

We approve this approach in 4-CP electro degradation in acidic solutions on anodes Pt/Ti with 15 wt.% (control) and 38 wt.% of Pt. Date of table 3 and 4-CP dimer image are shown above.

Conclusions

The activity of IrO₂ and SnO₂ covered Ti anodes towards 3-CP and 4-CP degradation is higher than Pt/Ti activity. In spectral electrolysis analysis long-wave band $\lambda=293$ nm should be used. Electrolysis involves CPs dimmers. It is possible to substitute routine spectral control or more complex GC analysis by CV method in monitoring of CPs degradation during electrolysis.

References

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SYNGAS PRODUCTION BY CO₂ REFORMING OF CH₄ OVER Ni-CONTAINING XEROGEL Al₂O₃-ZrO₂(Yb₂O₃) WITH POLYVINYLPIRROLIDON

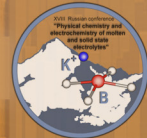
N.E. Vakhrushev, Z.V. Murga, I.I. Mikhailenko

*Peoples' Friendship University of Russia (RUDN University), Moscow, Russia
corresponding_author@e-mail.com*

Abstract

The dry reforming of methane (DRM) reaction $\text{CO}_2 + \text{CH}_4 \leftrightarrow 2\text{CO} + 2\text{H}_2$ shows great potential in conversion two greenhouse gases into high-purity syngas as feedstock for synthesis of higher hydrocarbons and oxygenates (Fischer-Tropsch process). Ni-based supported alumina or silica systems are good cost-effective catalysts but their practical applications restrict high temperatures of reaction that leads to catalyst deactivation by carbon deposits, sintering, phase transformation.

In our study supported 5% wt. Ni catalysts with hybrid mixed oxides support Ni/AZ(Yb)PVP (sol-gel technique with polymer addition) were prepared and tested in DRM reaction in compare with Ni/Al₂O₃. Catalysts were examined using BET XRD, XPS, ESR, SEM, TEM methods. and «worked» DRM tests were performed at atmospheric pressure in U-shape quartz reactor (flow rate of 20 ml/min, molar ratio CO₂-CH₄, gas chromatograph Crystal-2000 on line, Ar gas carrier). For only calcinated Ni/AZ(Yb)PVP samples catalytic tests were with heating-cooling 723 → 1023 → 723 K cycles. The



different type of temperature hysteresis ("clockwise" for CH_4 and «anti-clockwise» for CO_2) with different apparent activation energy of product's formation was found. In reducing Ni^{+2} *in situ* by DRM reaction products we can obtain active and stable to carbon formation surface for Ni catalyst with composite support. For stationary activity molar ratio $\text{H}_2/\text{CO} \sim 1$ in heating mode, but $\text{H}_2/\text{CO} < 1$ when 5%Ni/AZ(Yb)PVP catalyst is cooling. Increasing Ni loading doesn't augment sufficiently the values of CO_2 and CH_4 conversion or CO , H_2 yields.

Keywords: dry reforming, nickel catalyst, alumina-zirconia-ytterbia support, sol-gel, polymer.

Introduction

One of the problems for nickel catalysts application in industry for DRM reaction is connected with catalyst deactivation and carbon deposition leading to loss of active-metal surface. Not only graphite-like, but a carbon nanotubes (CNTs) readily form during the reaction. The presence of specially introduced CNTs in Ni/silica by using catalytic chemical vapor deposition technique was found to enhance the catalyst activity and stability [1]. In our previous work [2] the different forms of "catalytic" carbon (nanotubes, octacarbon-C8 and grafite-3R,C, carbon fiber) were determined for 5%Ni/ Al_2O_3 with alumina specific area $105 \text{ m}^2/\text{g}$ and dispersed NiO phase formed after calcinations procedure. Catalyst's characterization by BET, SEM-EDS, XRD, XPS methods shown the redispersion and partial recrystallization of alumina (Al_2O_3 crystallite size 71 nm and 44 nm before and after 18 h of catalysis). For fresh, non reduced catalyst with low activity the auto-oscillations were observed for CO_2 and CH_4 content at reaction temperature 673 K.

The focus of this study is the compare the activities in DRM reaction of unreduced nickel catalyst supported on Al_2O_3 and composite $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{YbO}_2)$ with molar ratio $\text{Al}_2\text{O}_3:\text{ZrO}_2=1:1$ and doping by ytterbia as stabilizer of t- ZrO_2 and by porous regulating agent PVP.

Experimental

The catalysts 5%wt.Ni/ Al_2O_3 (reference sample) and 5%wt.Ni/ $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{YbO}_2)$ PVP /Ni/AZ(Yb)PVP/ were prepared by impregnation method using precursor $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The catalytic performance was done in U-shaped quartz reactor with catalyst loading 135 mg (feed gas mixture CH_4+CO_2 of molar ratio $\text{CH}_4/\text{CO}_2=1$ in flow 20 mL/min) under atmospheric pressure at temperatures of 723–1023 K. Methane, H_2 , CO_2 and CO were analyzed by a GC Crystal 2000 (Porapak-Q column, TCD, Ar). In order to examine the active Ni/CNTs fragments formation we exposed non reduced Ni/AZ(Yb)PVP catalyst by heating and cooling in reaction media.

