The effect of La in PdCe-zeolite catalysts for NO_x-SCR with CH_4

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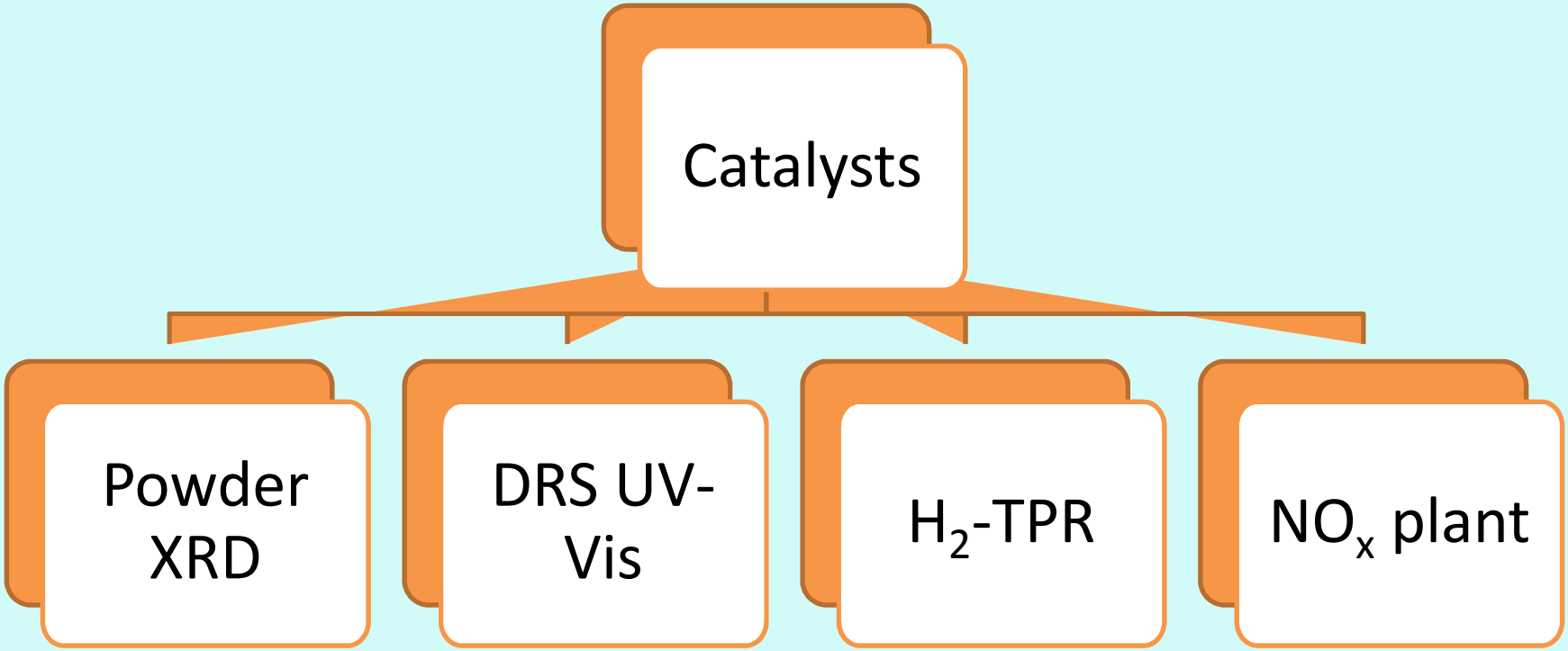
Work purpose

- The main goal of this work was to develop zeolite- based catalysts, showing a good catalytic behavior for $DeNO_x$ reduction with methane as reductant, even in the presence of water.

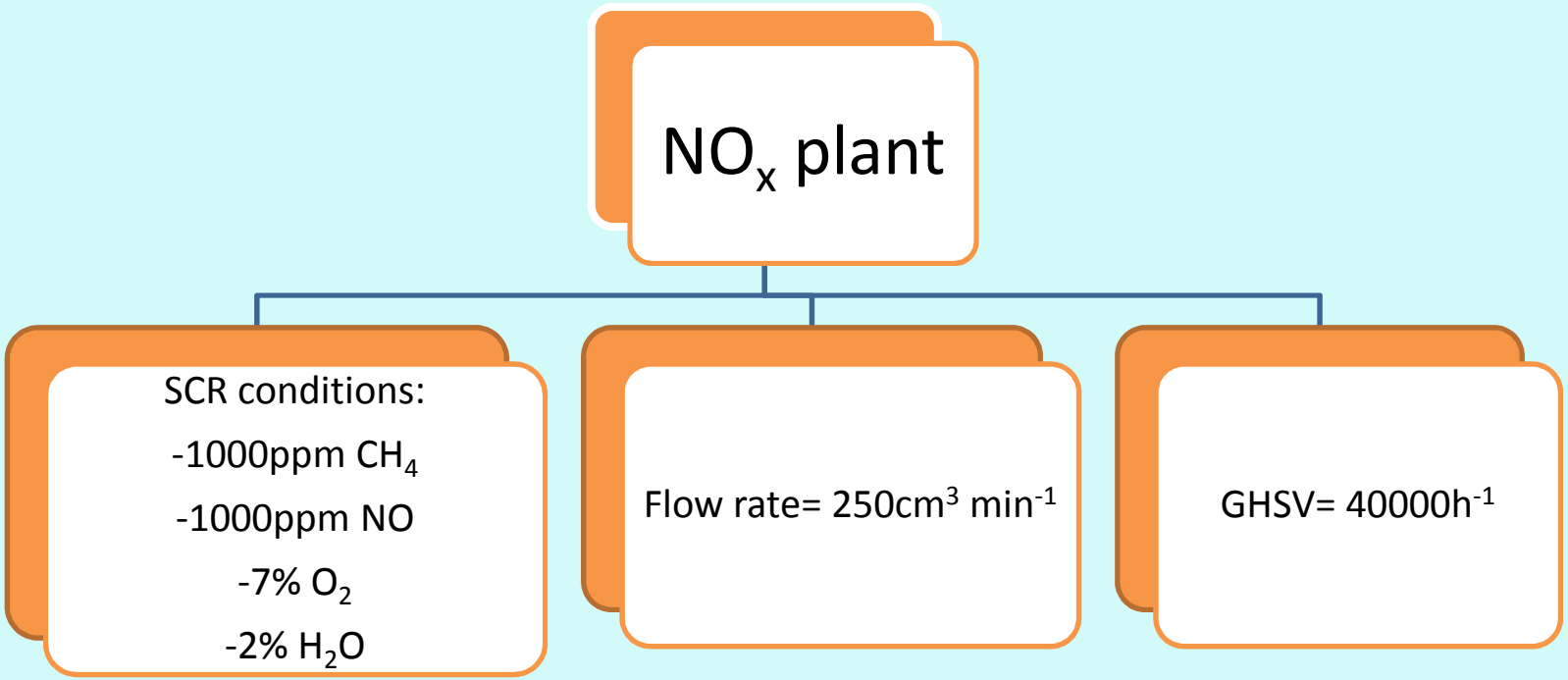
- Catalysts consisting of La, Ce and Pd, have been studied.

