Supplementary materials

1. **Calculation of efficient first-order rate constants of catalytic reactions and turn-over frequency TOF).**

Efficient first-order rate constant was calculated using the integral equation

$$k_{eff} = -\frac{\ln(1 - X_{CH_4})}{\tau} \quad ,$$

where X is degree of reagent (methane, ethanol) conversion at contact time τ (s)

Turnover frequency (TOF) is defined as the maximum number of chemical conversions of substrate molecules per unit time over a single catalytic site.

TOF was calculated as ratio of the initial reaction rate W_0 (mole s^{-1}) (being equal to $k_{eff.}$ *C^o) to the content of metal sites Z estimated by CO chemisorption (mol/g$_{cat}$) and catalyst bulk density ρ (g/l)

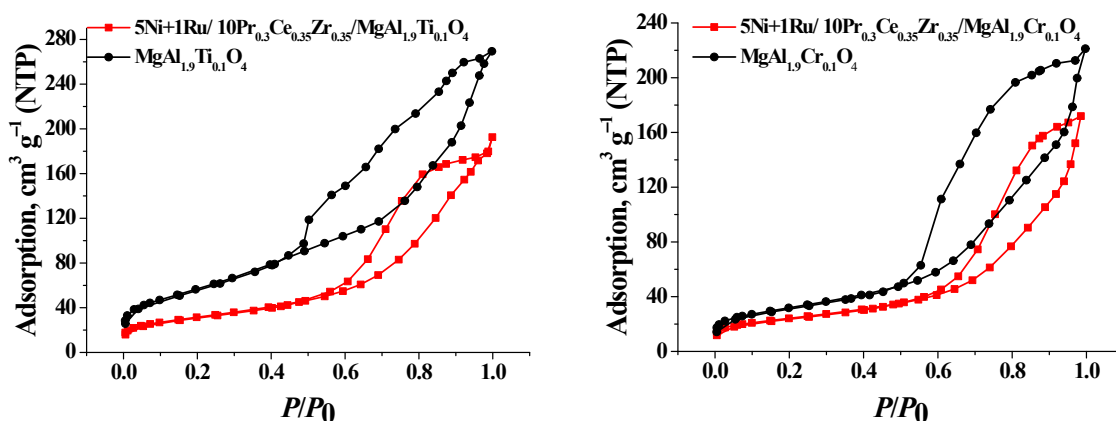$$TOF = \frac{k_{eff} \cdot C_{CH4}^0}{Z \cdot \rho}$$

2. **Texture**

Figure S1. Adsorption-desorption isotherms for doped MgAl$_2$O$_4$ mesoporous support and series 2 Ti2 and Cr2 catalysts

