

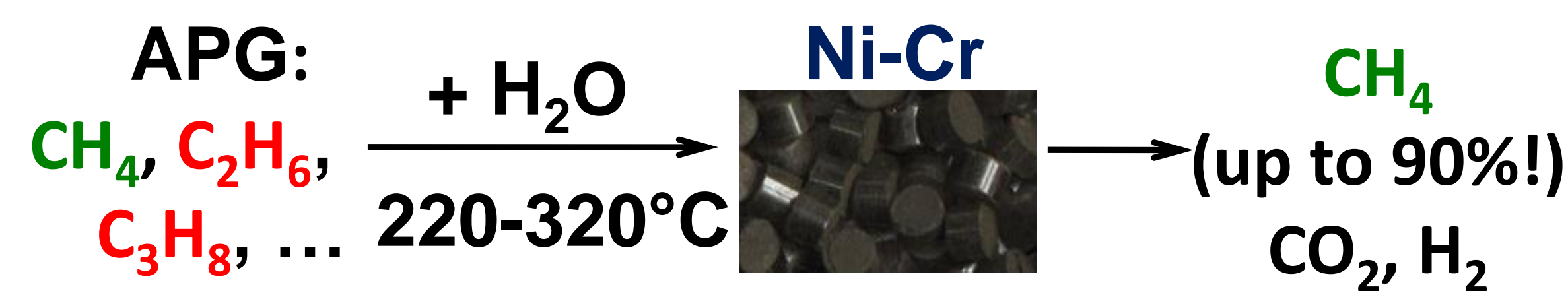
Introduction

In recent years, associated petroleum gas (APG) utilization approaches are focused mainly on the generation of electric power, which can be used for both local needs and transported for long distances. Direct use of APG as fuel for power generation is limited by low methane content, unstable gas composition, high coking and detonation risks that decreases service life and causes engine damage. Low-temperature catalytic steam reforming of light hydrocarbons (LTSR) represents a promising way to convert APG into methane-enriched gas fuel that can be used for electric power generation.

