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Steam Reforming of Bio-oil Model Compounds

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The steam reforming of bio-oil is a sustainable and renewable route to synthesis gas and hydrogen, where one of the main hurdles is carbon formation on the catalyst.

Liquid fuels, like diesel and gasoline, contain hydrocarbons and currently the only route for producing these fuels in a sustainable manner is from biomass. Biomass can through pyrolysis be converted to bio-oil, which has up to ten times higher energy density.

Steam reforming (SR) of bio-oil can be used to produce syngas for production of liquid fuels or H₂ to upgrade the bio-oil to transportation fuels through hydrodeoxygenation [1].

SR of bio-oil can be performed over supported Ni or noble metal catalysts, however, carbon deposition causes short lifetimes of catalysts, so new catalysts must be developed to make SR of bio-oil feasible [2;3].

Experimental

In the present work different Ni based catalysts has been synthesized by wet impregnation. The effect of the support material was investigated over four different types of supports and their properties are shown in table 1.

Catalyst	BET surface area [m ² /g]		Ni particle size [nm]		C _{Dep} [mg/(g _{Cat} h)]
	Fresh	Spent	Fresh	Spent	
Ni/CeZrO ₄	90	42	15-20	20-28	94
Ni/CeO ₂	113	37	10	27	19
Ni/MgAl ₂ O ₄	69	66	7	11	21
Ni/CeZrO ₄ /MgAl ₂ O ₄	63	53	6	9	15

Table 1: Properties of fresh and spent catalyst determined by XRD and BET-measurements. ¹Carbon deposition determined based on 4 hours experiment at 580-590°C and S/C of 5.3-6.0.

Effect of support material

Temperatures above 600°C are needed for full conversion (see fig. 1) and at these temperatures the product distribution resembled the thermodynamic equilibrium.

CeZrO₄ seems to be an interesting support due to a high conversion. The stability of this catalyst was also high as no activity loss was observed for up to 24 h. The better performance of CeZrO₄ could be ascribed to increased steam dissociation [4] and internal gasification of the deposited carbon on the redox active support.

Addition of 10 wt% of both CeO₂ and ZrO₂ to MgAl₂O₄ increased activity and decreased carbon deposition, probably due to an increased water dissociation and internal gasification of carbon.