3. **XPS spectra**

In Figures S2-S5 1, 2, and 3 spectra correspond to 5%Ni+1%Ru/10%Pr$_{0.3}$Ce$_{0.35}$Zr$_{0.35}$/ MgAl$_{1.9}$Fe$_{0.1}$O$_4$ (Fe1), 5%Ni+1%Ru/10%Pr$_{0.3}$Ce$_{0.35}$Zr$_{0.35}$/MgAl$_{1.9}$Ti$_{0.1}$O$_4$ (Ti1) , and 5%Ni+1%Ru/10%Pr$_{0.3}$Ce$_{0.35}$Zr$_{0.35}$/MgAl$_{1.9}$Cr$_{0.1}$O$_4$ (Cr1) catalysts, respectively.
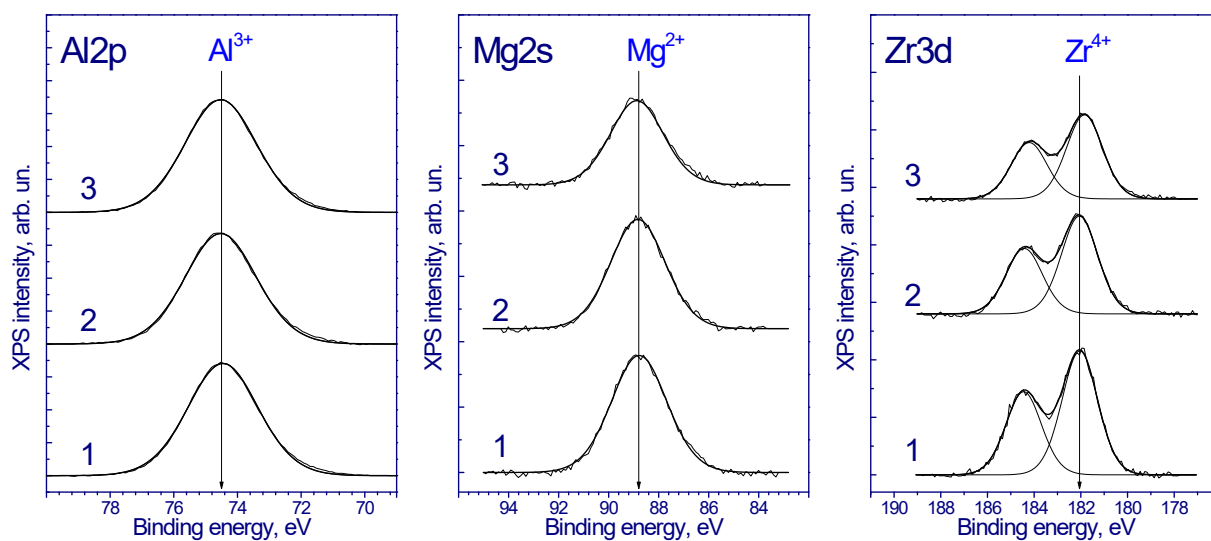
Figure S2. Al2p, Mg2s and Zr3d core-level spectra of the catalysts. The spectra are normalized on the total concentration of Al and Mg.
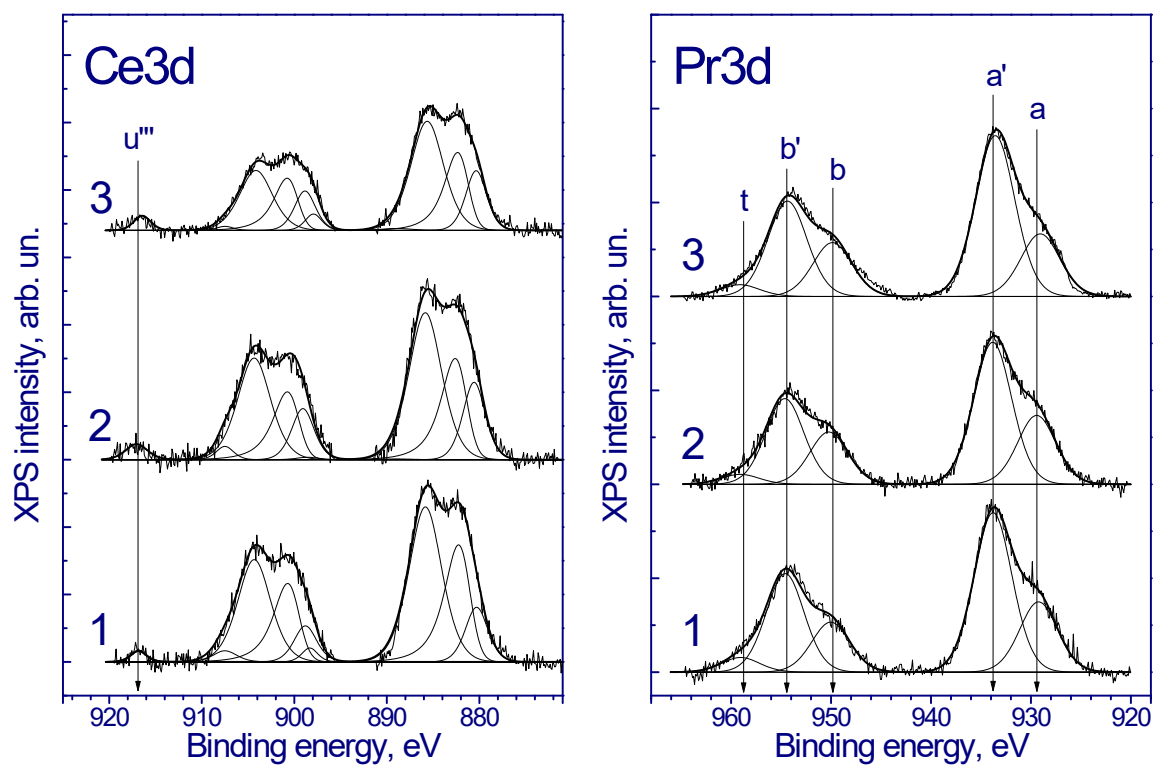

