Methane reforming to hydrogen over supported catalysts

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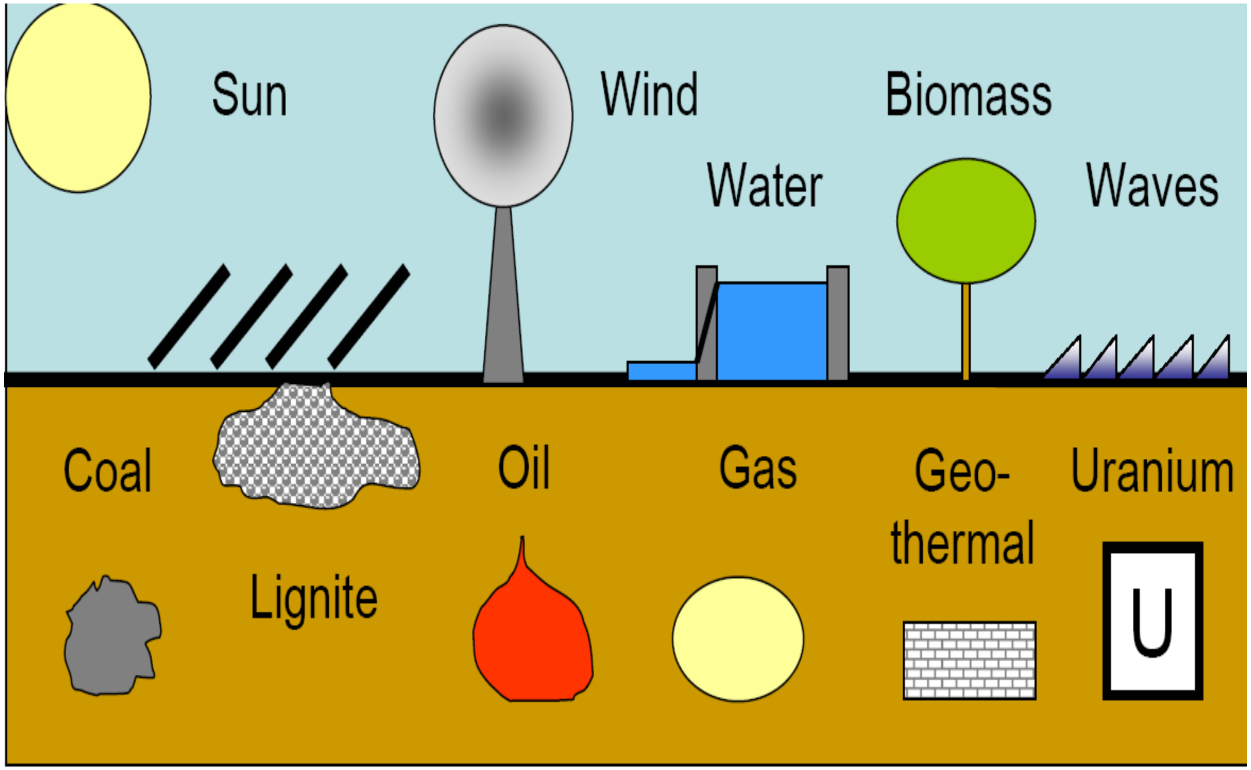
Feedstock for energy production



← *Above ground*

← *Under ground*

Advantages and disadvantages of different energy sources

Energy sources	Cost (€/MWh) 2005- 2030	GHG emissions (kgCO$_2$eq/MWh	EU-27 Import dependency 2005 - 2030	Environmental/ damage estimate (billion $)
Nat. gas	45 - 70	*440*	57 - 84%	867
Oil	80 - 95	*550*	*82 - 93%*	*1853*
Coal	35 - 45	*800*	39 - 59%	1625
Nuclear	40 - 45	15	100% for U	-
Biomass	25 - 85	30	-	-
Wind	50 -170	10	-	-
Hydro	25 - 90	20	-	-
Solar	140-430	25	-	-

Hydrogen - fuel of the future

Hydrogen has the potential to solve two major challenges:

- to reduce the dependence on imported petroleum
- to reduce the pollution and greenhouse gas emissions

- Hydrogen in fuel cells:
  - extremely clean as the only byproduct is water
- Currently H_2 is mainly produced from fossil fuel (natural gas)
- It is desirable to incorporate renewable resource for its generation to support sustainable energy development

The development of clean, sustainable, and cost-competitive hydrogen production processes is the ***key*** to a viable ***future hydrogen economy***

Key drivers affecting renewable energy economy

- The fossil fuels, which meet the most of the world's energy demand today, will begin deplete fast in the near future

- Global population and economic growth, and the need for new clean energy supplies at affordable prices

- Global climate change and the need to reduce greenhouse gas emissions and pollutions

- Reducing dependence on imported fuels, stopping global warming and climate change, doing more with a lower consumption of energy, identifying new technologies and developing renewable energy sources

Biomass – the major renewable energy resource

- Biomass is an attractive petroleum alternative because it is a renewable energy resource, ensuring a sustainable energy supply and reducing GHG emissions

- Two-third of the total energy produced from renewable resources in Europe comes from biomass

- Biomass is an abundant domestic resource for many countries

- Biomass can be oriented to obtain ethanol, methane and/or biogas, as CH_4 and CO_2 are the main components of the biogas composition.

Catalytic processes for CH_4 conversion

Steam reforming:

$CH_4 + H_2O \rightarrow CO + 3H_2$

$CO + H_2O \Leftrightarrow CO + H_2$ **WGSR**

Partial oxidation:

$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$

Dry reforming (biogas reforming):

$CH_4 + CO_2 \rightarrow CO + 2H_2$

$CO + H_2O \Leftrightarrow CO + H_2$ **WGSR**

Autothermal reforming:

$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$

$CH_4 + H_2O \rightarrow CO + 3H_2$

$CO + H_2O \Leftrightarrow CO + H_2$ **WGSR**

Carbon deposition:

$2CO \rightarrow CO_2 + C$ and $CH_4 \Leftrightarrow 2H_2 + C(s)$

Employed catalytic materials for methane reforming

Carriers: Al_2O_3, CeO_2, ZrO_2, CeO_2-Al_2O_3, CeO_2-ZrO_2, CeO_2-La_2O_3-Al_2O_3, Pr_2O_3-Al_2O_3, zeolites – NaY, USY, ZSM-5

Supported noble metal catalysts: Rh, Ru, Pt, Pd

Advantages:

- high conversion
- high carbon resistant

Disadvantages:

- high cost
- limited availability

Supported Ni catalysts – the most widely used catalysts

Advantages:

- low cost
- high conversion
- wide availability

Disadvantages:

- quick deactivation at high T_{reac} due to: (i) Ni sintering and (ii) coke formation

CeO_2 – promoted catalysts

Suppression of coke deposition

The unique properties of CeO_2:

- High reducibility
- Oxygen mobility
- High oxygen storage capacity due to the redox couple Ce^{3+}/Ce^{4+}
- The main problem of ceria is the decrease of its surface area at high thermal treatment and in reductive atmosphere – loss of OSC
- The dopant cations with ionic radius and electronegativity close to that of ceria are good modifiers of the structure and electronic properties of ceria
- Doped CeO_2 with divalent or trivalent cations can generate oxygen vacancies and to increase the mobility of oxygen species that results in high OSC of CeO_2.

Pt/CeO_2-La_2O_3-Al_2O_3 catalysts for steam reforming and partial oxidation of methane

Subject: To study the effect of the support kind on the structure, electronic and catalytic properties of Pt/CeO_2-La_2O_3 catalyst for steam methane reforming and partial oxidation of methane

Preparation

Carriers:

$CeO_2(x)$-$La_2O_3(1-x)$-Al_2O_3 oxides

Sol-gel method:

Solutions of $Ce(NO_3)_3.6H_2O$, $La(NO_3)_3.6H_2O$, $Al(OC_4H_9)_3$

Drying and calcination of xerogels at r.t and at 1223 K fo 6 h, respectively

Total metal content - 12 wt%

Pt/CeO_2-La_2O_3-Al_2O_3 catalysts:

Impregnation method:

Solution of H_2PtCl_6 (40%)

Drying at 383 K for 12 h

Calcination at 773 K for 4 h under synthetic air

Pt content - 1 wt%.