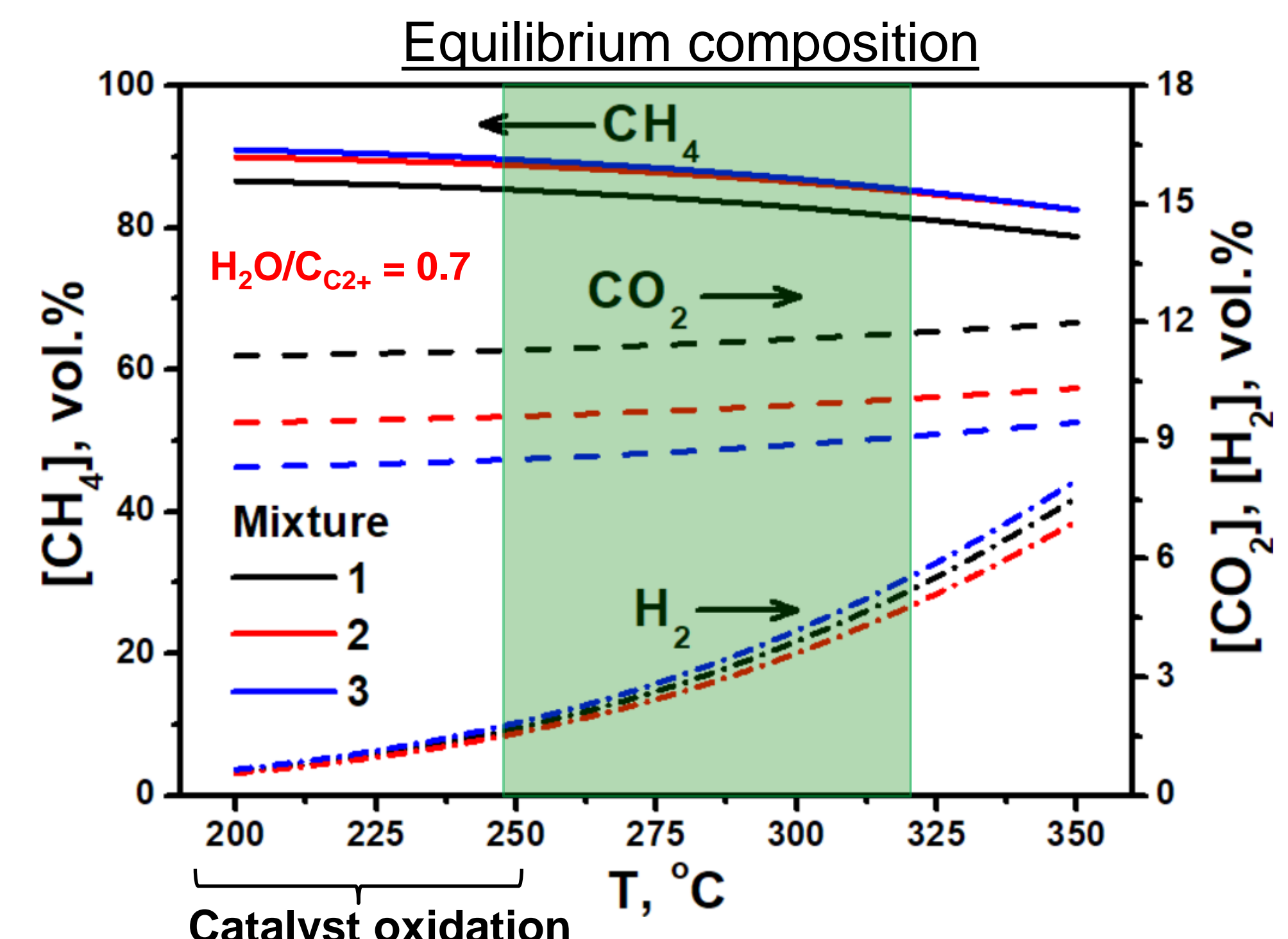
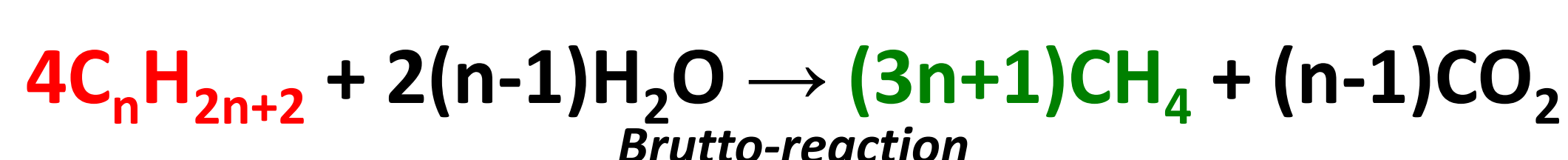
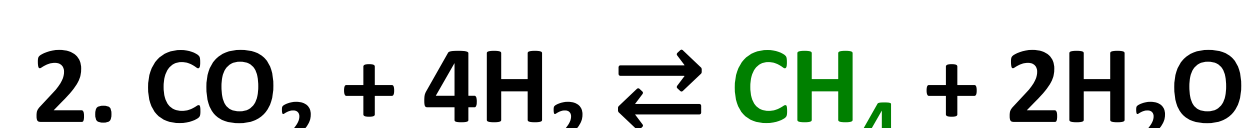
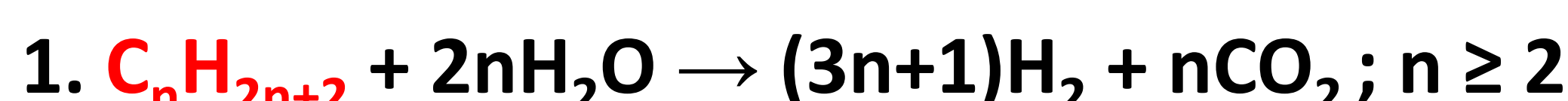
Solution: low-temperature steam reforming of C₃₊-alkanes over the Ni-based catalysts

- ✓ Cheap Ni-based catalysts
- ✓ Compact power plants
- ✓ Temperature below 320°C
- ✓ 100% conversion of C₅₊-alkanes
- ✓ High methane content in the products

In total we get normalized fuel for satisfying the oil field needs in electric power!