Figure S3. Ce3d and Pr3d core-level spectra of the catalysts. The spectra are normalized to the total concentration of Al and Mg.
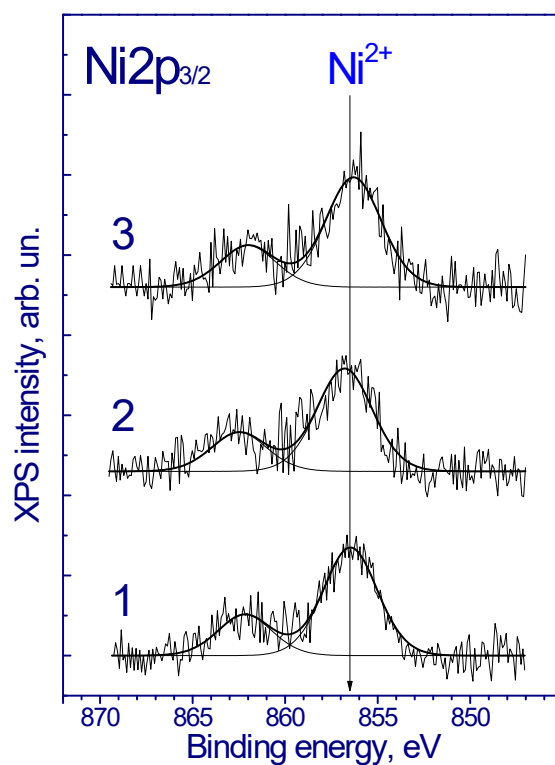
Figure S4. $Ni2p_{3/2}$ core-level spectra of the catalysts. The spectra are normalized to the total concentration of Al and Mg.
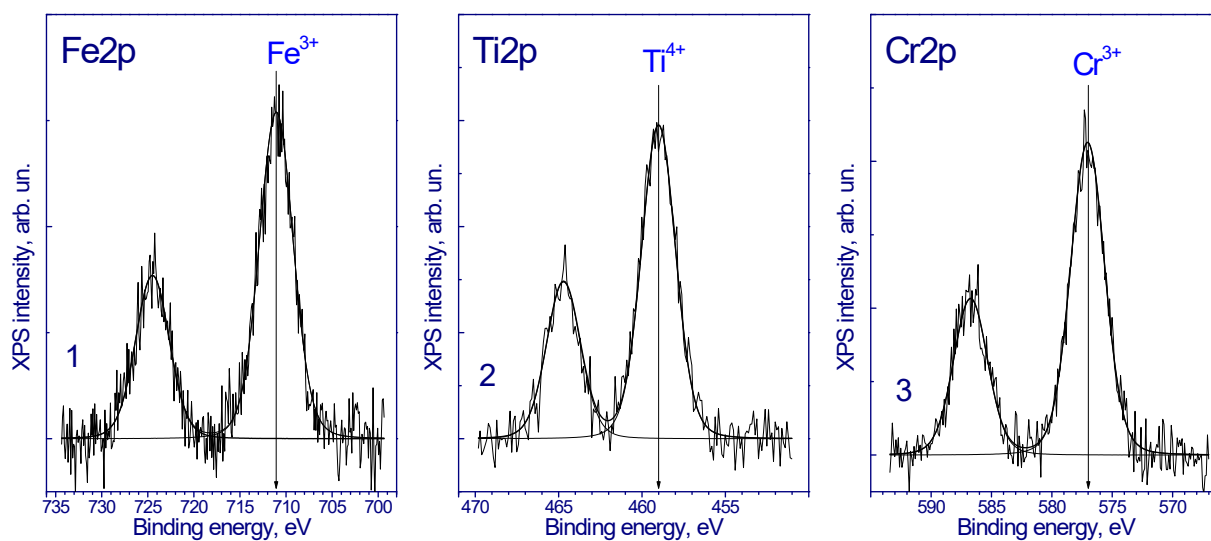