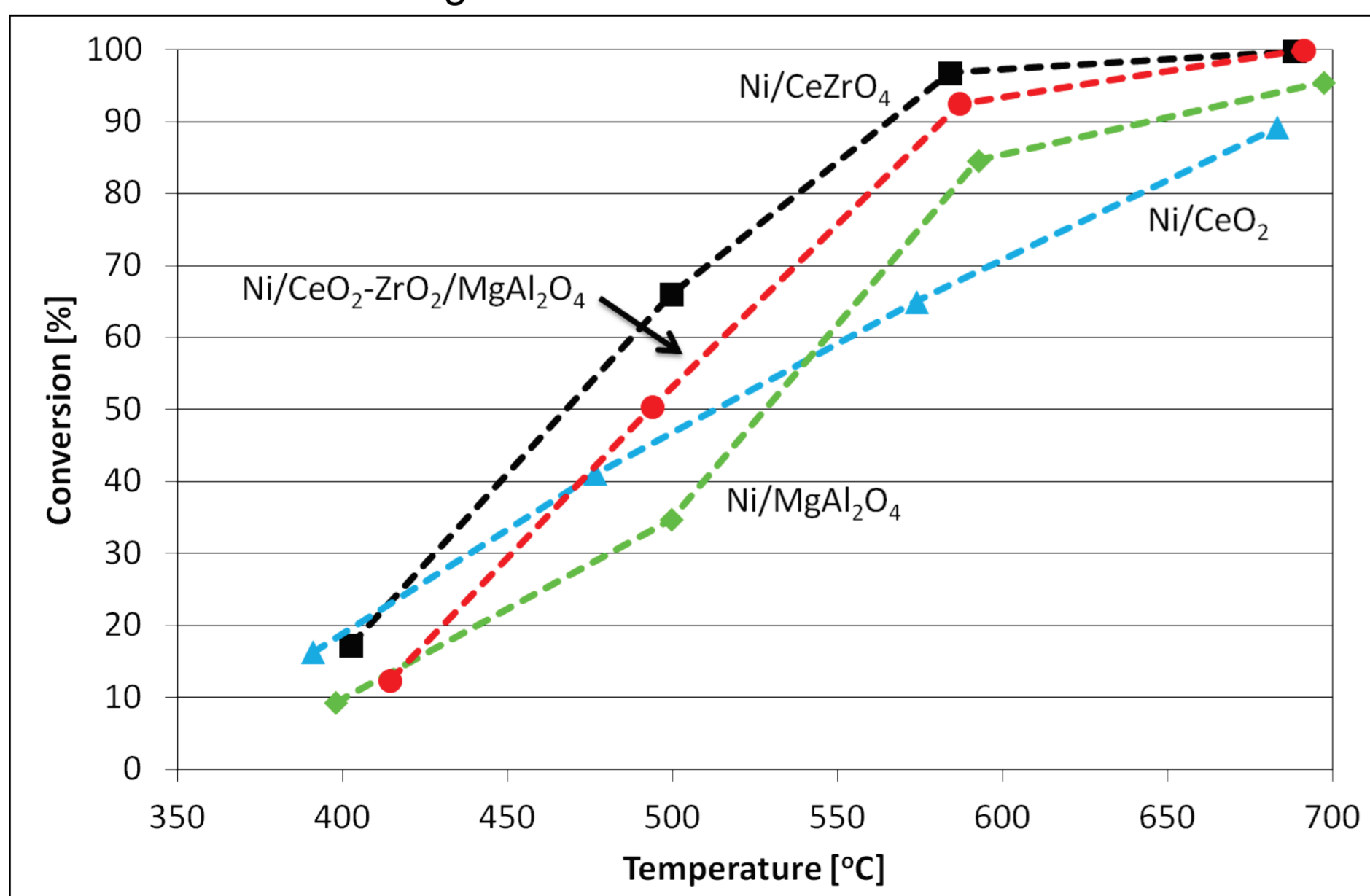


Figure 1: The conversion as function of temperature over Ni-based catalysts. m_{cat} : 0.5 g, Ni loading: 8.0-8.2 wt%, p: atmospheric, S/C: 5.3-6.0, Temp.: 400-700 °C, F_T =1.5-1.6 NL/min, x_{Eth} =3.2-3.5 %, x_{H_2O} =38.6-39.2 %, N₂ as balance.

Deactivation of the catalysts was observed and the cause was both sintering and carbon deposition as indicated in table 1.

Carbon deposition was most pronounced on Ni/CeZrO₄. TEM images showed that carbon whiskers were formed on Ni/CeZrO₄, which partly could explain the high activity despite a significant carbon deposition.

Ni/CeZrO₄ and Ni/CeO₂ sintered significantly, while Ni/MgAl₂O₄ and Ni/CeZrO₄/MgAl₂O₄ were more thermally stable, as especially the overall surface area did not decrease significantly over 60-70 h.

Effect of additives

Addition of K, CeO₂, ZrO₂, or mixtures hereof to Ni/MgAl₂O₄ was investigated to see if the catalyst performance could be enhanced.

