it has been shown that gallium nitride exhibits a catalytic activity towards the direct non-oxidative methane aromatization in a continuous flow reactor. Small surface area (8 m² g⁻¹) and lower residence time (1 – 4 s) necessitate temperatures above 650 °C to initiate benzene formation, yet at these temperatures coke formation becomes inevitable. Increasing the surface area as well as the number of exposed m-planes of the gallium nitride material is in progress to achieve higher benzene yields.

Acknowledgements

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List of Figures

Figure 1 TEM image of the GaN nanoparticles showing the c-plane (inset) and m-plane (inset)

Figure 2 Influence of temperature on (A) methane conversion, (B) benzene formation and (C) hydrogen formation (methane GHSV: $360 \text{ ml}_N \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$). Note. Symbols represent experimental data point and dotted lines are for guidance only.

Figure 3 Influence of catalyst mass and methane partial pressure at 670°C on (A) methane conversion, (B) benzene formation and (C) hydrogen formation (for variable mass: methane flow rate: $180 \text{ ml}_N \text{ h}^{-1}$; GHSV for 40 vol% methane is $228 \text{ ml}_N \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$ based on methane). Note. Symbols represent experimental data point and dotted lines are for guidance only.

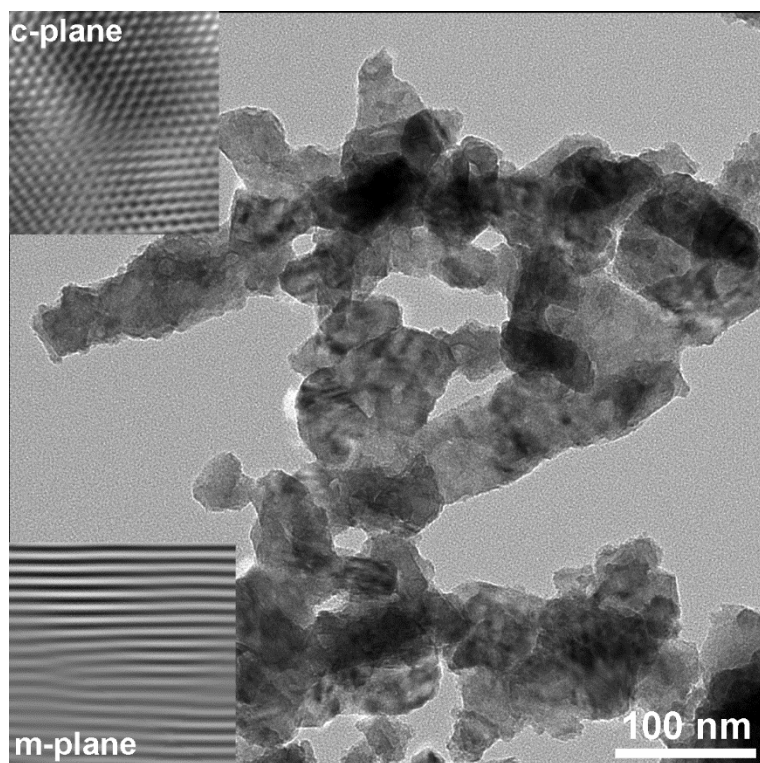


Figure 1

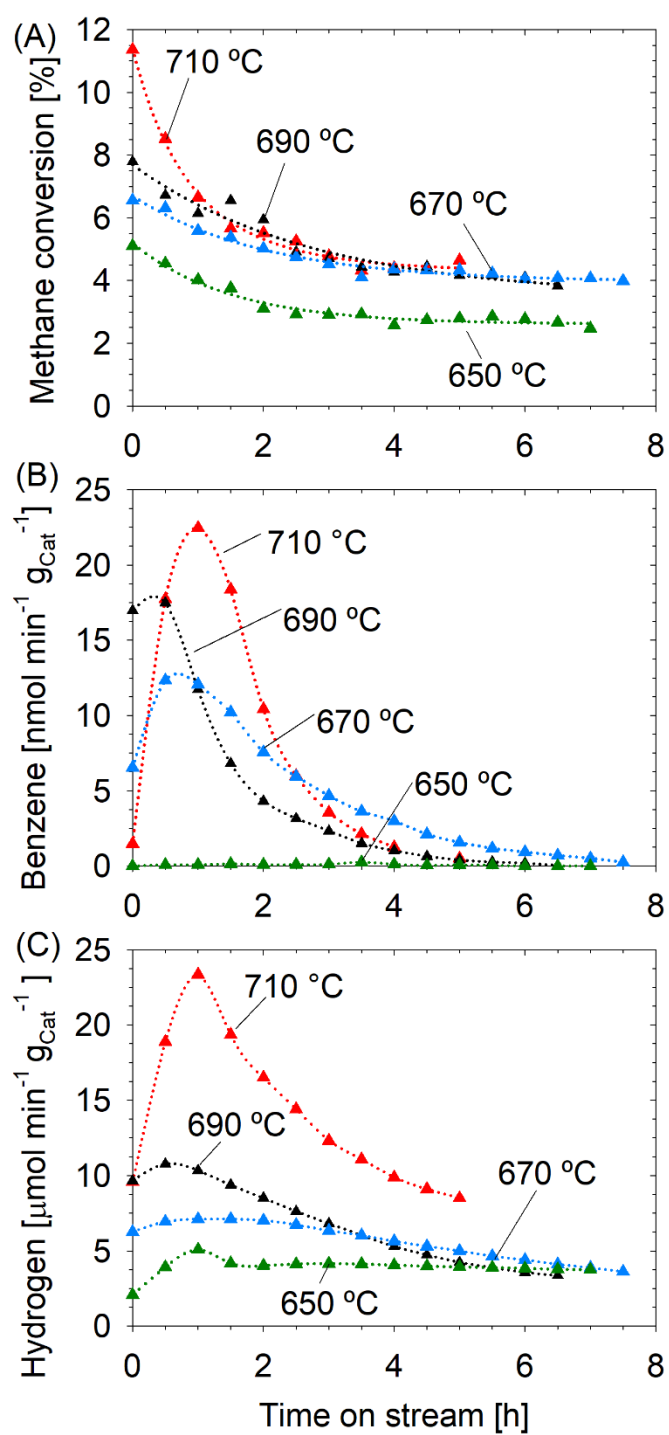


Figure 2

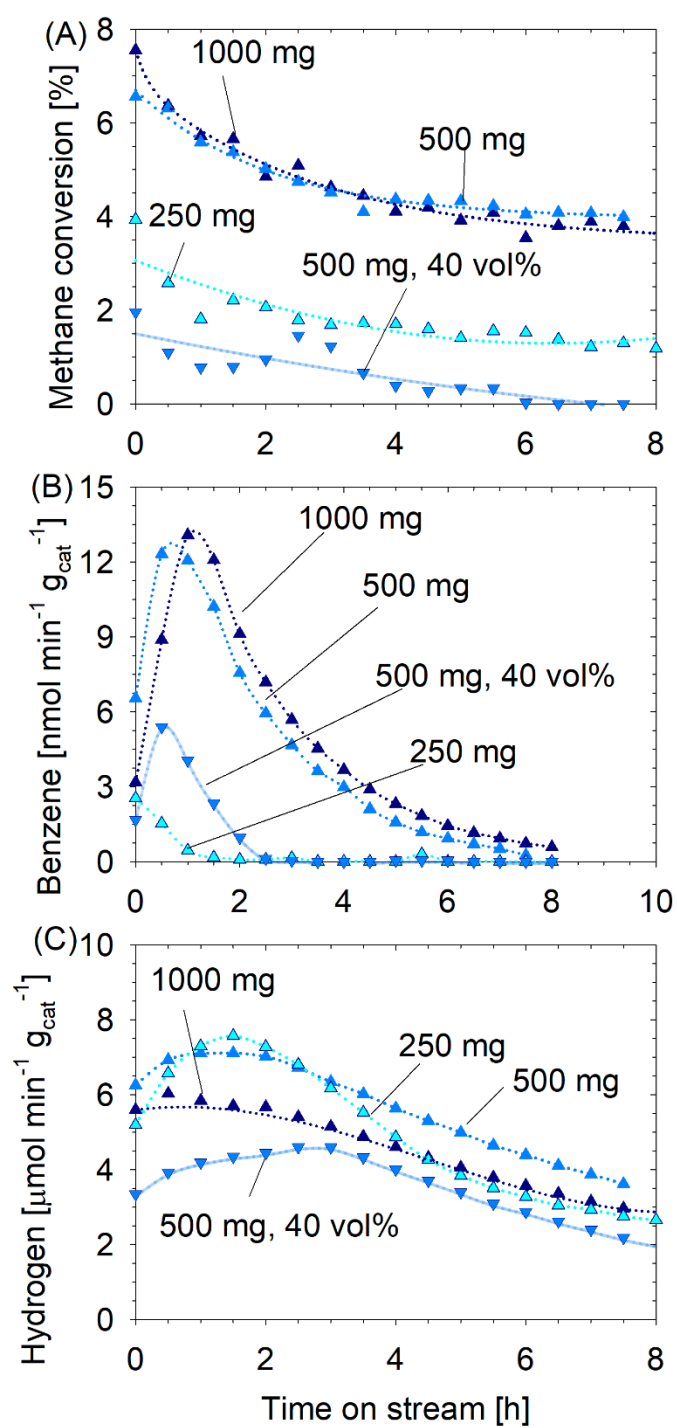


Figure 3