Methods for characterization

- N_2 adsorption-desorption isotherms
- X-ray diffraction (XRD)
- UVvis diffuse reflectance spectroscopy (DRS)
- *In-situ* temperature-resolved X-ray absorption near structure (XANES)
- Fourier transformed infrared spectroscopy (FTIR) of CO adsorbed
- Temperature programmed reduction (TPR)
- TGA/TD analysis
- High resolution transmission electron microscopy (HRTEM)
- Cyclohexane dehydrogenation reaction for metal dispersion evaluation

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Steam methane reforming and partial oxidation of methane

Steam methane reformig reaction (SMR):

$T_{reaction}$ = 693^0-783 K; reaction mixure: CH_4:H_2O:H_2 ratio of 1:3:0.5; total flow rate of 100 ml

Partial oxidation of methane (POM):

$T_{reaction}$ = 800 ^oC; CH_4:O_2:N_2 = 2:1:0.9, Flow rate=130 ml/min

Before reaction the catalysts were reduced in situ at 773 K for 1h in 10% H_2/N_2 flow (50 ml/min)

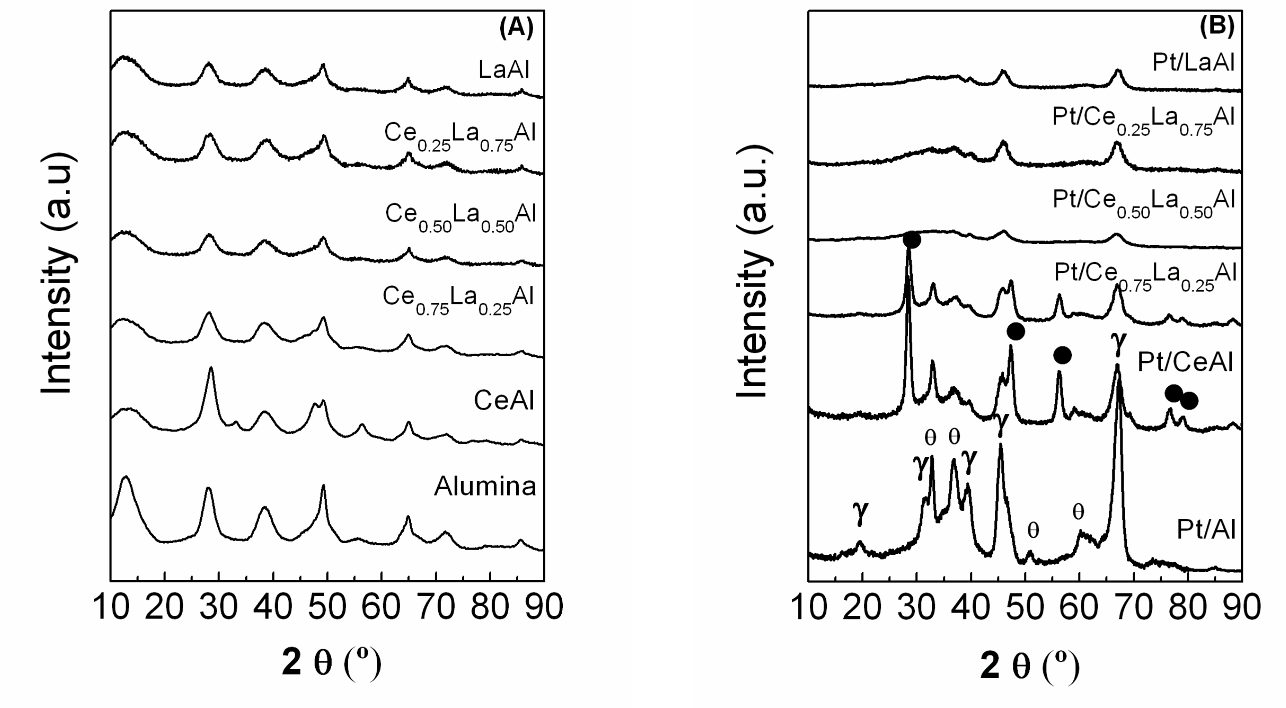
Textural properties of mixed oxides and Pt/CeO_2-La_2O_3-Al_2O_3 catalysts

Samples	S_{BET} m^2/g	V_{pore} cm^3/g	D_{pore} nm	D_{AlOOH} nm
Alumina	182	0.28	6.1	2.2
Mixed oxides				
CeAl	156	0.20	4.6	1.6
$Ce_{0.75}La_{0.25}Al$	95	0.16	6.2	1.5
$Ce_{0.50}La_{0.50}Al$	124	0.18	4.9	1.5
$Ce_{0.25}La_{0.75}Al$	90	0.13	5.3	1.4
LaAl	104	0.12	5.2	1.6
Catalysts				
Pt/Al	179	0.30	5.7	-
Pt/CeAl	135	0.17	4.3	-
Pt/$Ce_{0.75}La_{0.25}Al$	92	0.16	6.1	-
Pt/$Ce_{0.50}La_{0.50}Al$	118	0.17	5.0	-
Pt/$Ce_{0.25}La_{0.75}Al$	102	0.14	5.0	-
Pt/LaAl	100	0.16	5.9	-

Mesoporous materials, type IV isotherms

Physicochemical characteristics of Pt/CeO_2-La_2O_3-Al_2O_3 catalysts

XRD of CexLayAl xerogels (A) and calcined Pt/CexLayAl catalysts (B)



- Addition of La and/or Ce oxide species to alumina stabilize its structure
- CeO_2 formation with fluorite structure
- Pt/CeAl-size of CeO_2-10 nm
- Pt/Ce0.75La0.25 – size of CeO_2–8 nm

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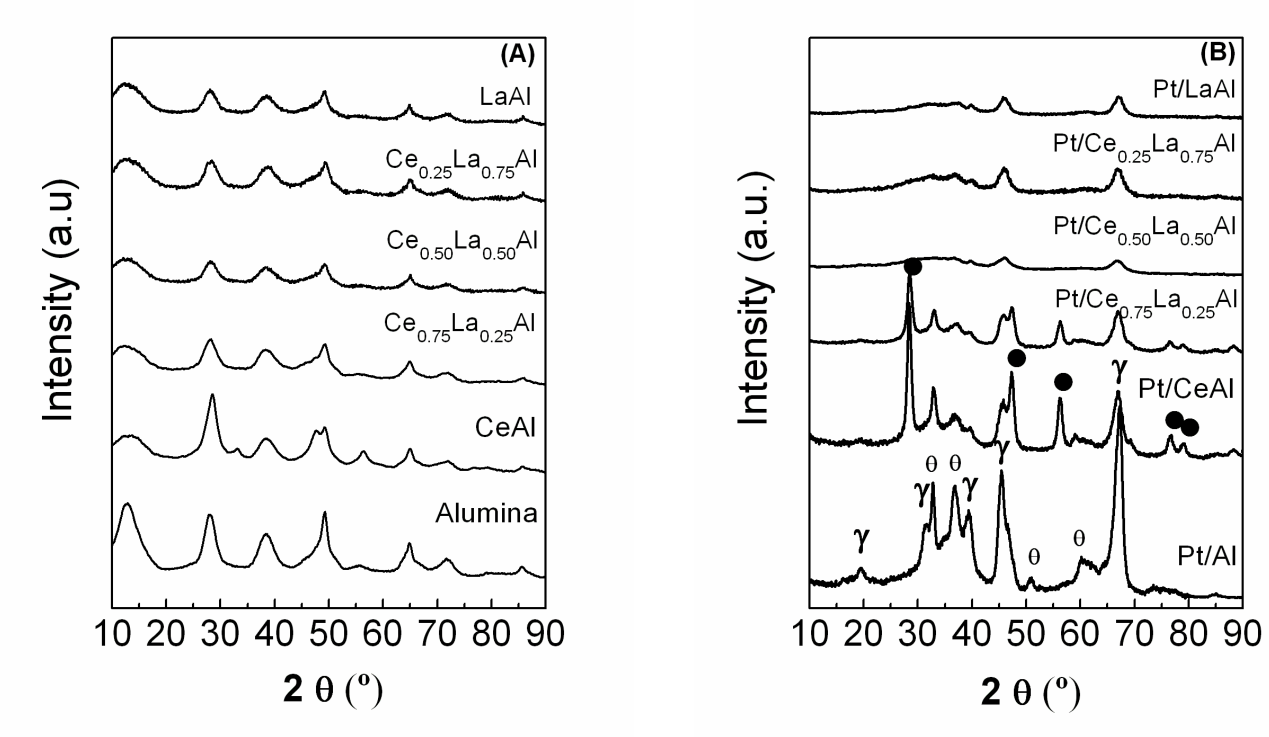

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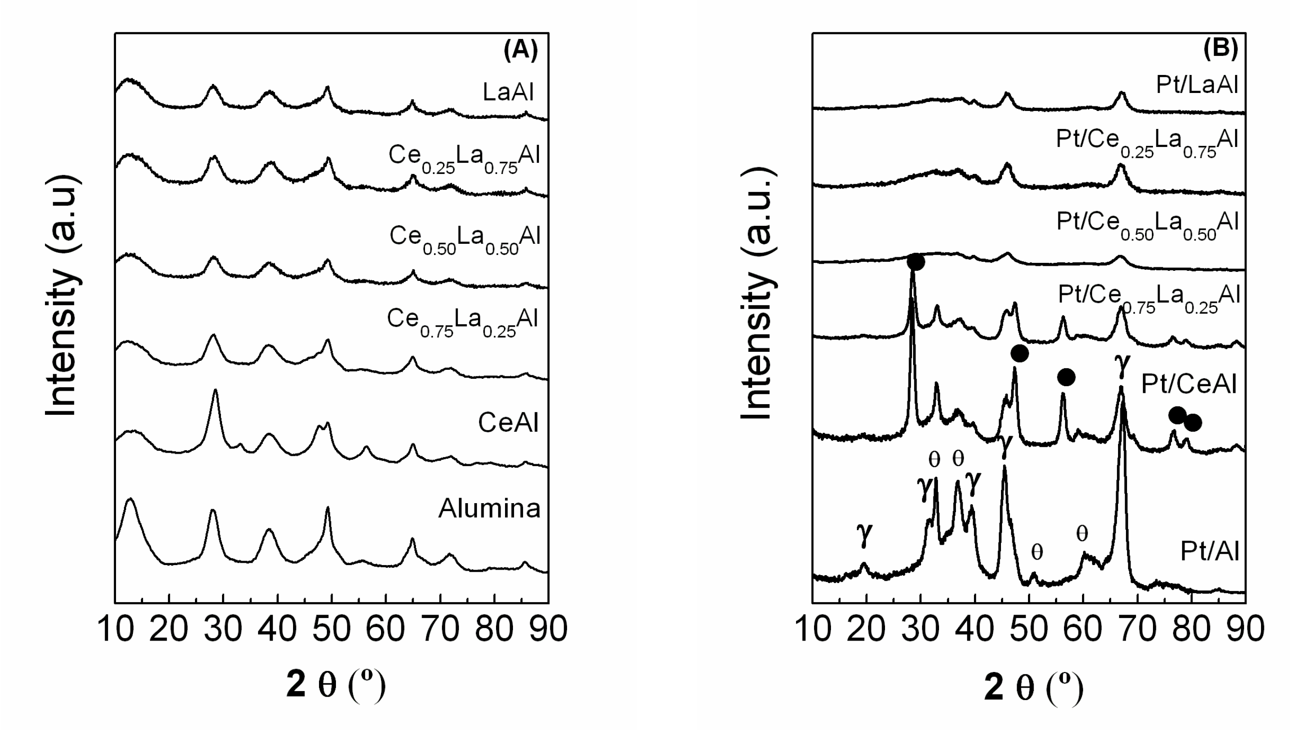

