HYTHANE PRODUCTION VIA LOW-TEMPERATURE STEAM REFORMING OF NATURAL GAS

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Introduction

Methane-hydrogen mixtures (hythane, a pre-prepared mixture of natural gas with ~20% hydrogen) have a number of advantages compared to conventional fuels: lower toxicity of emissions by 1.5-2 times, relatively low cost, no harmful impurities, high hydrogen content which ensures complete combustion of fuel in the absence of carbon deposits and environmental friendliness. One of the most promising areas is gas turbine installations in idle modes, when full turbine power is not necessary and it is possible to use diluted mixtures with hydrogen-initiating additives as fuels. The scheme for converting an engine to hydrogen-containing fuel was considered by car manufacturers in the USA, Canada, and China, but it did not receive wide practical application due to the need to produce hydrogen, its intermediate storage and transportation to a gas station. In addition, the inability to quickly change the composition of the methane-hydrogen mixture does not allow efficient organization of the turbine's working process. Therefore it is reasonable to use methane-hydrogen mixtures (obtained from pipeline natural gas) instead of adding hydrogen gas to natural gas.

Experimental

$Ce_{0.75}Zr_{0.25}O_2$ (CeZr), 50% $Ce_{0.75}Zr_{0.25}O_2$ + 50% Al_2O_3 (CZA), and $Ce_{0.4}Zr_{0.5}Y_{0.05}La_{0.05}O_2$ (Optalys-14) were used as carriers. The catalysts were prepared by incipient wetness impregnation using $Ni(NO_3)_2$ and ethylene glycol (EG) [1]. NIAP-07-05 (36% Ni + 12% Cr_2O_3/Al_2O_3), an industrial catalyst of carbon oxides methanation and 30%Ni-20%MgO-50%Al_2O_3 prepared by the Pechini technique were chosen as reference samples.
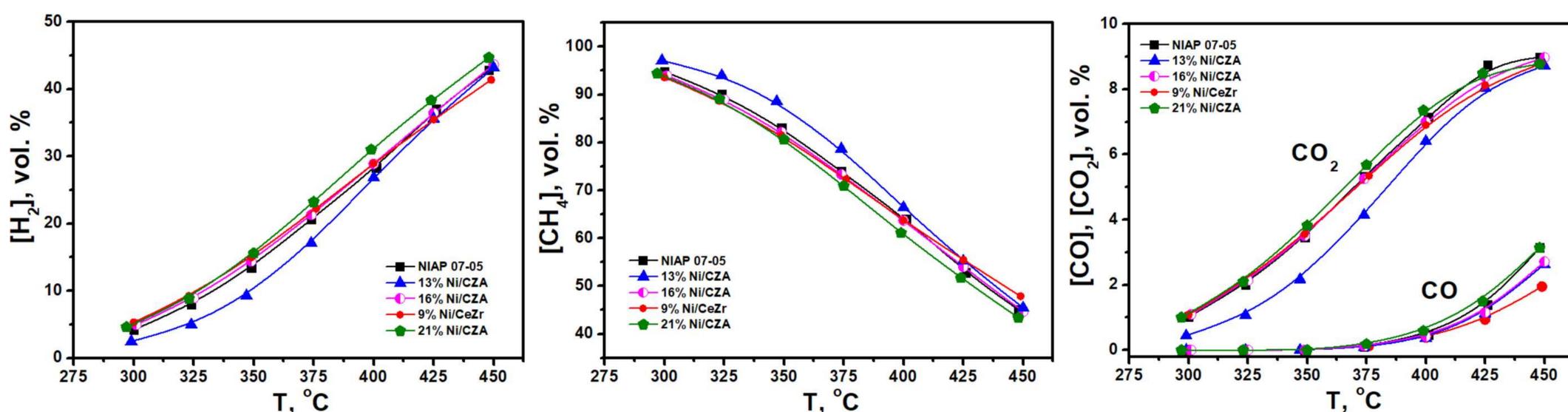
Results