Figure S5. Fe2p, Ti2p, and Cr2p core-level spectra of the catalysts. The spectra are normalized to the total concentration of Al and Mg.
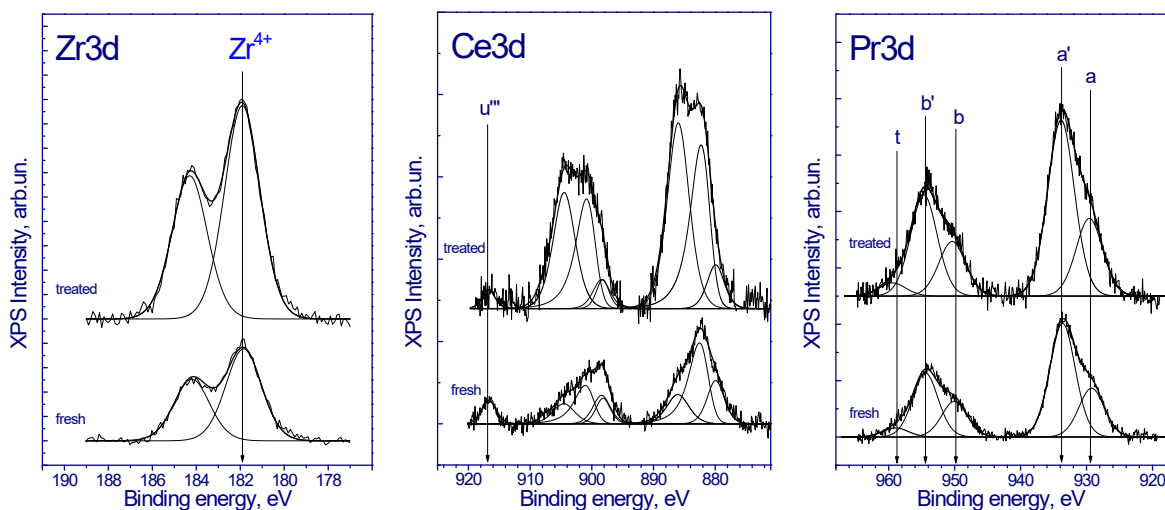
Figure S6. Zr 3d, Ce 3d and Pr3d core-level spectra of the Cr2 catalyst in fresh and treated states. The spectra are normalized to the total concentration of Al and Mg.
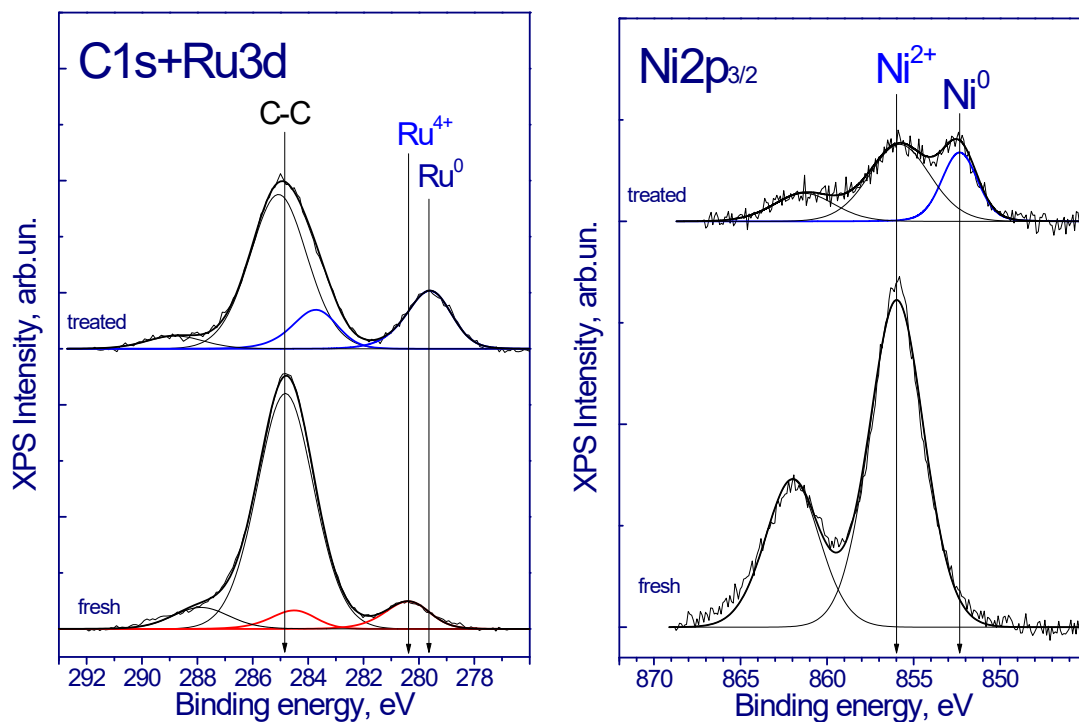