Results and discussion

After hydrothermal treatment or training in mixture of CH_4+CO_2 (no DRM reaction occurred) good initial morphology of Al_2O_3 with clear faces and ribs (Fig.1) was broken. The H_2/CO molar ration in reaction over $\text{H}_2\text{-}$

reduced 5%wt.Ni/Al₂O₃ with stationary activity showed the values less than 1 (Fig.2) that increased with temperature rise from 0.7 to 0.83.

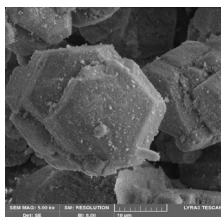


Figure 1. SEM image of Al₂O₃ grain

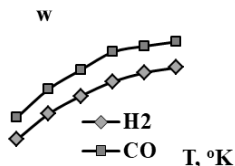


Figure 2. The temperature dependence of the rate (w in mole·g⁻¹·h⁻¹) of products formation over 5%/Ni/Al₂O₃

Apparent activation energies of H₂ and CO formation were lower for H₂-reduced catalyst, but deposition of carbon inactive form increased E_a value (table). One example of TEM images for CNTs with incorporated Ni particles, formed in DRM reaction with 5%/Ni/Al₂O₃ catalyst is shown in Fig 3. Two types of CNTs are known with corresponding peaks on TGA curves: less stable CNTs decompose in the temperature range 673–813 K and highly stable in 813–1023 K. Non reduced in H₂ treatment 5%/Ni/AZ(Yb)PVP catalyst (sample 4) showed low activity with E_a values 134 and 68 kJ/mole for H₂ and CO formation respectively. After 5 h of catalytic training in methane reforming the active metallic Ni sites appeared and E_a value dropped up to 32 kJ mol⁻¹. So, H₂ and CO may be involved in reduction Ni⁺² to Ni⁰ species with Ni⁰ stabilization by CNTs formed in DRM accompanied reactions CH₄→C+2H₂ at high temperatures or 2CO→ C+CO₂ at low temperatures. In case of 10%/Ni/AZ(Yb)PVP (sample 6) the value E_a CO increased in two times.

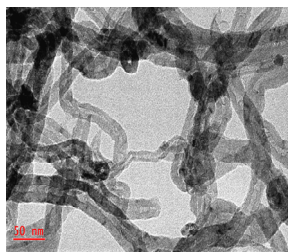


Figure 3. Formation of CNTs in DRM reaction

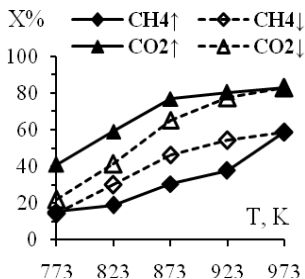
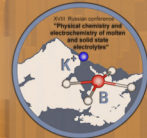


Figure 4. CO₂ and CH₄ conversion over 5%/Ni/AZ(Yb)PVP catalyst



For active sample 5 with high CH₄ and CO₂ conversions we observed hysteresis effect of different type for CO₂ and CH₄ in slow made heating-cooling cycle (Fig. 4).

Apparent activation energy of DRM reaction products formation over supported nickel catalysts;

1 – unreduced, 2 – reduced in H₂ flow, 623, 2 h, 3 – carbonized sample 2 (18 h DRM tests),

4 – unreduced, 5,5*,6 – reduced by CH₄ reforming products in heating (5) and cooling (5*) cycle

Catalyst	5%/Ni/Al ₂ O ₃			5%Ni/AZ(Yb)PVP			10%Ni/AZ(Yb)PVP
Sample number	1	2	3	4	5	5*	6
Ea H ₂ kJ mol ⁻¹	53	35	57	134	32	52	56
Ea CO kJ mol ⁻¹	41	29	47	68	32	26	54

Conclusions

Unreduced Ni/AZ(Yb)PVP was applied in DRM and showed the auto activation by reaction products with thermal hysteresis effect. Activation energies of products formation were obtained.

References

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PHYSICOCHEMICAL PROPERTIES OF THE DISPERSE SYSTEM MgO / (Li₂CO₃-Na₂CO₃-K₂CO₃)_{eut} PROMISING FOR MCFC

I.D. Zakiryanova*, E.V. Nikolaeva, I.V. Korzun

Institute of High-Temperature Electrochemistry, Yekaterinburg, Russia

** e-mail address: optica96@ihte.uran.ru*

The study of the physicochemical properties of high-temperature disperse systems based on molten alkali metal carbonates is necessary to search for optimal working environments for carbonate fuel cells (MCFC).