Macrokinetic approach for process describing



No	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆	CO ₂	N ₂
1	70.45	7.92	7.95	4.36	1.46	1.09	4.30	2.45
2	70		30					
3	74	10	10	5	1			

} Realistic APG
} Model mixtures

Possible C formation!

Experimental

Ce_{0.75}Zr_{0.25}O₂ (CeZr) and Ce_{0.4}Zr_{0.5}Y_{0.05}La_{0.05}O₂ (Optalys) were used as carriers. The catalysts were prepared by incipient wetness impregnation using Ni(NO₃)₂ and ethylene glycol (EG). NIAP-12-05 (63%Ni + 37%Cr₂O₃), an industrial catalyst of gas purification from O₂, CO and CO₂ and NIAP-07-05 (36%Ni + 12%Cr₂O₃ on Al₂O₃), an industrial catalyst of carbon oxides methanation were chosen as reference samples.

Results and discussion

In the present work we studied X% Ni/CeZr (X = 5, 9, 12, 15) and X% Ni/Optalys (X = 9, 18, 31) prepared via incipient wetness impregnation of the corresponded carriers. These catalysts demonstrated high Ni dispersion (Table 1) which kept unchanged after catalytic tests. The catalysts were studied in the LTSR of a model propane-methane mixture and compared with industrial NIAP-07-05 and NIAP-12-05 catalysts (Fig. 1).