Figure S7. Ru 3d and Ni2p$_{3/2}$ core-level spectra of the Cr2 catalyst in fresh and treated states. The spectra are normalized to the total concentration of Al and Mg.

Pr*3d* spectra have a complex shape, since, first, due to spin-orbital interaction 3d-level is splitted on two sublevels Pr*3d$_{5/2}$* и Pr*3d$_{3/2}$*, which results in appearance of a doublet with the ratio of intensity lines as 3:2; second, each component of the doublet is splitted into three lines – a/b, a'b', a''/b'' and t (additional peak in spectrum of Pr*3d$_{3/2}$*) [Borchert, H., Frolova, Y.V., Kaichev, V.V., Prosvirin, I.P., Alikina, G.M., Lukashevich, A.I., Zaikovskii, V.I., Moroz, E.M., Trukhan, S.N., Ivanov, V.P., Paukshtis, E.A., Bukhtiyarov, V.I., Sadykov, V.A., J. Phys. Chem. B **2005**, 109, 5728-5738]. In

spectrum of pure Pr_2O_3 where Pr is in 3+ state a''/b'' doublet is not observed. In Pr$3d$ spectra (Figs. S3 and S7) doublet a''/b'' is absent, hence, Pr is mainly in Pr^{3+} state.

Table S1. Binding energies and states of metals in fresh and treated R2 catalysts

Sample	Zr3d$_{5/2}$	Ce3d$_{5/2}$ (u''')	Ni2p$_{3/2}$		Ru3d$_{5/2}$		Pr3d$_{5/2}$	Al2p	Mg2s
	Zr^{4+}		Ni^0	Ni^{2+}	Ru^0	Ru^{4+}	Pr^{3+}	Al^{3+}	Mg^{2+}
Fresh	181.8	916.6	–	856.1	–	280.3	929.3 933.7	74.5	88.8
Treated	181.9	916.7	852.6 (28%)	855.8 (72%)	279.5	–	929.6 933.9	74.5	88.8

Table S2. Surface concentration of elements normalized on the total concentration of Al+Mg and Mg/Al ratio determined by XPS in fresh and treated R2 catalysts