- Metals combination, the amount and the order of La introduction in the catalysts were considered.

Experimental



Test conditions



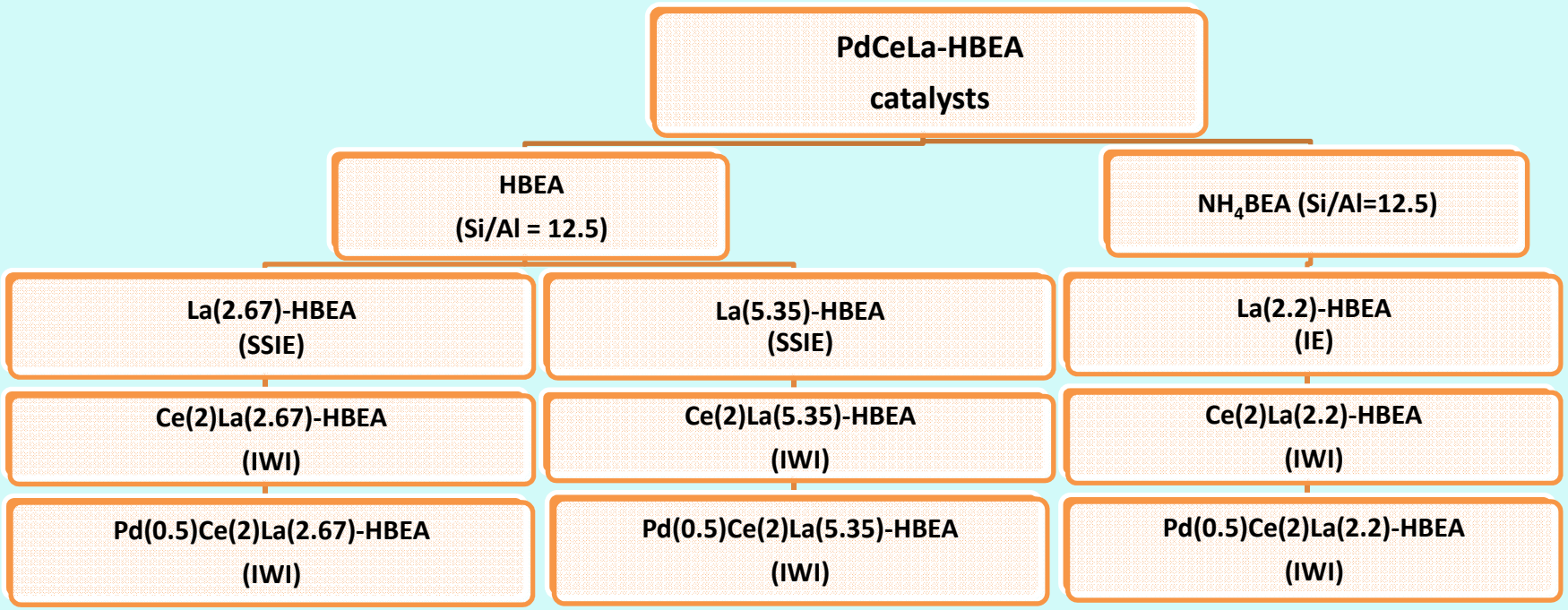
Catalytic tests were performed using the following cycles:

(1) a run under dry conditions, from 300°C to 500°C – *1st isothermal* dry,

(2) a run under water vapor (2% vol. H_2O), from 300°C to 500°C – *isothermal wet*,