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Pt/CeO_2-La_2O_3-Al_2O_3 catalysts for SMR

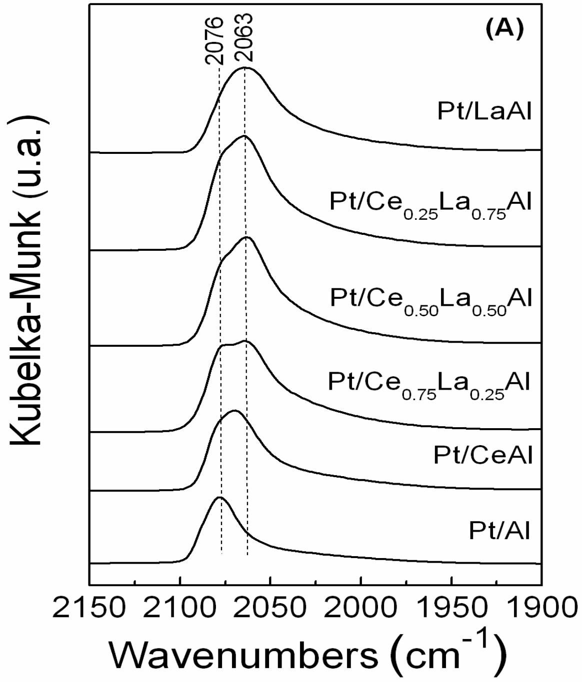
Catalytic properties of Pt/CexLayAl catalysts in SMR at 773 K

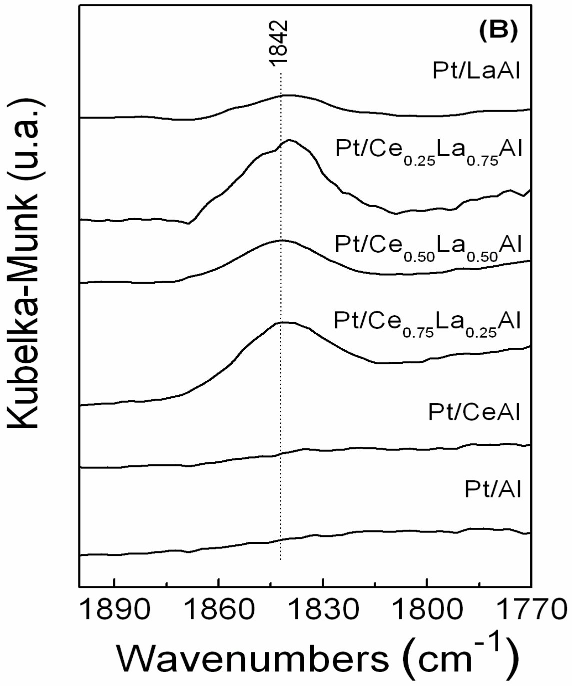
Sample	r_{CH4} **mol/s.**g_{ca} **t.** $^{10-5}$	E_a^{ap} **kJ/mol**	TOF^{ap}_{CH4} s^{-1}	Pt_D **%**
Pt/Al	4.65	67.8	1.7	59
Pt/CeO_2	4.84	67.1	3.0	33
Pt/$Ce_{0.75}La_{0.25}Al$	4.28	60.5	3.5	25
Pt/$Ce_{0.50}La_{0.50}Al$	5.21	65.8	3.5	30
Pt/$Ce_{0.25}La_{0.75}Al$	4.75	58.5	2.6	36
Pt/LaAl	5.08	70.6	3.0	35

- The both Pt/$Ce_{0.75}La_{0.25}Al$ and Pt/$Ce_{0.50}La_{0.50}Al$ catalysts exhibit the highest TOF_{CH4} , despite their lower dispersion of Pt.
- While other catalysts exhibit higher Pt dispersion and lower TOF_{CH4}
- It is expected that Pt/Al catalyst with the highest Pt dispersion will exhibit higher TOF_{CH4} , i.e a higher number of converted CH_4 molecule$_s$
- There is no relation between Pt dispersion and E_a, as well as between the dispersion and TOF_{CH4}
- It means that the dispersion does not play main role in SMR

Physicochemical characteristics of Pt/CeO_2-La_2O_3-Al_2O_3 catalysts

FTIR of CO adsorbed: HF region (A), LF region (B)





Linearly bonded CO species:

→Pt^{o} + $Pt^{\delta+}$ due to the strong interaction with support

→Heterogeneous distribution of Pt sites,i.e. with different electron density

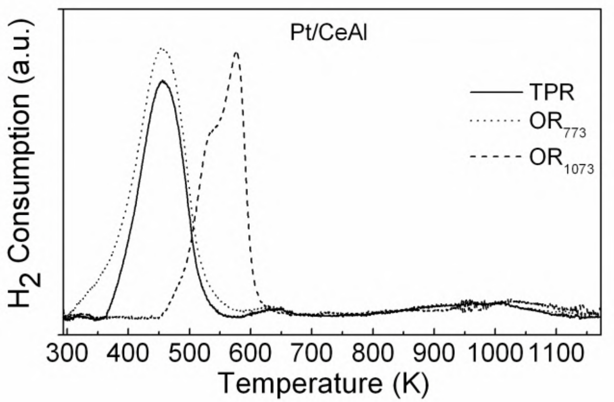
Bridge bonded CO species:

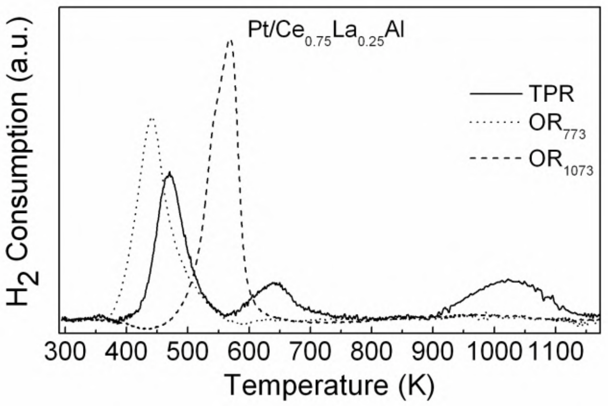
→ Pt/CeLaAl-1840 cm^{-1} - Pt^{o}

→ Pt/CeAl - SMSI → CeO_x

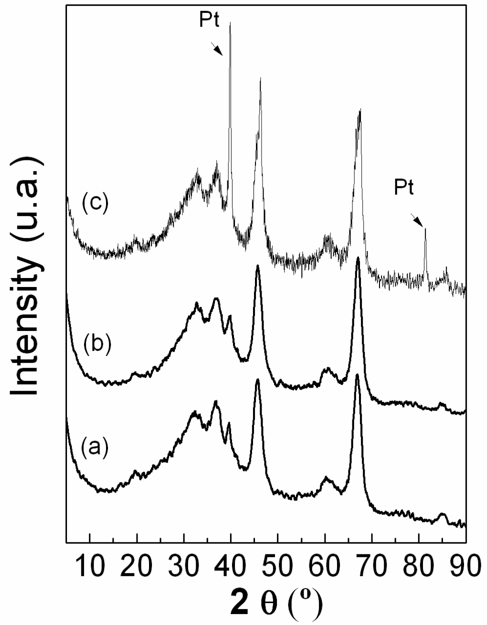
Physicochemical characteristics of Pt/CeO_2-La_2O_3-Al_2O_3 catalysts

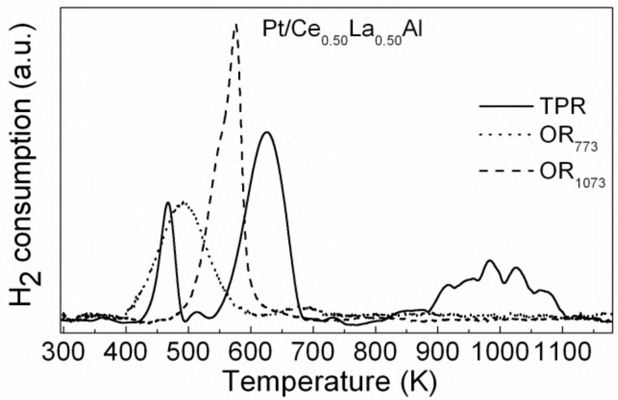
TPR and redox cycles: $OR_{773\ K}$ and $OR_{1073\ K}$