Sample	[C]	[O]	[Mg]/[Al]
Fresh	1.40	2.55	0.47
Treated	0.90	2.30	0.41

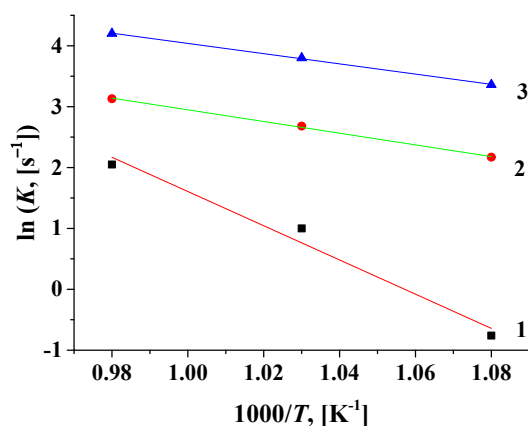## 4. Methane dry reforming

Fig. S8. Arrhenius plots of efficient first-order rate constants of methane dry reforming for series one catalysts: 1-Fe1, 2-Ti1, 3-Cr1. Feed 15%CH_4 + 15% CO_2 in He, contact time 15 ms.
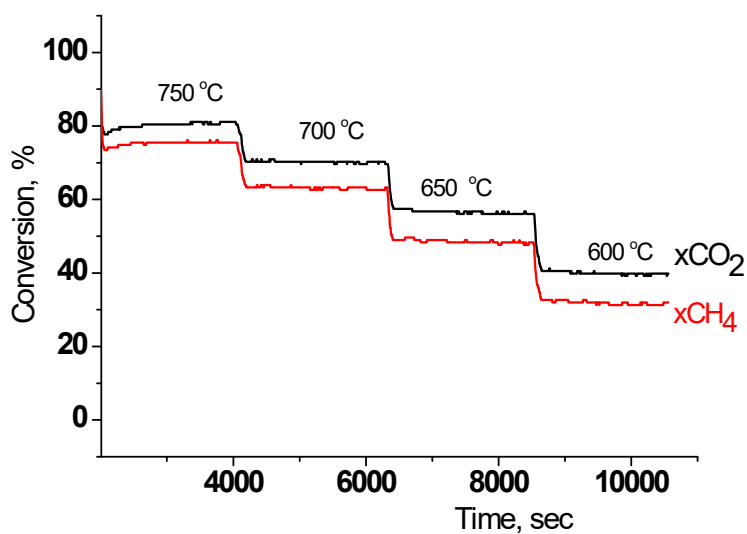
Fig. S9. Cr2 catalyst performance stability in the temperature range 750-600 °C. Feed 15 vol. % CH_4 +15 vol. % CO_2+ He balance, contact time 0.015 s

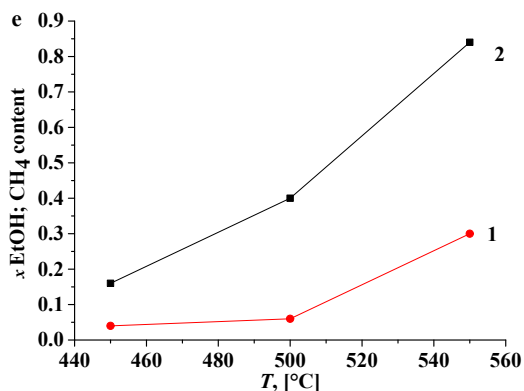## 5. Steam reforming of ethanol

Fig. S10. Temperature dependence of CH_4 content (1, %) and EtOH conversion (2, degree) in the low-temperature range 450-550 °C for   Cr2 catalyst. Feed 2% EtOH +8% H_2O in He, contact time 8 ms.
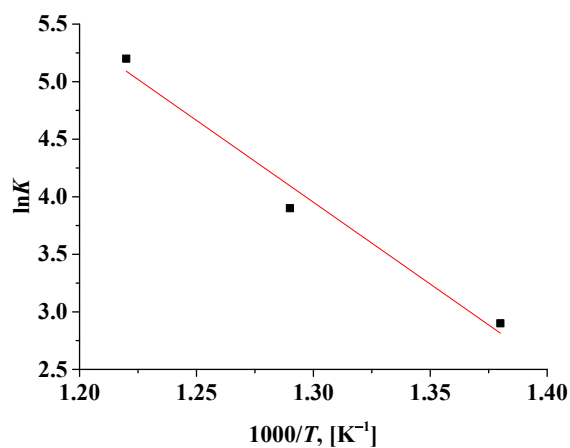
Fig. S11. Arrhenius plots of the efficient first-order rate constants of ethanol steam reforming on Cr2 catalyst. Feed 2% EtOH +8% H_2O in He, contact time 8 ms.
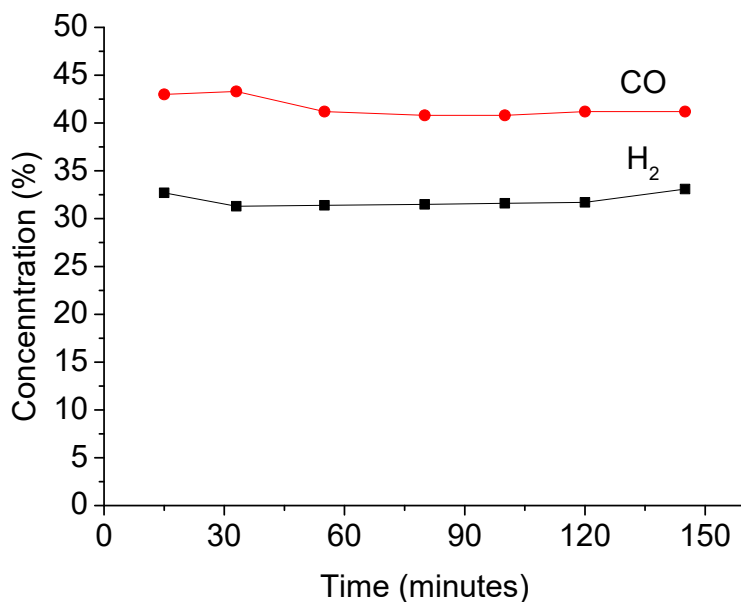
5. Stability of structured catalyst performance