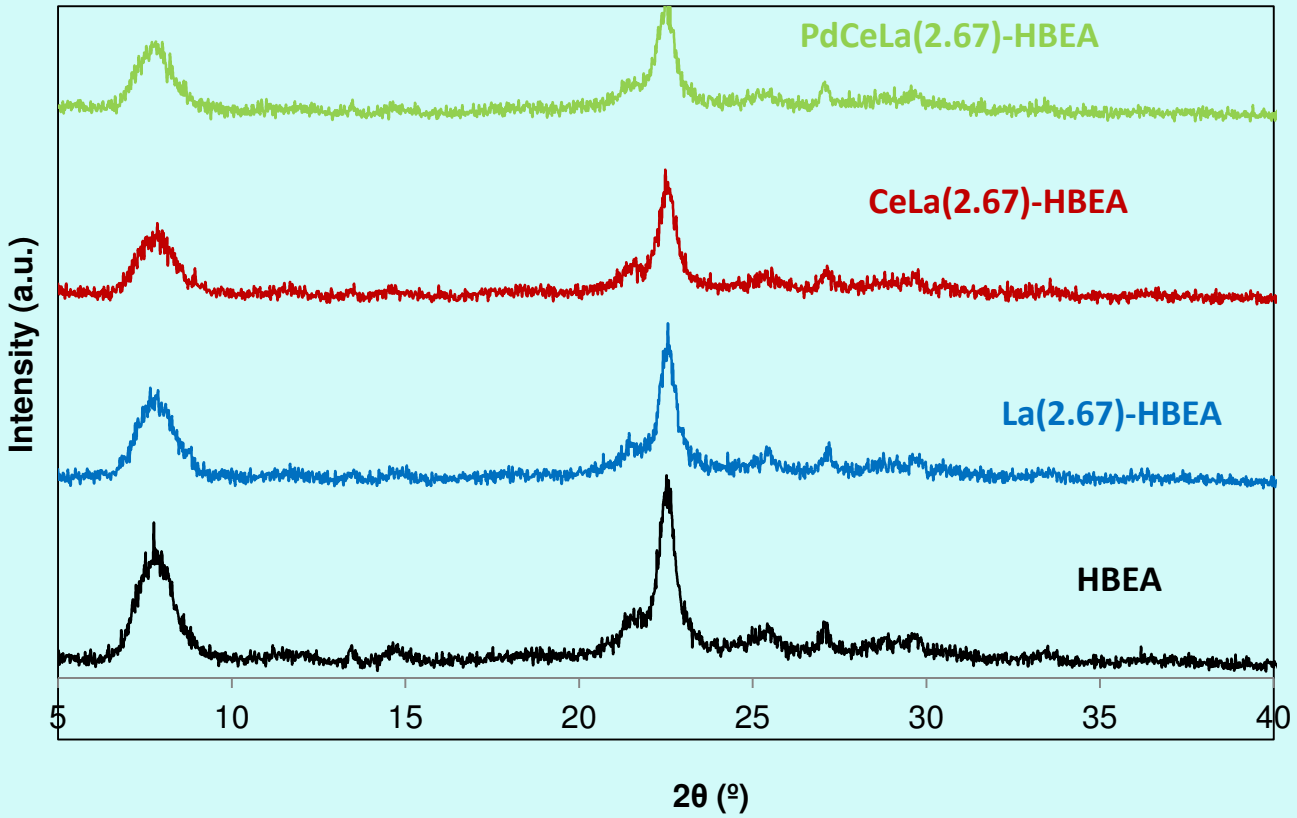
(3) a *2nd* run in dry conditions after water test, from 300°C-500°C – 2nd *isothermal dry.*

PdCeLa-HBEA



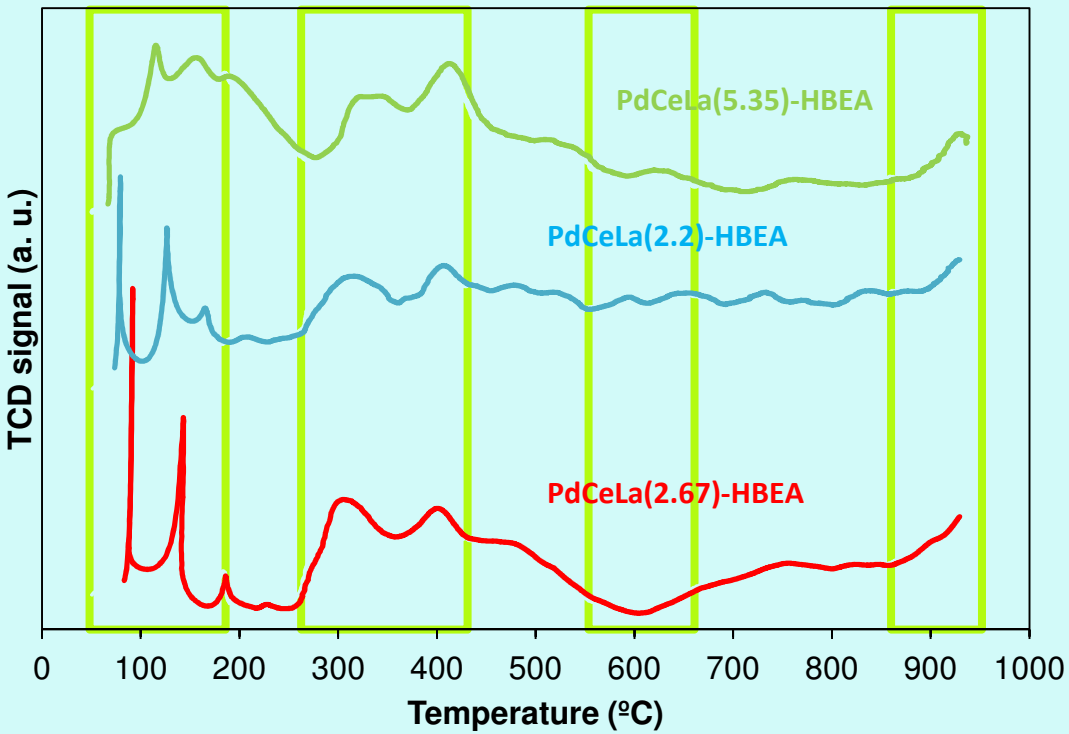
- Different amounts of La introduced using different methods,
- Equal Ce and Pd amount (2 wt.% and 0.5 wt.%, respectively), intoduced into all La catalysts,
- The same method of Pd and Ce ions introduction → incipiente wetness impregnation.