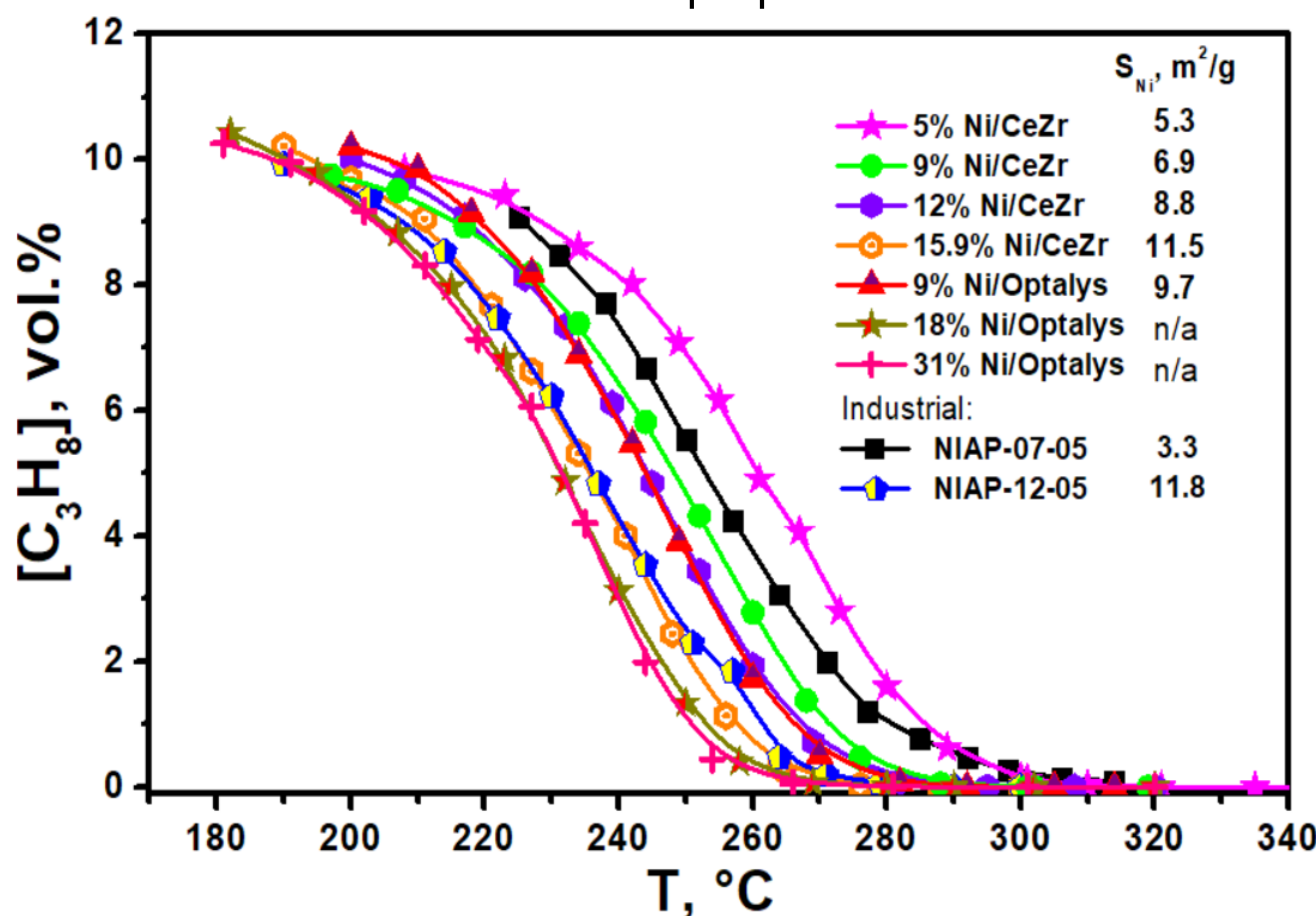


Fig. 1 Steam reforming of a propane-methane mixture. H₂O/C ratio = 2; [C₃H₈]⁰ = 10 vol.%, [CH₄]⁰ = 90 vol.%; WHSV = 2500 cm³·h⁻¹·g_{cat}⁻¹.

The kinetics of propane steam reforming was proved to be first order with respect to propane and approximately zero order with respect to the H₂O, CO₂, H₂ etc. Therefore we can estimate the rate constant of the process and normalize it to the area of metallic Ni:

$$k = \frac{\ln\left(\frac{[\text{C}_3\text{H}_8]_0}{[\text{C}_3\text{H}_8]}\right)}{\tau \cdot S_{\text{Ni}}}$$

The value of k allows us to estimate the specific catalytic activity of the samples per m² of metallic Ni (Fig. 2). S_{Ni} was determined by CO chemisorption (see Fig. 1).