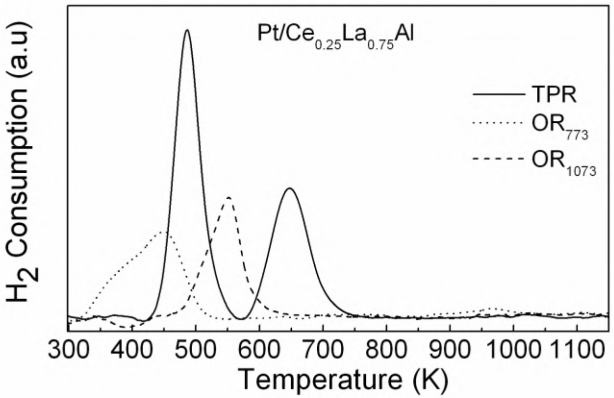




XRD of $Pt/Ce_{0.75}La_{0.25}Al$ after redox cycles







TPR - acceleration of the oxygen diffusion at interface La-Ce; maintaining $Pt^{\delta+}$; H_2 spillover effect from Pt to CeO_2-due to the intimate contact

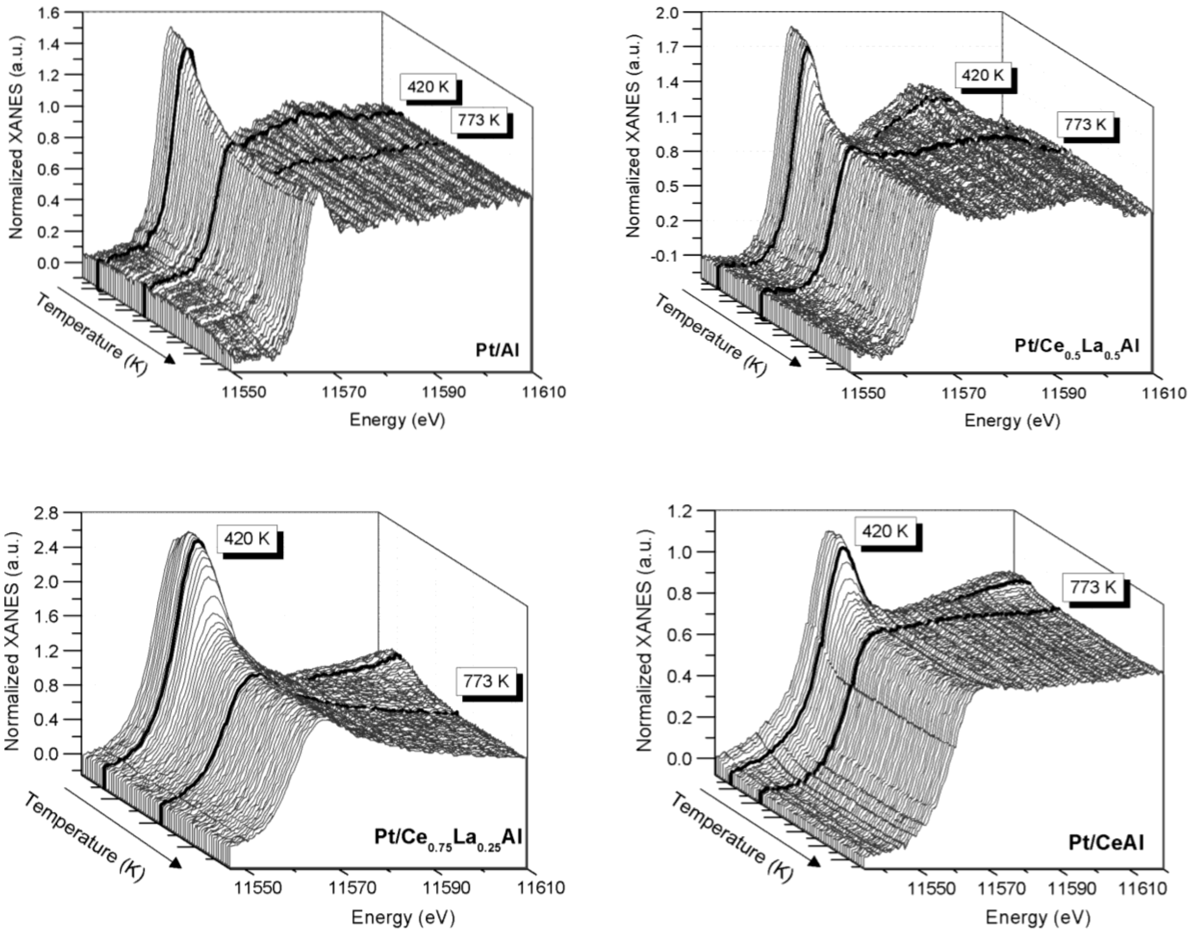
OR_{773} –Improved reducibility at lower temperatures; Overlapping of the peaks of reduced Pt and CeO_2;

- Disappearing of the peaks of surface and bulk reduction of CeO_2
- Small CeO_2 particles formation,

OR_{1073}- Shift of TPR to higher temperatures-agglomeration of Pt and Ce oxide species after redox cycles

Physicochemical characteristics of Pt/CeO_2-La_2O_3-Al_2O_3 catalysts

Pt L_{III}-edge XANES spectra of calcined Pt/CexLayAl subjected to TPR



- Intensive WL at a11567 eV and at about 423-430 K → presence of oxidized Pt, more visible for Pt/$Ce_{0.75}La_{0.25}$
- Low intensive WL → fully reduced Pt at 773 K

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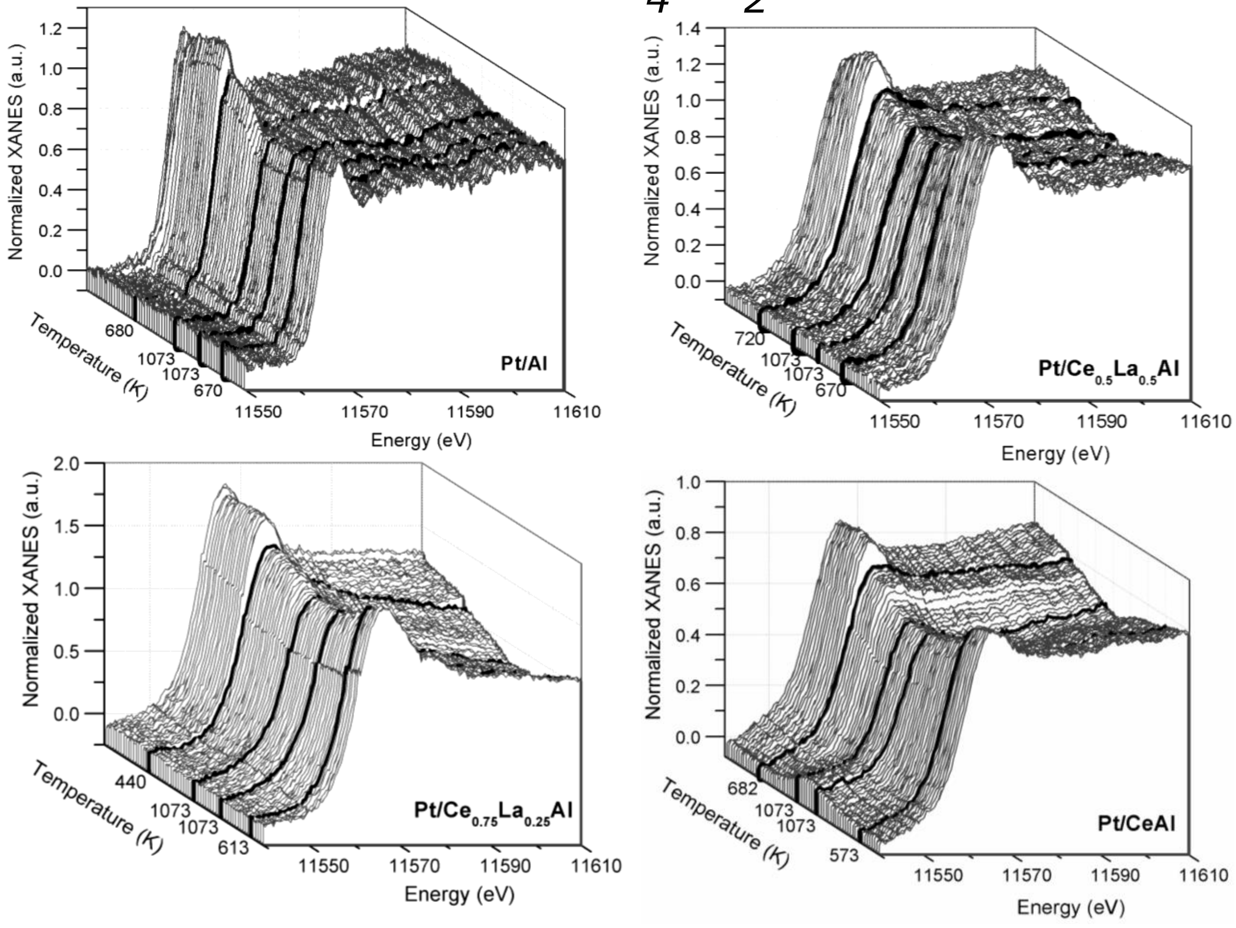
Pt/CeO_2-La_2O_3-Al_2O_3 catalysts for partial oxidation of methane