XRD patterns for La(2.67)-HBEA and CeLa(2.67)-HBEA catalysts and tri-metallic PdCeLa(2.67)-HBEA catalyst



- Crystallinity was not affected by metal exchanged.

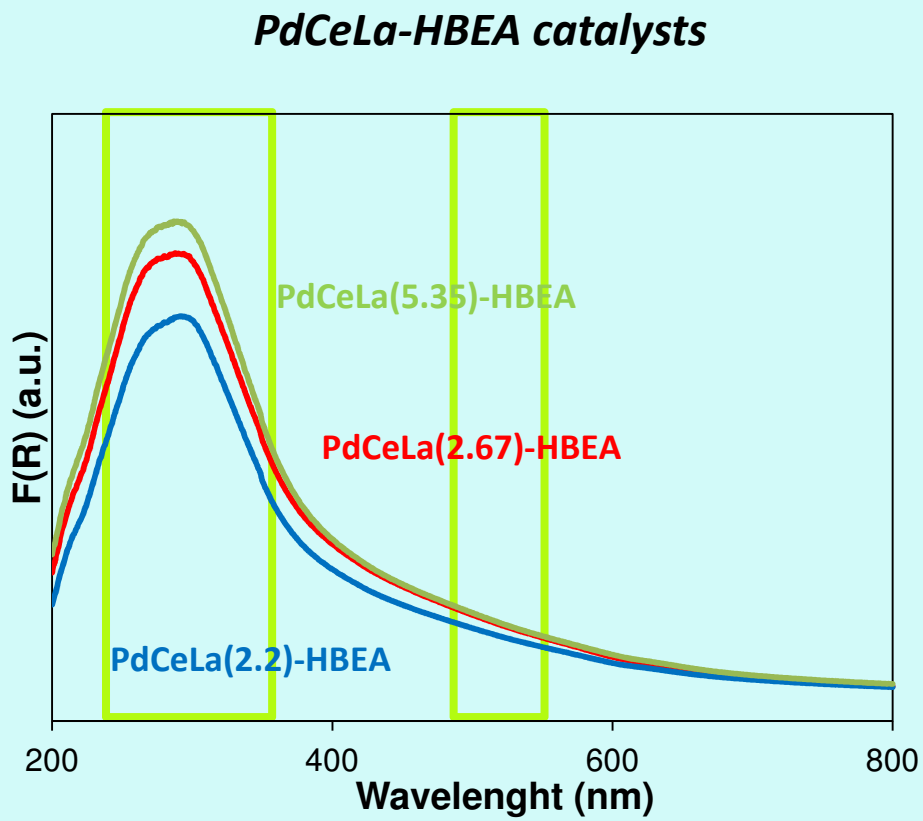
H_2-TPR profiles of tri-metallic PdCeLa –HBEA catalysts



- 100ºC → PdO species in interactions with CeO_2,
- 130ºC → reduction of Ce on the surface,
- 300-400ºC → reduction of surface Ce oxide species,
- 600ºC → reduction of bulk oxygen of Ce species,
- 900ºC → reduction of cerium (III) oxides [1-5].

[1] Saleh M. Saqer, Dimitris I. Kondarides, Xenophon E. Verykios, Applied Catalysis B: Environmental Vol. 103, (2011), 275–286.
[2] Córdoba L.F., Flytzani-Stephanopoulos M., Montes de Correa C., Applied Catalysis B: Environmental Vol. 33, (2001), 25–33.
[3] Feio L.S.F., Hori C.E., Damyanova S., Noronha F.B., Cassinelli W.H., Marques C.M.P., Bueno J.M.C., Applied Catalysis A: General Vol. 316, (2007), 107–116.
[4] WeyrichP.A., Trevin˜o H., Hölderich W.F., Sachtler W.M.H., Applied Catalysis A: General Vol. 163, (1997), 31–44.
[5] Yue L., He C., Zhang X., Li P., Wang Z., Wang H., Hao Z., Journal of Hazardous Materials Vol.244-245, (2013), 613-620.

Diffuse reflectance UV-vis spectra at room temperature for trimetallic PdCeLa-HBEA catalysts