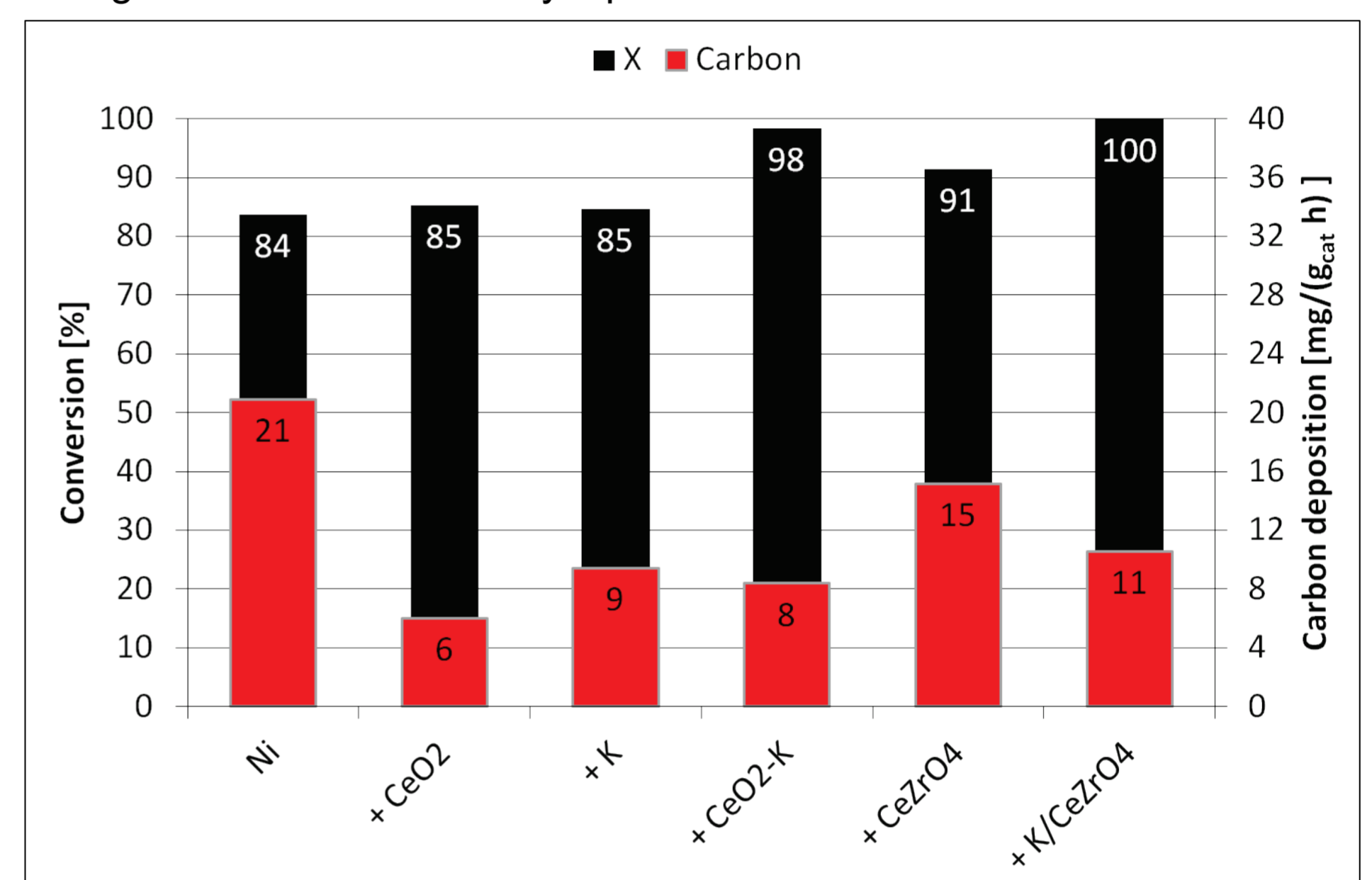


Figure 2: The conversion and carbon deposition for promoted Ni/MgAl₂O₄ catalysts. m_{cat} : 0.5 g, Ni loading: 8.0-8.2 wt%, p: atmospheric, S/C: 5.6-6.1, Temp.: 579-592°C, F_T =1.5 NL/min, x_{Eth} =3.2-3.6 %, x_{H_2O} =38.8-39.0 %, N₂ as balance.

The additives all enhanced the catalysts performance by decreasing carbon deposition, increasing conversion or both. The product distribution did not differ much with the different additives. A promising catalyst seems to be Ni/CeO₂-K/MgAl₂O₄ with high activity and low carbon deposition.

Effect of O₂ in the feed

Addition of oxygen to the feed might improve the stability of the catalysts due to oxidation of solid carbon on catalysts during operations.

Catalyst	Type	Conversion	C _{Dep}	H ₂ Production
		[%]	[mg/(g _{Cat} h)]	[mole/mole Eth converted]
Ni/CeZrO ₄	SR	96	94	4.2
Ni/CeZrO ₄	OSR	97	65	3.9
Ni/MgAl ₂ O ₄	SR	84	21	4.3
Ni/MgAl ₂ O ₄	OSR	100	22	3.7
Ni/CeO ₂	SR	75	19	4.1
Ni/CeO ₂	OSR	100	11	4.0
Ni/CeZrO ₄ /MgAl ₂ O ₄	SR	91	15	4.2
Ni/CeZrO ₄ /MgAl ₂ O ₄	OSR	100	6	4.0

Table 2: Comparison of conversion, carbon deposition, and H₂ production at SR and OSR conditions during a 4 hour experiment. m_{cat} =0.50 g, Ni loading: 8.0-8.2 wt%, S/C: 5.8-6.0; O/C: 0.23-0.28; Temp.: 579-592°C; F_T =1.5 NL/min, x_{Eth} =3.2-3.5 %, x_{H_2O} =38.4-38.6 %, x_{O_2} =0.1 %, N₂ as balance.

O₂ addition (OSR) increased conversion and decreased carbon deposition at the expense of lower H₂ production and a larger amount of CO₂ in the offgas. The effects were most pronounced for redox active supports.

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