Fig. S12. Stability of structured catalyst performance in natural gas (NG) dry reforming. Feed 42% NG+51% CO_2+N_2, 700 °C, contact time 1.22 s.
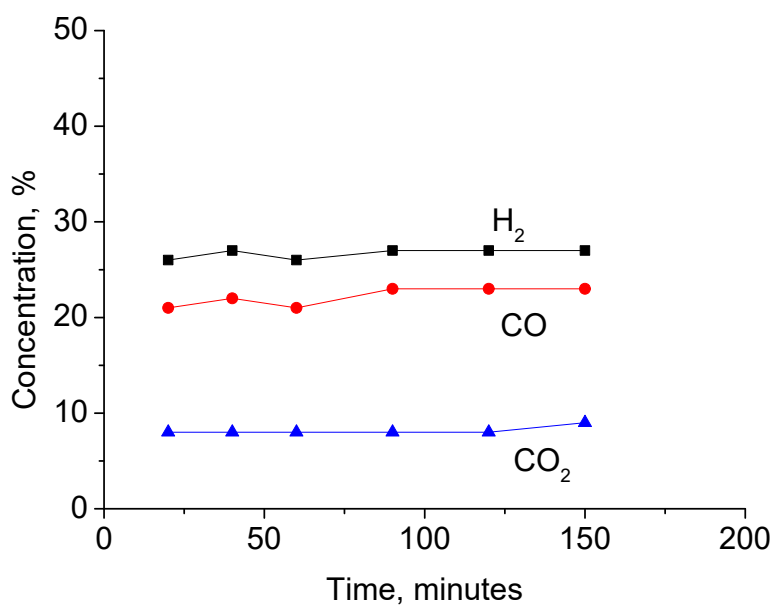

Fig. S13. Stability of structured catalyst performance in ethanol dry reforming. Feed 22% EtOH +21% CO_2 +N_2, 780 °C, contact time 0.33 s.