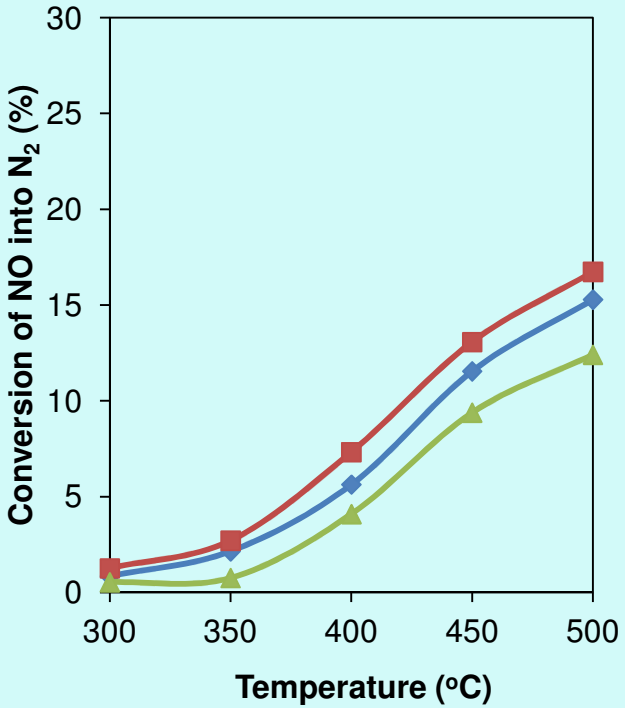
- 210 nm → disperse Ce^{3+} species,
- 240nm → palladium clusters,
- 260 nm → 4f-5d transitions of Ce^{3+} ions,
- 310 nm → cerium (IV) oxides,
- 500nm → palladium oxides [2-5].

[2] Córdoba L.F., Flytzani-Stephanopoulos M., Montes de Correa C., Applied Catalysis B: Environmental Vol. 33, (2001), 25–33.
[3] Feio L.S.F., Hori C.E., Damyanova S., Noronha F.B., Cassinelli W.H., Marques C.M.P., Bueno J.M.C., Applied Catalysis A: General Vol. 316, (2007), 107–116.
[4] WeyrichP.A., Trevin˜o H., Hölderich W.F., Sachtler W.M.H., Applied Catalysis A: General Vol. 163, (1997), 31–44.
[5] Yue L., He C., Zhang X., Li P., Wang Z., Wang H., Hao Z., Journal of Hazardous Materials Vol.244-245, (2013), 613-620.

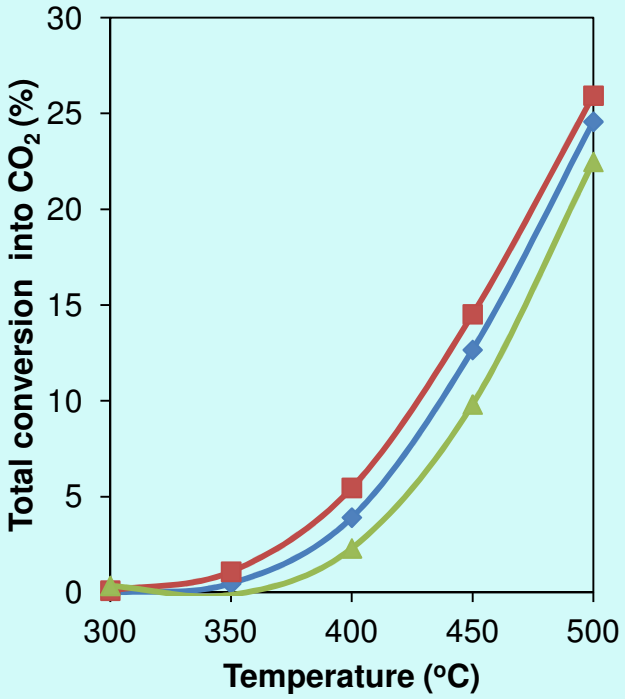
NO_x SCR steady-state catalytic test results, over tri-metallic catalysts

PdCeLa(2.67)-HBEA, PdCeLa(2.2)-HBEA and PdCeLa(5.35)-HBEA

NO_x conversion into N_2



CH_4 conversion into CO_2



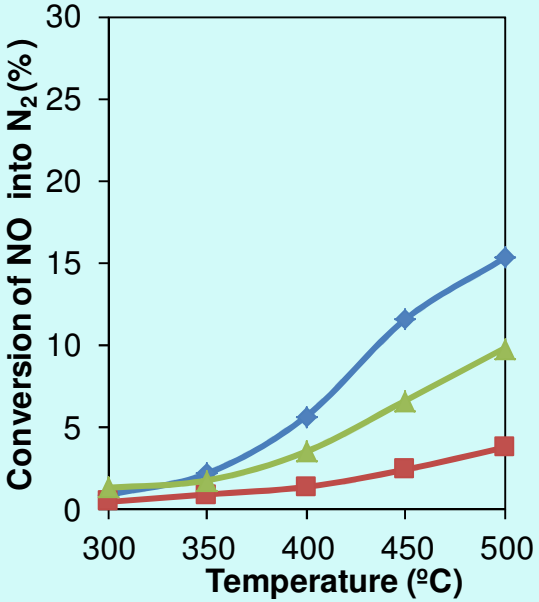
- The best catalytic performance was observed over PdCeLa(2.67)-HBEA catalyst.

Conversions during the whole catalytic cycle, obtained over PdCeLa-HBEA catalysts

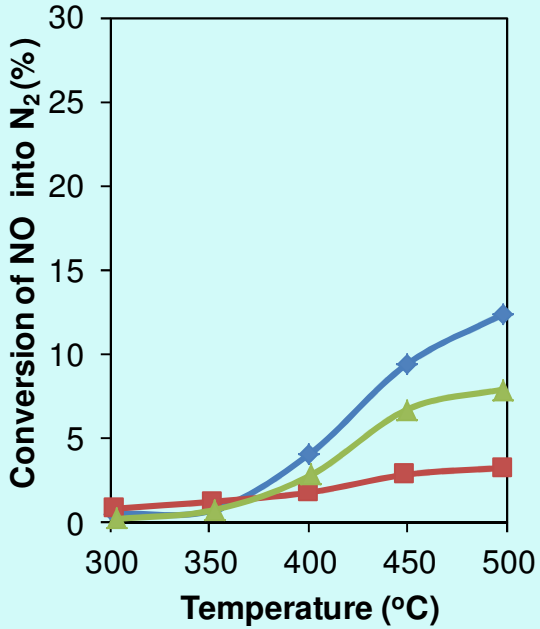
Isothermal, Isothermal wet , Isothermal 2nd dry