In-situ temperature resolved Pt L_{III}-edge XANES-POM spectra of Pt/CexLayAl catalysts up to 1073 K under reaction mixture of CH_4:O_2 = 2:1 diluted with He



- Pt is oxidized at the beginning of reaction – high intensive WL
- Intensity of WL is beginning to decrease at 678 K due to reduction of Pt species
- However, for Pt/Al is
- All Pt species are reduced under reaction at 1073 K
- Re-oxidation of Pt with decreasing the reaction temperature, more visible for Pt/Ce_xLa_yAl due to high oxygen mobility at metal-support interface

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Pt/CeO_2-La_2O_3-Al_2O_3 catalysts for SMR

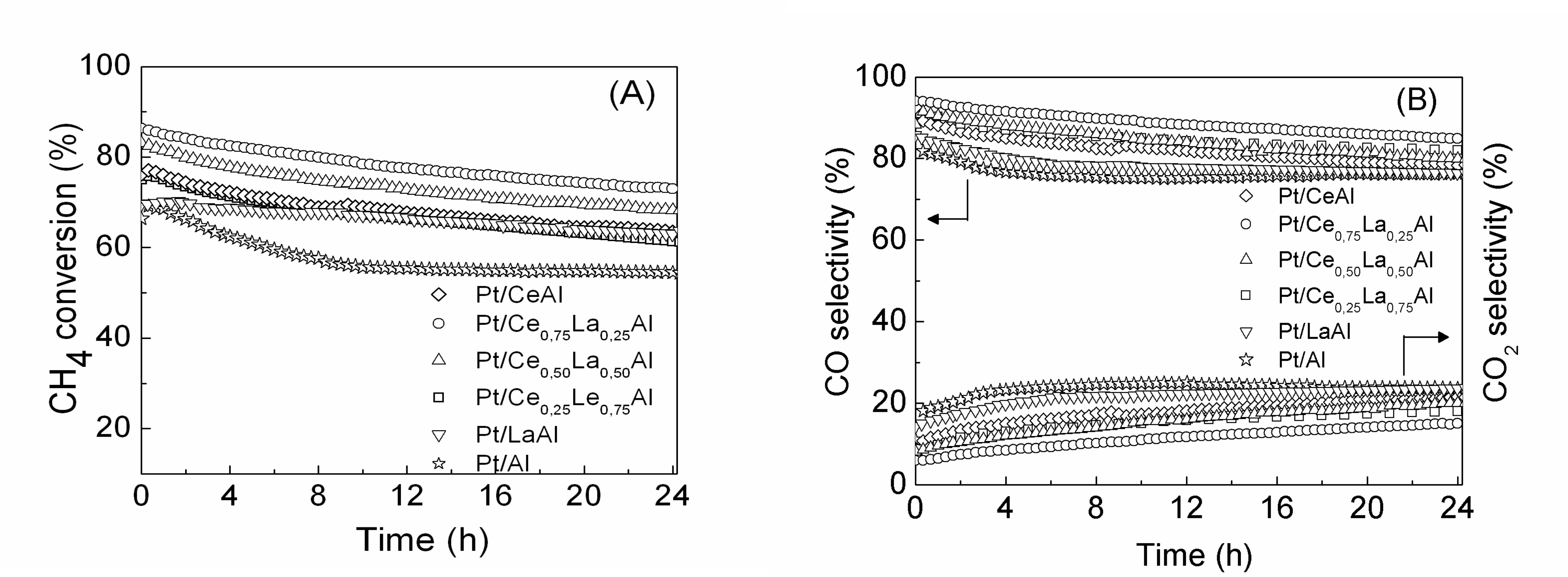
Catalytic properties of Pt/CexLayAl catalysts in SMR at 773 K

Sample	r_{CH4} mol/s.g_{ca} t.$^{10-5}$	E_a^{ap} kJ/mol	TOF^{ap}_{CH4} s^{-1}	Pt_D %
Pt/Al	4.65	67.8	1.7	59
Pt/CeO_2	4.84	67.1	3.0	33
Pt/$Ce_{0.75}La_{0.25}Al$	4.28	60.5	3.5	25
Pt/$Ce_{0.50}La_{0.50}Al$	5.21	65.8	3.5	30
Pt/$Ce_{0.25}La_{0.75}Al$	4.75	58.5	2.6	36
Pt/LaAl	5.08	70.6	3.0	35

- The equilibrium between the rate of methane decomposition over exposed metal particles and the rate of carbon cleaning will define the overall stability of the catalys
- The coexistence of the $Pt^0/Pt^{\delta+}$ and Ce^{4+}/Ce^{3+} redox couples leads to the increase of the CH_4 conversion and carbon resistance over Pt catalysts due to the OSC of $CeO_{2,}$ i.e. a great number of active metal sites is exposed to the reactant molecules

Pt/CeO_2-La_2O_3-Al_2O_3 catalysts for partial oxidation of methane

Catalytic behavior of Pt/Ce$_x$La$_y$Al catalysts in POM with time on stream



- The coexistence of Pt^{o}/Pt$^{\delta+}$ and Ce^{3+}/Ce^{4+} couples is responsible for: (i) the high CH_4 conversion and (ii) carbon cleaning due the OSC of CeO_2
- Comparing the XANES of ex in-situ reduced catalysts with those of catalysts under POM, the intensity of WL for working catalyst is higher at the beginning of reaction due to the oxidation of reduced Pt under oxygen rich atmosphere. However, most of the Pt particles are reduced over catalyst surface at 1073 K which re-oxidized again after decreasing the reaction temperature at about 673 K.
- The deactivation of Pt/Al catalyst is due to the strong agglomeration of Pt

Pt/CeO_2-La_2O_3-Al_2O_3 catalysts for SMR and POM

Conclusions

Results clearly show the effect of the of CeO_2(La_2O_3) content, as well as the atmosphere and temperature pretreatment on the structure and surface properties of Pt catalysts supported on the mixed $x$$CeO_2$-y$La_2O_2O_3$ oxides. (*i*) Well dispersed Pt particles on the surface of the mixed $xCeO_2$-yLa_2O_3-Al_2O_3 oxides after calcination and reduction at 773 K are obtained due to the strong interaction between modified alumina and Pt. (*ii*) The presence of the both promoters (CeO_2 and La_2O_3) leads to distribution of Pt sites with different electron density on the surface of reduced catalysts (Pt^0 and $P^{\sigma+}$). (*iii*) The improved low-temperature reducibility of the high CeO_2-loaded Pt catalysts subjected to the redox cycle of 773 K is related to the reduction of small Pt particles as well as to the support reduction associated with the formation of more anionic oxygen vacancies caused by the incorporation of La into the CeO_2 framework.

The different behaviors of Pt/Ce*x*La*y*Al and Pt/Al catalysts under reaction conditions of steam reforming and partial oxidation of methane is mainly assigned to the support kind. The high activity and stability of the Pt/Ce*x*La*y*Al catalysts in SMR and POM is related to the metal-support interface and the high oxygen mobility in support. The strong initial deactivation of alumina-supported Pt catalyst in POM is caused by Pt sintering.

Reforming of methane with CO_2

Reforming of CH_4 with CO_2 (dry reforming of methane (DRM) or biogas reforming) to synthesis gas or hydrogen rich synthesis gas has increasing attention last years.

Biogas contain two green houses gases: CH_4 and CO_2 that can be converted into value products

DRM yields a synthesis gas with molar ratio of H_2/CO near 1 that is suitable for Fisher-Tropsh synthesis

Due to the high endothermicity of DRM the catalysts deactivate very fast at high reaction temperature of the process. This is the main reason this process to no be applied at industrial scale now days.

The subject is to develop effective catalysts exhibiting high activity and high stability by using suitable carriers and promoters to enhance the catalyst efficiency.

Ni/CeO_{2}- Al_2O_3 catalysts for reforming of CH_4 with CO_2

Preparation

Carriers:

xCeO_2-Al_2O_3 oxides

Wetness impregnation method →

γ-Al_2O_3, solution $Ce(NO_3)_3.6H_2O$

Drying at 110°C in air for 12 h

Calcination at 600 °C K for 5 h

CeO_2 content-1, 3, 6, 12 wt%

Catalysts:

Ni/xCeO_2-Al_2O_3

Wetness impregnation method →

solution of $Ni(NO_3)_2.6H_2O$

Drying at 110°C for 12 h

Calcination at 550°C in air for3 h

Ni content – 10 wt%

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Ni/CeO_{2}- Al_2O_3 catalysts for reforming of methane with CO_2

- *Methods:*
- N_2 adsorption-desorption isotherms
- X-ray diffraction (XRD
- Uvvis Diffuse reflectance spectroscopy (DRS))

X-ray photoelectron spectroscopy (XPS)

- Raman spectroscopy
- Temperature programmed reduction (TPR)
- Temperature programmed oxidation (TPO); TG/TDA
- High resolution transmission electron microscopy (HRTEM)

Reforming of methane with CO_2:

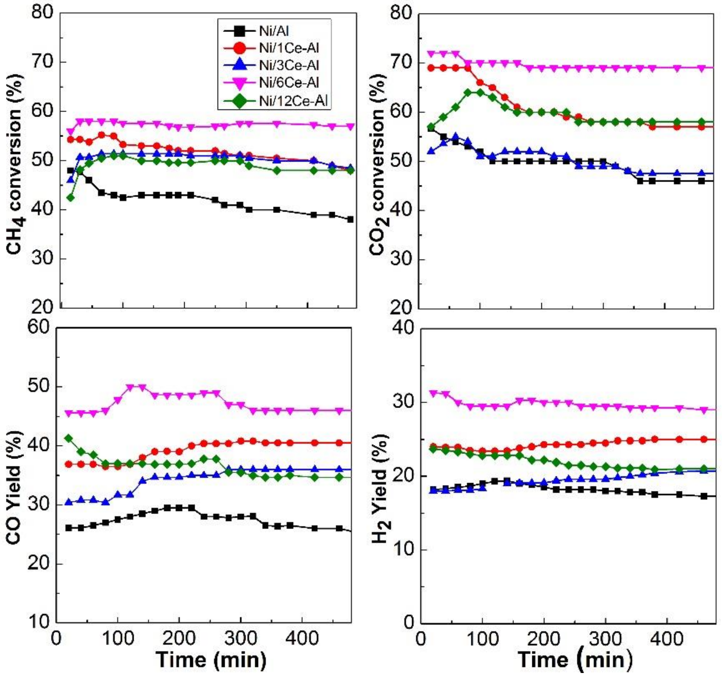
at $T_{reaction} = 450^0$-650^0C

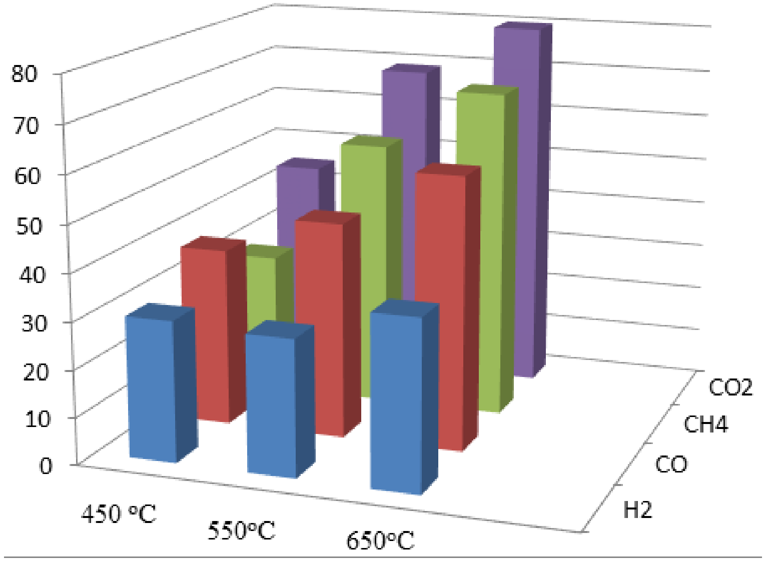
CH_4:CO_2=1/1

$m_{cat} = 0.05$ g

Catalyst pretreatment in flow of 10%H_2/N_2 at 550^0C for 1.5 h

Catalytic test of Ni/CeO_2-Al_2O_3 catalysts in reforming of methane with CO_2





Catalyst	XCH4	XCO2	YH2	YCO	H2/CO
Ni/Al	45	56.7	18.5	27.0	0.63
Ni/1Ce-Al	53	61.3	24.3	37.2	0.61
Ni/3Ce-Al	43	52	19.1	31.7	0.65
Ni/6Ce-Al	57	69	30.2	45.2	0.60
Ni/12Ce-Al	50	60	22.8	37.1	0.61

Physicochemical characteristics of Ni/CeO_2-Al_2O_3 catalysts

Textural properties

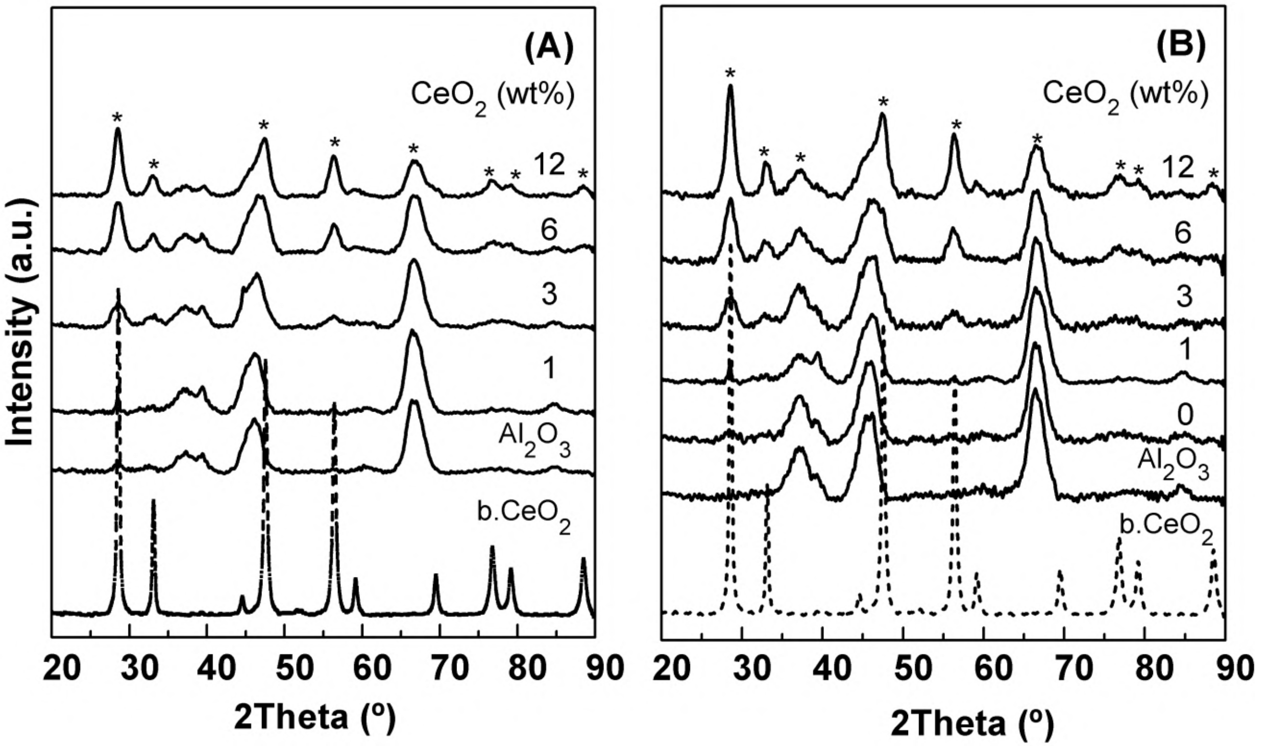
Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	D_p (nm)	D_{XRD} CeO_2 (nm)
Al_2O_3	248	0.92	14.6	-
Ni/Al	187	0.55	11.7	-
Ni/1Ce-Al	193 (228)[a]	0.66 (0.91)[a]	13.2 (15.7)[a]	-
Ni/3Ce-Al	190 (222)	0.70 (0.87)	13.6 (15.7)	5.5 (5.3)[a]
Ni/6Ce-Al	173 (231)	0.65 (0.86)	14.2 (15.7)	6.2 (6.2)
Ni/12Ce-Al	158 (198)	0.48 (0.79)	12.1 (15.4)	9.3 (9.2)

[a] xCeO_2-Al_2O_3 carriers

Stabilization effect of CeO_2 on the textural properties up to 6 wt%

Physicochemical characteristics of Ni/CeO_2-Al_2O_3 catalysts

XRD of CeO_2-Al_2O_3 oxides (A) and Ni/CeO_2-Al_2O_3 catalysts (B)



Agglomeration of CeO_2 with fluorite structure
with increasing the CeO_2 content

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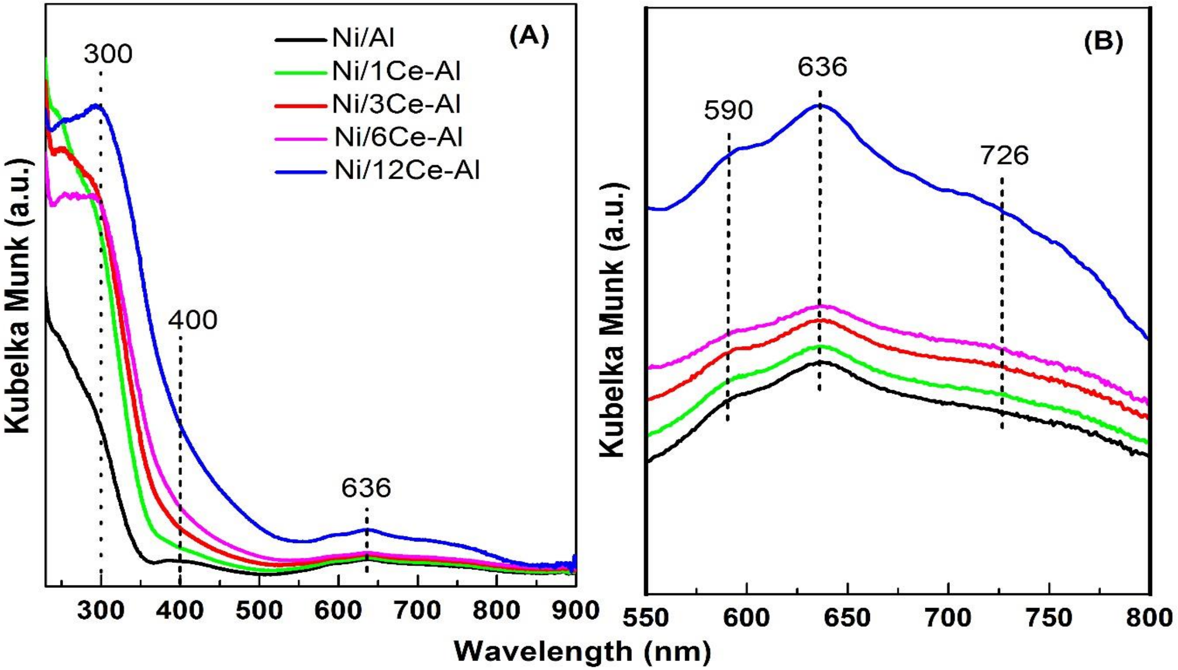
Physicochemical characteristics of Ni/CeO_2-Al_2O_3 catalysts