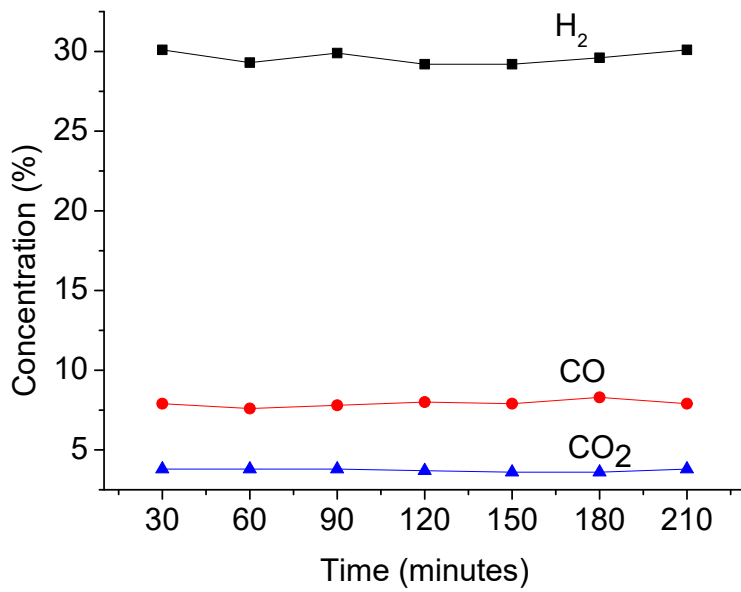**Fig. S14** . Stability of structured catalyst performance in ethanol steam reforming. Feed 10.3% EtOH+40.7%H_2O+N_2, 710 ℃, contact time 0.23 s
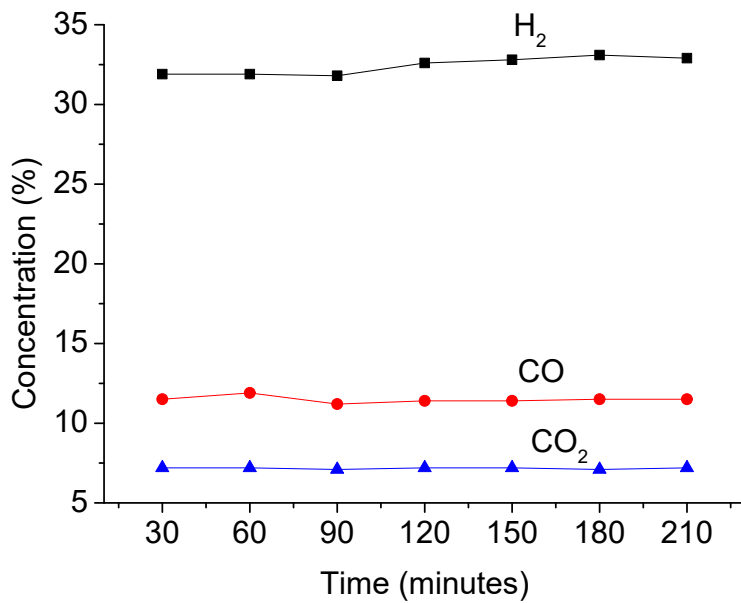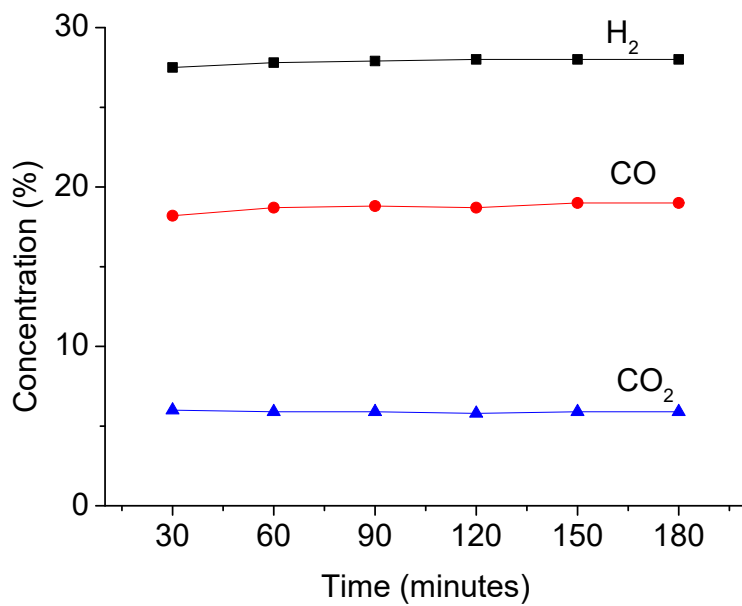

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Fig. S15. Stability of structured catalyst performance in ethanol oxysteam reforming. Feed 12.4%EtOH+ 49%H_2O+ 8.1%O_2+N_2, 760 ℃, contact time 0.25 s

d

Fig. S16. . Stability of structured catalyst performance in ethanol mixed steam-dry reforming. Feed 20 % EtOH +11.5% CO_2+7.4%H_2O +N_2 , 750 °C, contact time 0.35 s