$NO_x \rightarrow N_2$

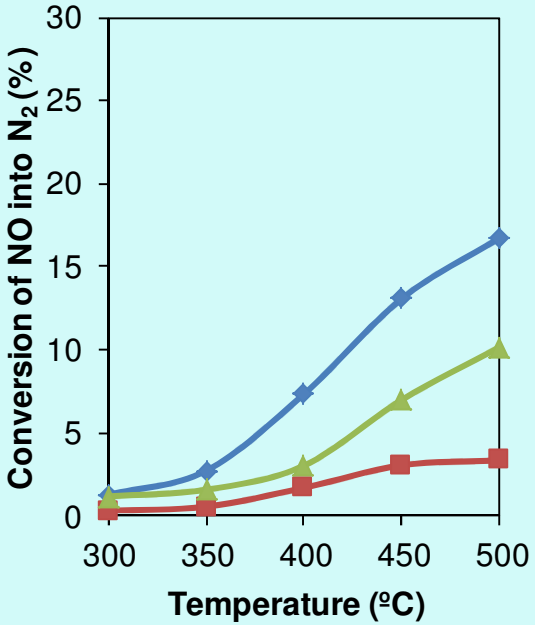
PdCeLa(2.2)-HBEA



PdCeLa(5.35)-HBEA



PdCeLa(2.67)-HBEA



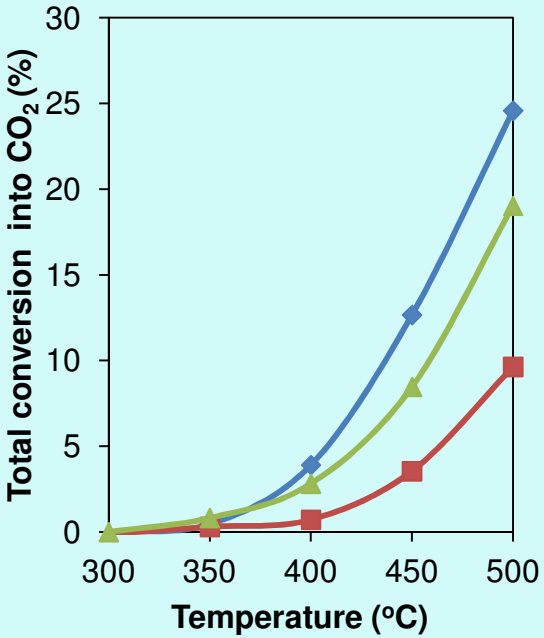
- Stability of all presented PdCeLa-HBEA was greatly affected by water presence,
- Initial conversion obtained during 1st isothermal tests, were not restored after the reaction with 2% of water in the reaction mixture.

Conversions during the whole catalytic cycle, obtained over PdCeLa-HBEA catalysts

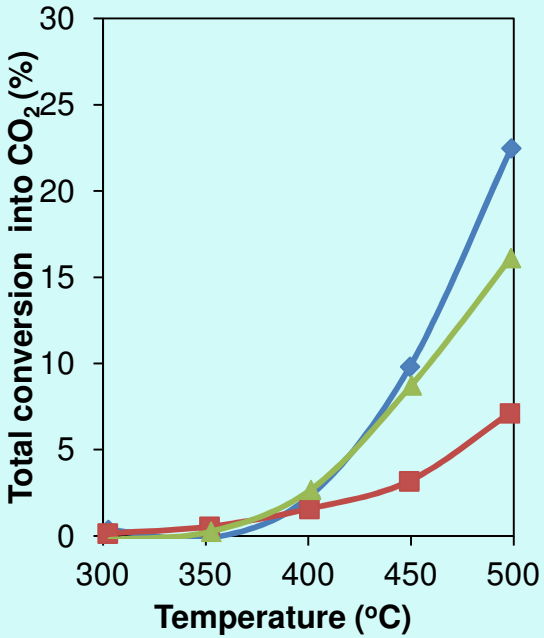
Isothermal, Isothermal wet , Isothermal 2nd dry