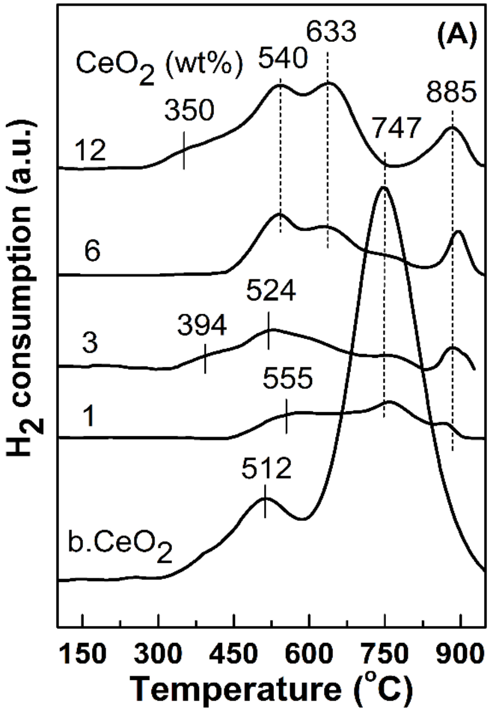
UVvis DRS

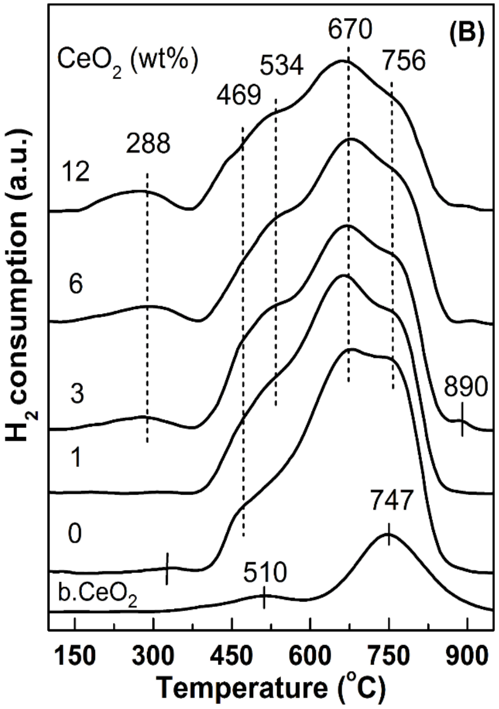


- 230-490 nm: $O^{2-} \rightarrow Ce^{4+}$ and $O^{2} \rightarrow Ce^{3+}$ electron charge transfer
- ; 230-350 nm $O^{2-} \rightarrow Ni^{2+}$electron charge transfer
- Doublet at 590-636 nm → Ni^{2+} ions in tetrahedral configuration: $NiAl_2O_4$;
- Broad band at 720-780 nm for Ni^{2+} ions → in octahedral coordination: NiO

Physicochemical characteristics of Ni/CeO_2-Al_2O_3 catalysts

TPR of CeO_2-Al_2O_3 oxides (A) and Ni/CeO_2-Al_2O_3 catalysts (B)





Stepwise reduction of bulk CeO_2:
Superficial reduction → oxygen vacancies and Ce^{3+} ions

Bulk reduction → formation of Ce_2O_3
Easy reduction of supported CeO_2
Formation of $CeAlO_3$

Reduction of complex of Ni oxide species in more intimate contact with CeO_2

Decrease of the formation of surface non-stoichiometric spinel $NiAl_2O_4$ at 756ºC and disappearing of CeAlO3 at higher CeO_2 content

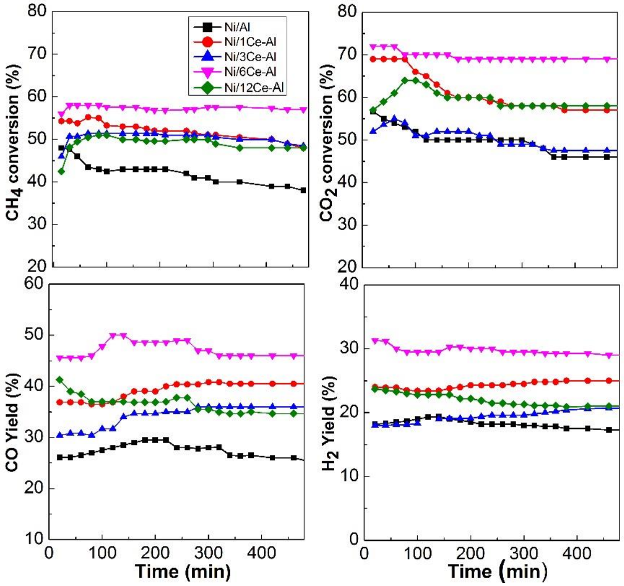
XPS parameters of calcined, reduced and spent $Ni/xCeO_2$-Al_2O_3 catalysts

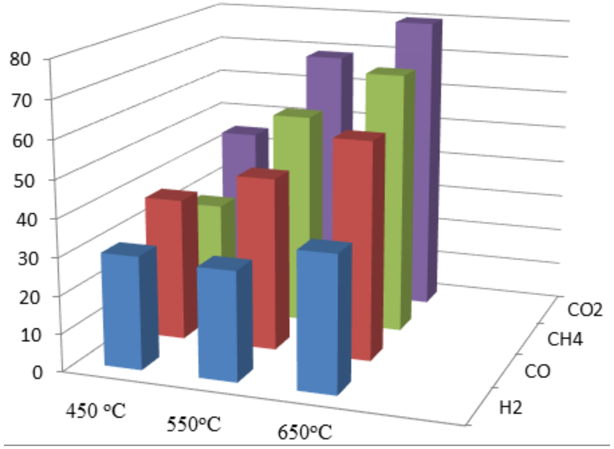
Sample	**Ni $2p_{3/2}$**		**$Ce3d_{5/2}$**	**Ce^{3+}/ (Ce^{4+}+Ce^{3+})**	**Ce/Al**	**Ni/(Al+Ce)**	**Ni/Ce**	**C/Al**
	Ni2+	**Ni^{o}**						
				Calcined samples				
Ni/Al	855.8	-	-	-	-	0.06	-	-
Ni/1Ce-Al	855.8	-	882.1	32 (33)[b]	0.015	0.089	5.96	-
Ni/3Ce-Al	855.8	-	881.9	36 (22)	0.016	0.089	5.38	-
Ni/6Ce-Al	855.8	-	882.1	15 (34)	0.015	0.070	4.58	-
Ni/12Ce-Al	855.8	-	882.3	0 (32)	0.014	0.079	5.46	-
				Reduced samples				
Ni/Al	856.1(91)[a]	852.3(9)[a]	-	-	-	0.03	-	-
Ni/1Ce-Al	856.1(94)	852.5(6)	881.7	35	0.007	0.040	4.95	-
Ni/3Ce-Al	856.1(95)	852.3(5)	882.3	33	0.009	0.040	4.30	-
Ni/6Ce-Al	855.8(97)	851.8(3)	882.4	24	0.009	0.059	5.80	-
Ni/12Ce-Al	856.1(98)	852.4(2)	882.0	34	0.010	0.059	5.47	-
				Spent catalysts				
Ni/Al	856.4(86)[a]	852.7(14)[a]	-	-	-	0.05	-	0.175
Ni/1Ce-Al	856.4(87)	852.7(13)	881.5	36	0.013	0.048	3.85	0.085
Ni/3Ce-Al	856.3(88)	852.8(12)	881.4	31	0.014	0.057	4.14	0.074
Ni/6Ce-Al	856.2(80)	852.7(20)	881.7	32	0.012	0.058	4.75	0.135
Ni/12Ce-Al	856.3(92)	852.8 (8)	881.3	40	0.016	0.057	3.88	0.069