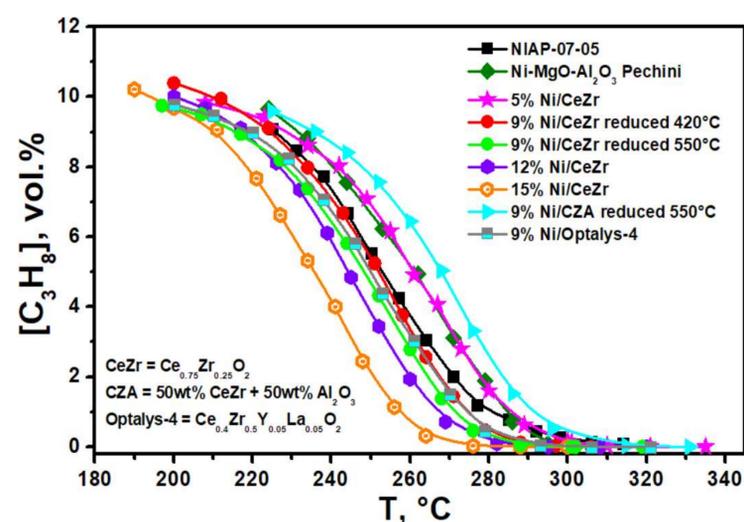**Fig. 1 Catalyst activity in methane steam reforming. H_2O/C ratio = 1. GHSV = 37600 h^{-1}.**

Fig. 2 Steam reforming of a propane-methane mixture.
$[C_3H_8]$ = 10 vol.%, $[CH_4]$ = 90 vol.%, H_2O/C ratio = 2.
WHSV = 2500 $cm^3/(h \cdot g_{cat})$.

The kinetics of propane steam reforming was proved to be first order with respect to propane and approximately zero order with respect to the H_2O, CO_2, H_2 etc. Therefore we can estimate the rate constant of the process and normalize it to the area of metallic nickel:

$$k = \frac{\ln\left(\dfrac{[C_3H_8]_0}{[C_3H_8]}\right)}{\tau \cdot S_{Ni}}$$

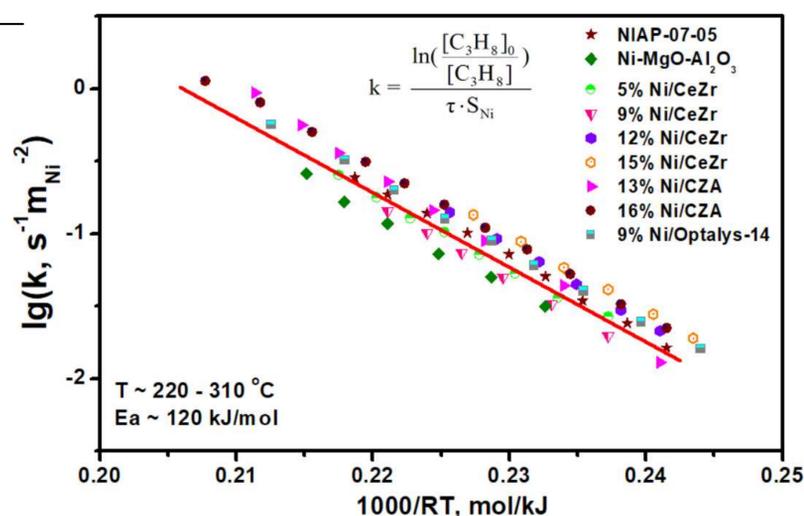The value of k allows us to conclude about the specific catalytic activity of the samples per m^2 of metallic Ni.

Fig. 3 Arrhenius dependences of the rate constants of propane steam reforming on various catalysts. Experimental conditions: $[C_3H_8]$ = 10 vol.%, $[CH_4]$ = 90 vol.%, H_2O/C ratio = 2. WHSV = 2500 $cm^3 \cdot h^{-1} \cdot g_{cat}^{-1}$.

The dependences shown in Fig. 3 are linear which means the catalytic process can be described by the first-order kinetics. The observed activation energies are close for all the catalysts and are about to 120±15 kJ/mol. Thus, the LTSR of propane in methane excess proceeds in the same way over nickel catalysts of various compositions prepared by different methods. Thus, the specific catalytic activity of nickel catalysts in low-temperature steam reforming of C_{2+}-hydrocarbons does not directly depend on the catalyst composition and preparation method. The activity of catalysts is determined by the specific surface area of metallic nickel.

Conclusions

1. Catalysts x% $Ni/Ce_{0.75}Zr_{0.25}O_2$ (x ≈ 5, 9, 12, 15) prepared by incipient wetness impregnation using an aqueous glycolic solution of nickel nitrate demonstrate high catalytic activity. The corresponding preparation method proved to be simple and effective.
2. An increase in the amount of nickel on the support increases the activity of the catalyst in the steam reforming reaction.
3. The most active catalyst of the series is a catalyst with a nickel content of 15 wt.%. This catalyst has a higher catalytic activity than the industrial nickel catalyst NIAP-07-05, containing 36 wt.% Ni.

[1] D.I. Potemkin et.al, Catalysis Today, 2020, doi.org/10.1016/j.cattod.2020.06.070