$CH_4 \rightarrow CO_2$

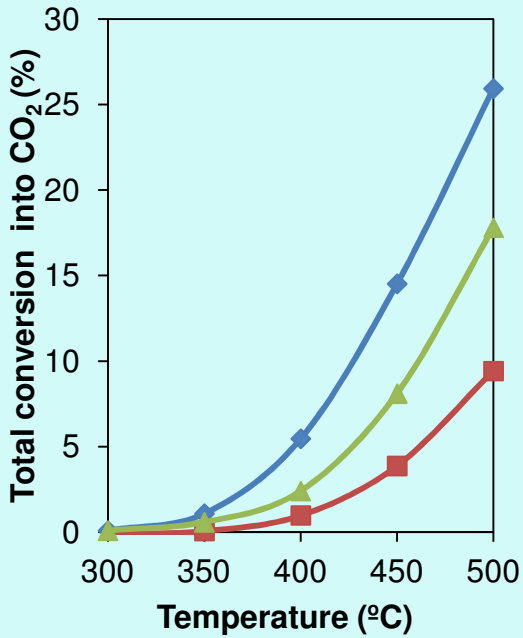
PdCeLa(2.2)-HBEA



PdCeLa(5.35)-HBEA



PdCeLa(2.67)-HBEA



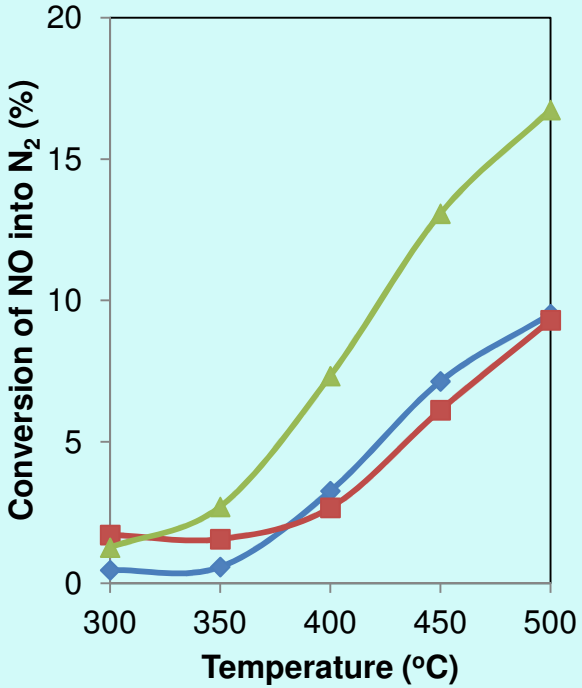
- All trimetallic catalysts that have been studied during these researches, showed better conversions for the reaction of methane combustion.

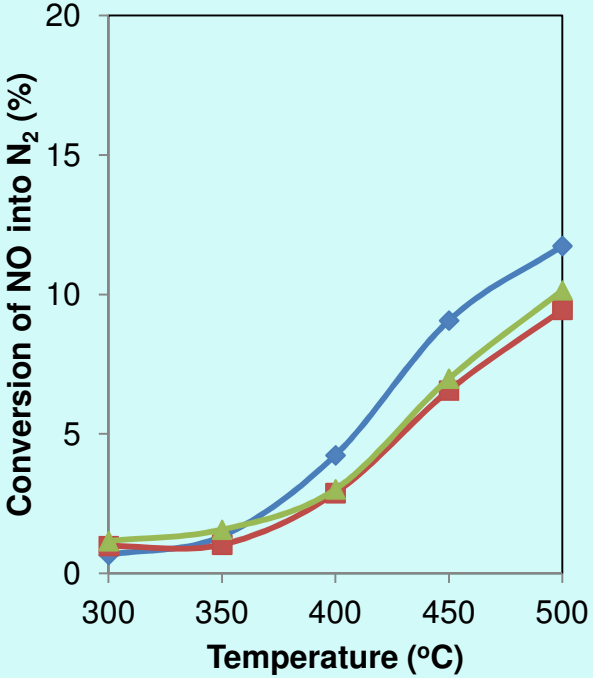
Results obtained over La(2.67)-HBEA and CeLa(2.67)-HBEA catalysts vs tri-metallic PdCeLa(2.67)-HBEA

NO_x conversion into N_2 during 1st isothermal catalytic test

NO_x conversion into N_2 during 2nd isothermal catalytic test

La(2.67)-HBEA, CeLa(2.67)-HBEA, PdCeLa(2.67)-HBEA





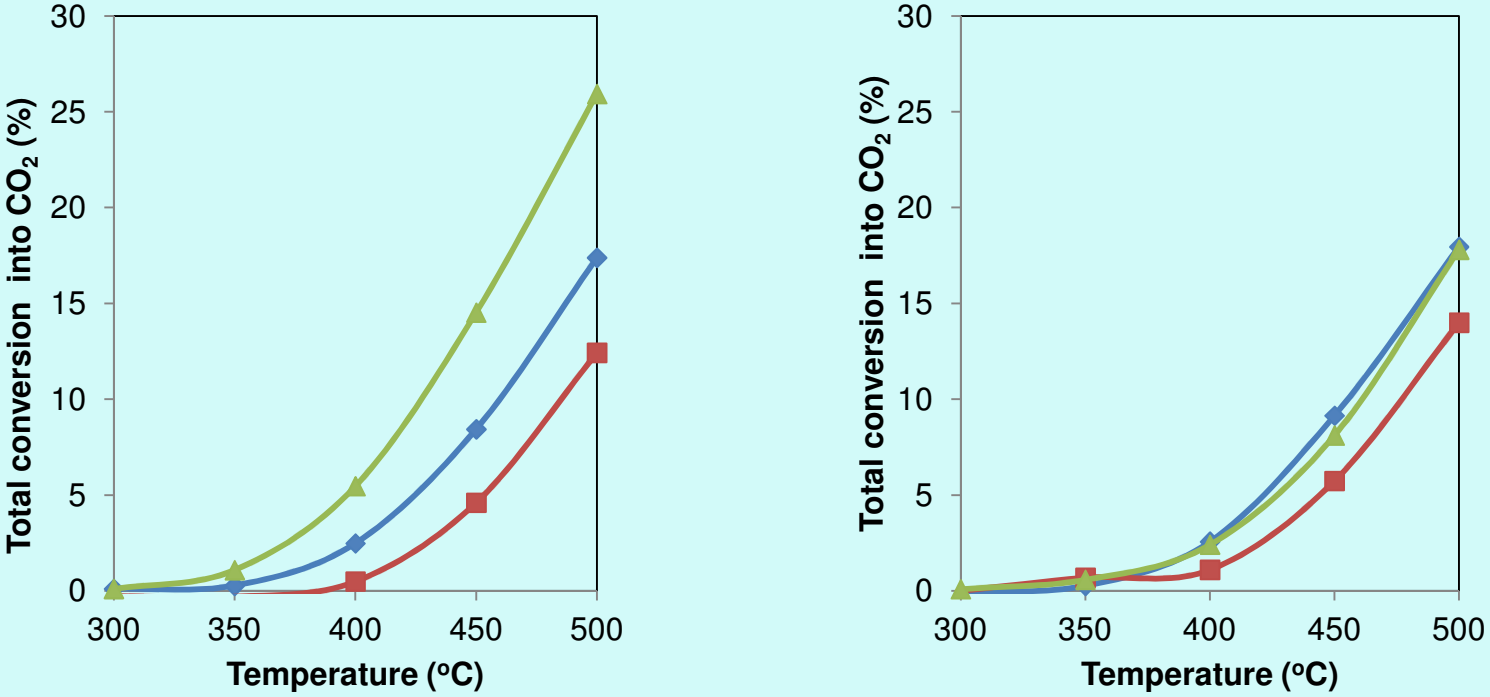
- Introduction of Ce did not produced the expected improvement in catalytic activity. This aim was observed only after the introduction of palladium.