[b] carriers

Ni^{o}/Ni^{2+} and Ce^{3+}/Ce^{2+} pairs

Catalytic test of Ni/CeO_2-Al_2O_3 catalysts in reforming of methane with CO_2





CH_4:CO_2=1:1

T_{reac}=550 °C

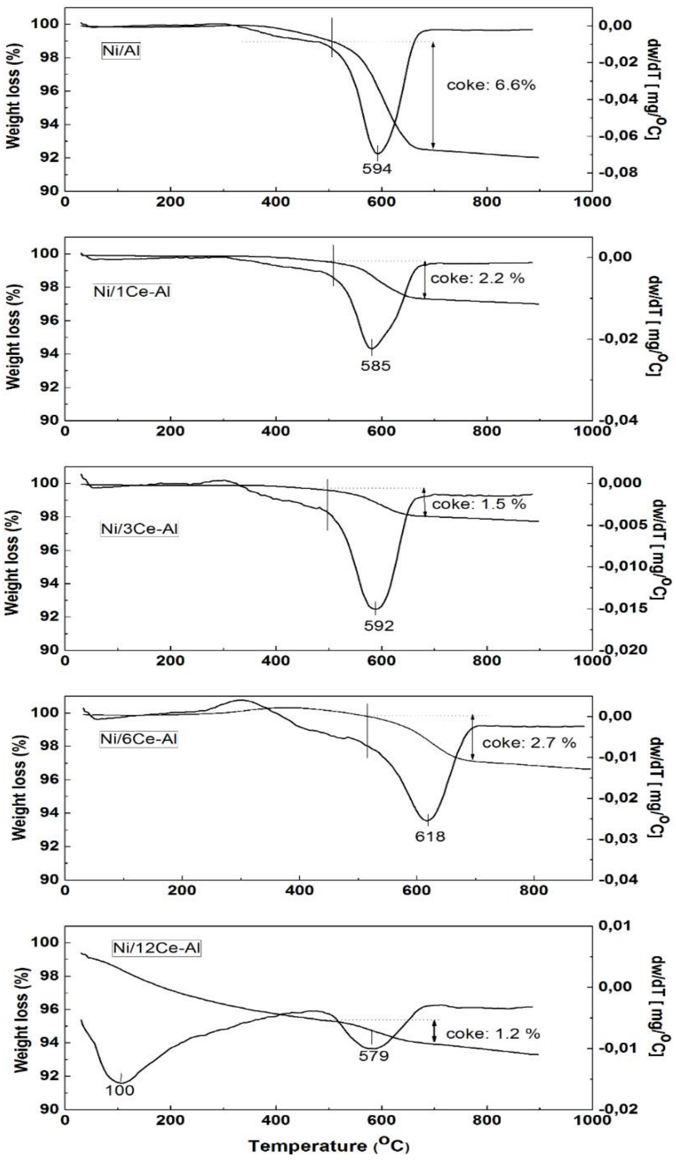
m=0.05 g

Catalyst	XCH4	XCO2	YH2	YCO	H2/CO
Ni/Al	45	56.7	18.5	27.0	0.63
Ni/1Ce-Al	53	61.3	24.3	37.2	0.61
Ni/3Ce-Al	43	52	19.1	31.7	0.65
Ni/6Ce-Al	57	69	30.2	45.2	0.60
Ni/12Ce-Al	50	60	22.8	37.1	0.61

$$CO_2 > CH_4 \rightarrow \quad CO + \underleftarrow{H_2O \Leftrightarrow H_2} + CO_2 \quad \text{WGSR}$$

Physicochemical characteristics of Ni/CeO_2-Al_2O_3 catalysts

TPO



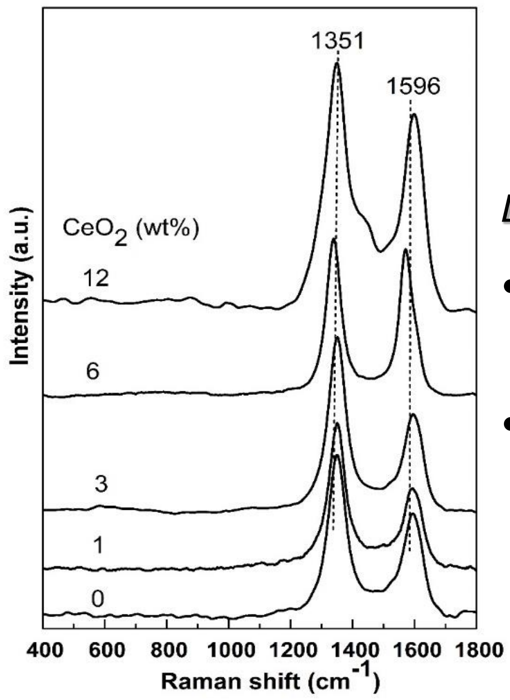
*Carbon formation v*ia several reactions:

- CH_4 decomposition: $CH_4 \Leftrightarrow 2H_2 + C_s$
- CO disproportionation: $2CO \Leftrightarrow CO_2 + C$

Weight loss increase:

Ni/12Ce-Al < Ni/3Ce-Al < Ni/1Ce-Al < Ni/6Ce-Al < Ni/Al

Raman spectra



Different structure of deposited carbon:

- (D) → 1351 cm^{-1} - amorphous carbon, defective filaments
- (G) → 1596 cm^{-1} – graphitic type carbon

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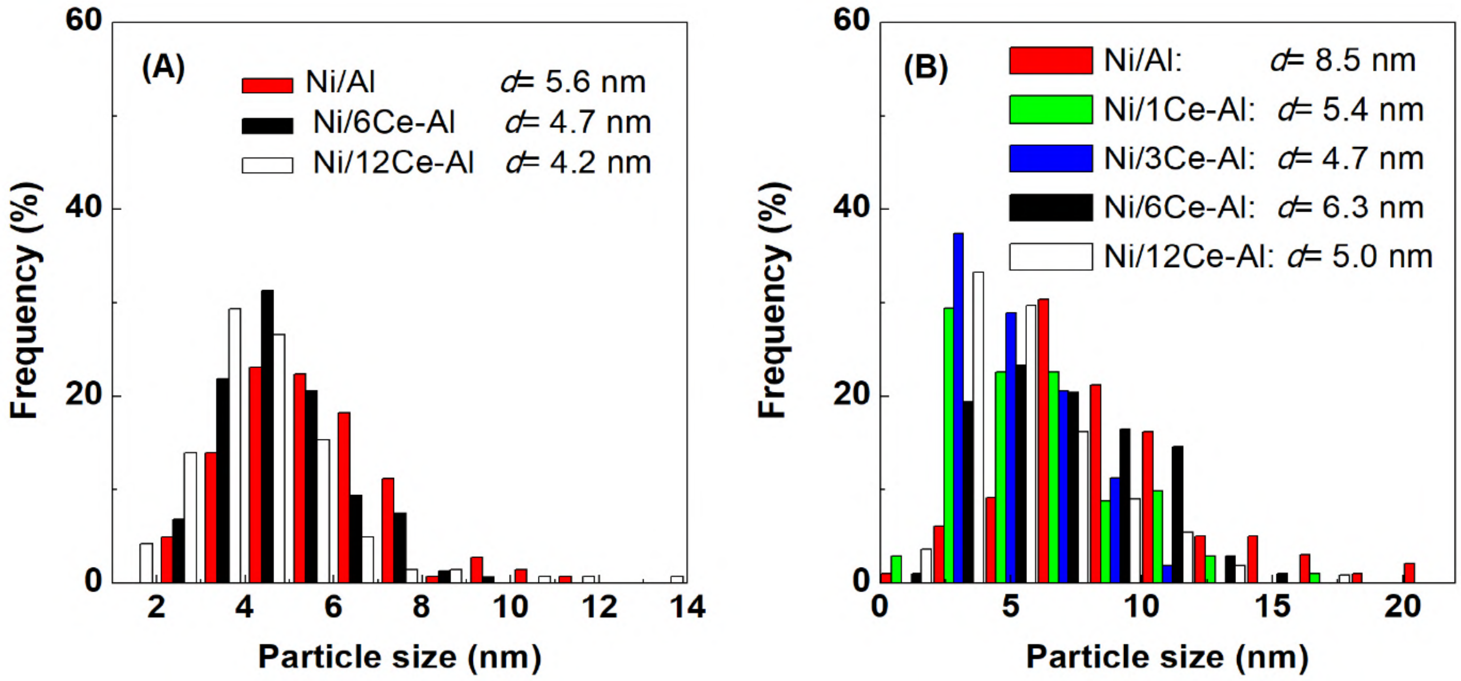
Physicochemical characteristics of Ni/CeO_2-Al_2O_3 catalysts

Particle size distribution for reduced and spent catalysts



Ni/Al catalyst: Agglomeration of Ni; Heterogeneous distribution of metal particles up to 20 nm
Ni/6Ce-Al catalyst: homogeneous distribution

Appl.Catal.B:Envir. 225 (2018) 340-453

Conclusions

- The synthesized mixed CeO_2-Al_2O_3 oxides with different CeO_2 content (1, 3, 6 and 12 wt.%) are suitable carriers for supported Ni catalysts.
- The nature of nickel-support interaction in Ni/Al_2O_3 and Ni/*x*CeO_2-Al_2O_3 catalysts systems causes different accessibility and reducibility of both, the nickel and cerium species. Increasing the CeO_2 loading leads to agglomeration of CeO_2 phase with fluorite structure.
- The XPS analysis suggests that the intimate contact between nickel and cerium species depends on the CeO_2 content. The Ce^{3+}/Ce^{4+} and Ni^{o}/Ni^{n+} couples are the active sites
- CeO_2-containing Ni catalysts exhibit high coke resistance due to the presence of small nanoparticles with average particles size of 5-6.3 nm.
- Two kinds of deposited carbon on the surface of spent catalysts are registered: more ordered and less ordered carbon. The heterogenous nickel particle size distribution from 0.5 nm to 20 nm, established for non-promoted with ceria alumina-supported Ni catalyst, causes the formation of nanofibers and catalyst deactivation.
- The most active catalyst in dry reforming of CH_4 is Ni/6Ce-Al. The CeO_2 content of 6 wt.% is optimal to ensure a more intimate contact between the nickel and cerium oxide species leading to a change in the electronic properties of Ni and Ce atoms and to increase the accessibility of the active sites for that catalyst.

Thank you

for your kind attention