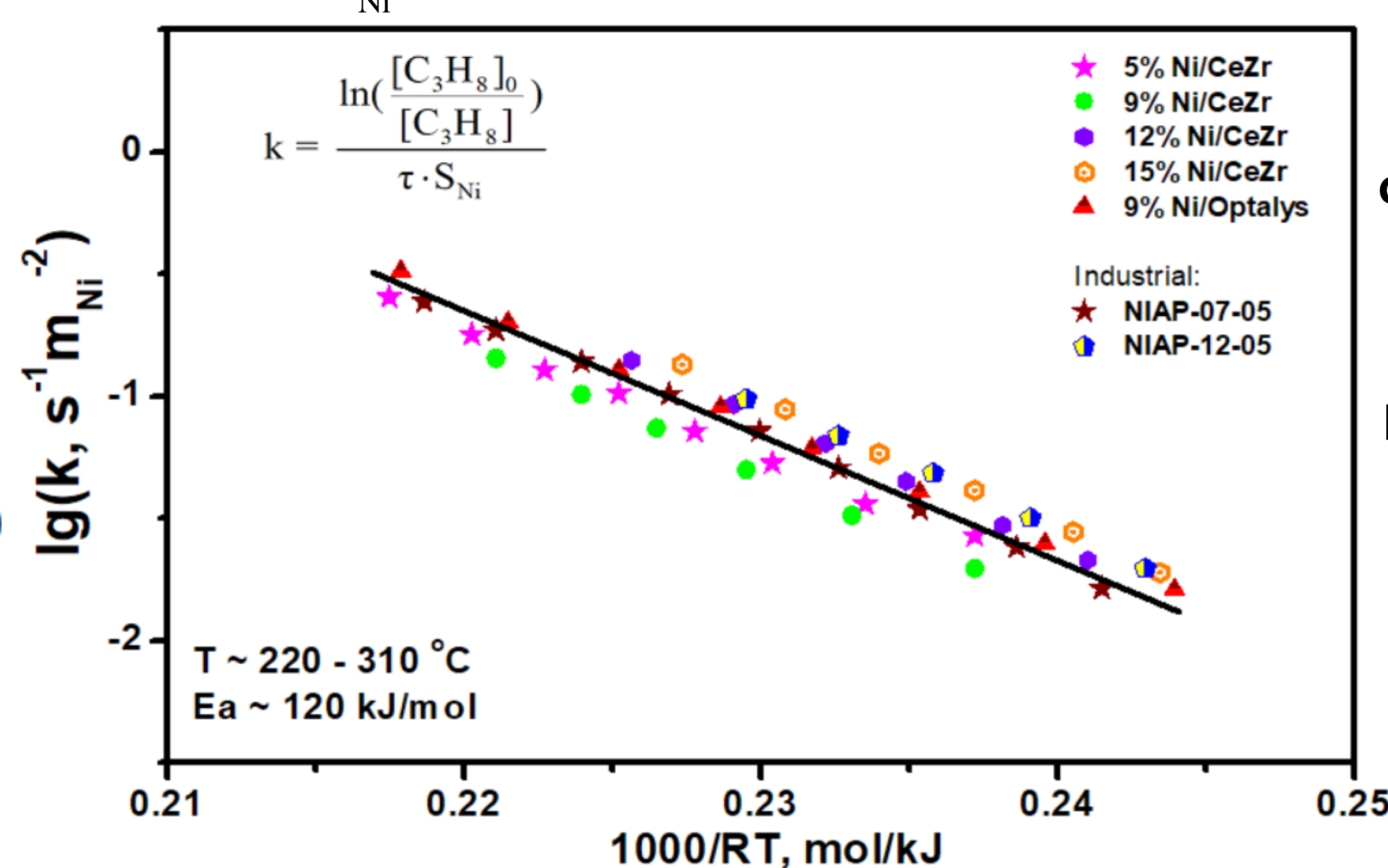


Fig. 2 Arrhenius dependences of the rate constants of propane steam reforming on various catalysts.

Experimental conditions: H₂O/C ratio = 2; [C₃H₈]⁰ = 10 vol.%, [CH₄]⁰ = 90 vol.%; WHSV = 2500 cm³·h⁻¹·g_{cat}⁻¹.

The dependences shown in Fig. 2 are linear and observed activation energies are close for all the catalysts and are about 120±15 kJ/mol. This indicates that the LTSR reaction proceeds in the same way over nickel catalysts of various compositions prepared by different methods. Thus, the activity of catalysts is determined by the specific surface area of metallic Ni.

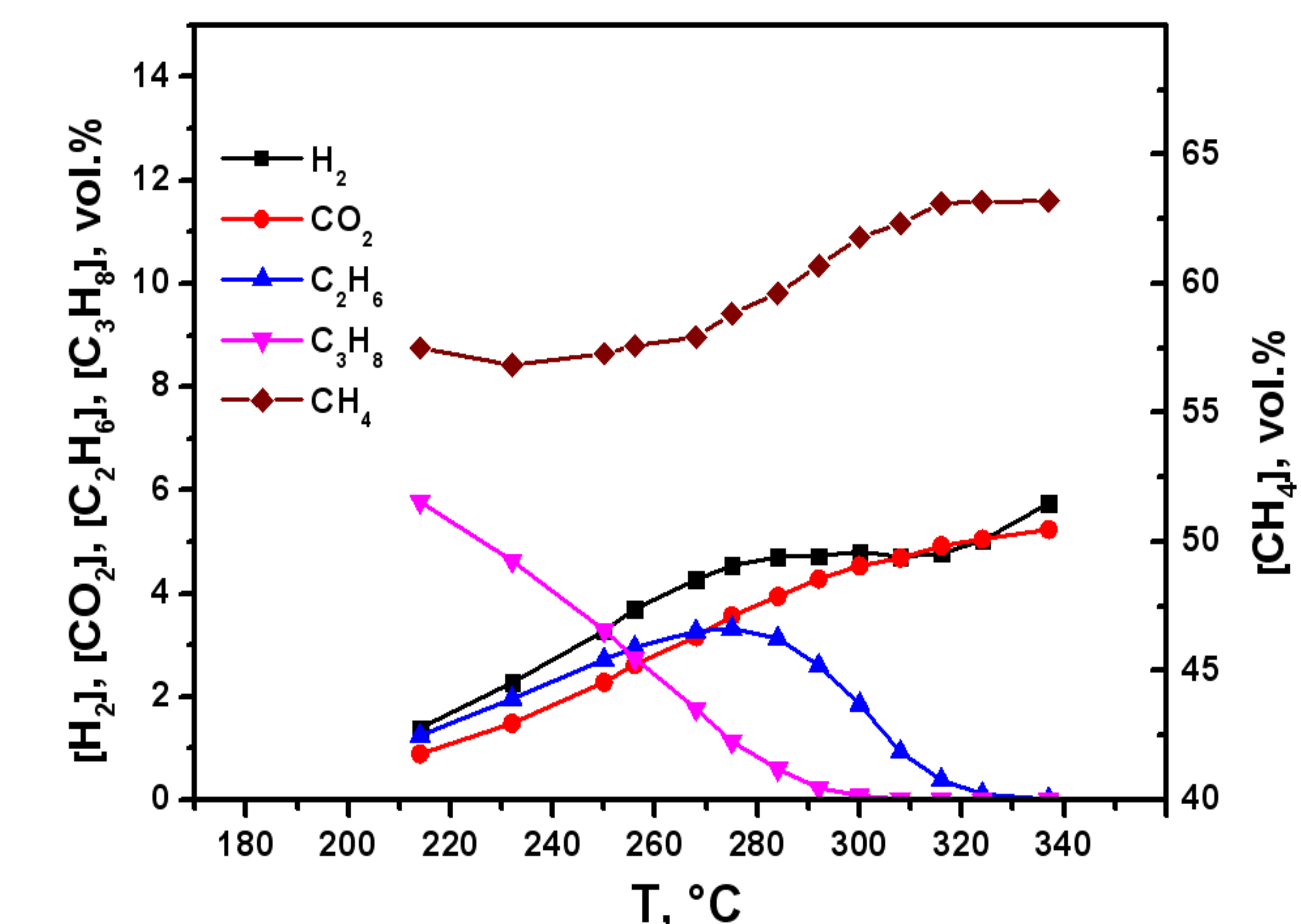


Fig. 3 Steam reforming of a propane-methane mixture. [H₂O]⁰ = 40 vol.%; [C₃H₈]⁰ = 6 vol.%, [CH₄]⁰ = 54 vol.%; WHSV = 2500 cm³·h⁻¹·g_{cat}⁻¹.

New results on LTSR over Rh/CeZr catalysts

Steam reforming of propane in excess of methane on a rhodium catalyst (1% Rh/CeZr) was also investigated (Fig. 3). The active component (Rh) was deposited by sorption-hydrolytic deposition. Complete conversion of propane is observed at 300 °C, and ethane is formed in the reaction products. The formation of ethane is observed at 200-280 °C, after which its amount decreases. Probably, a hydrogenolysis reaction occurs in the system with the formation of ethane and methane with the absorption of hydrogen formed during steam reforming. Ethane is formed as an intermediate product in the steam reforming of propane in excess of methane. This creates the prerequisites for its accumulation in the region of "intermediate" temperatures. Ethane in its calorific value is superior to methane, therefore, its formation in the fuel mixture is beneficial to compensate for the amount of CO₂ generated, which reduces the total heat of combustion of the resulting fuel. Therefore, from the point of view of useful utilization of APG into fuel gas, the study of catalysts based on rhodium is justified, since it is possible to regulate the formation of a certain amount of ethane, which can change the properties of the resulting fuel gas for the better.

Conclusions:

1. Catalysts x% Ni/Ce_{0.75}Zr_{0.25}O₂ (x ≈ 5, 9, 12, 15) and X% Ni/Optalys (X = 9, 18, 31) prepared by incipient wetness impregnation demonstrated high catalytic activity. The corresponding preparation method proved to be simple and effective. An increase in the amount of nickel on the support increases the activity of the catalyst in the steam reforming reaction. The most active catalyst of the series is 18 wt.% Ni/Optalys. This catalyst has a higher catalytic activity than industrial nickel catalysts NIAP-07-05 and NIAP-12-05 that have higher Ni content.