Results obtained over La(2.67)-HBEA and CeLa(2.67)-HBEA catalysts vs tri-metallic PdCeLa(2.67)-HBEA

CH_4 conversion into CO_2 during 1st isothermal catalytic test

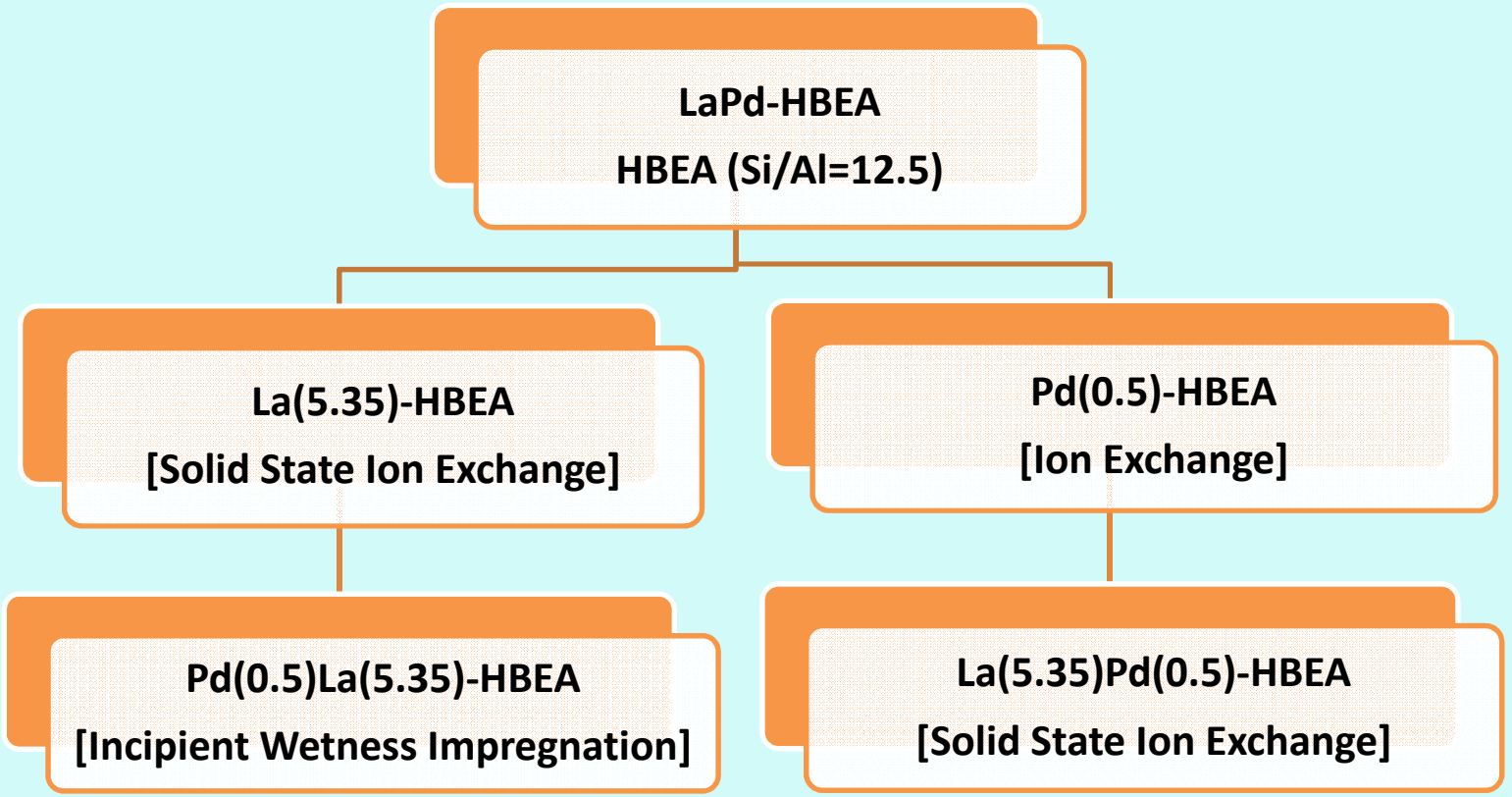
CH_4 conversion into CO_2 during 2nd isothermal catalytic test

La(2.67)-HBEA, CeLa(2.67)-HBEA, PdCeLa(2.67)-HBEA



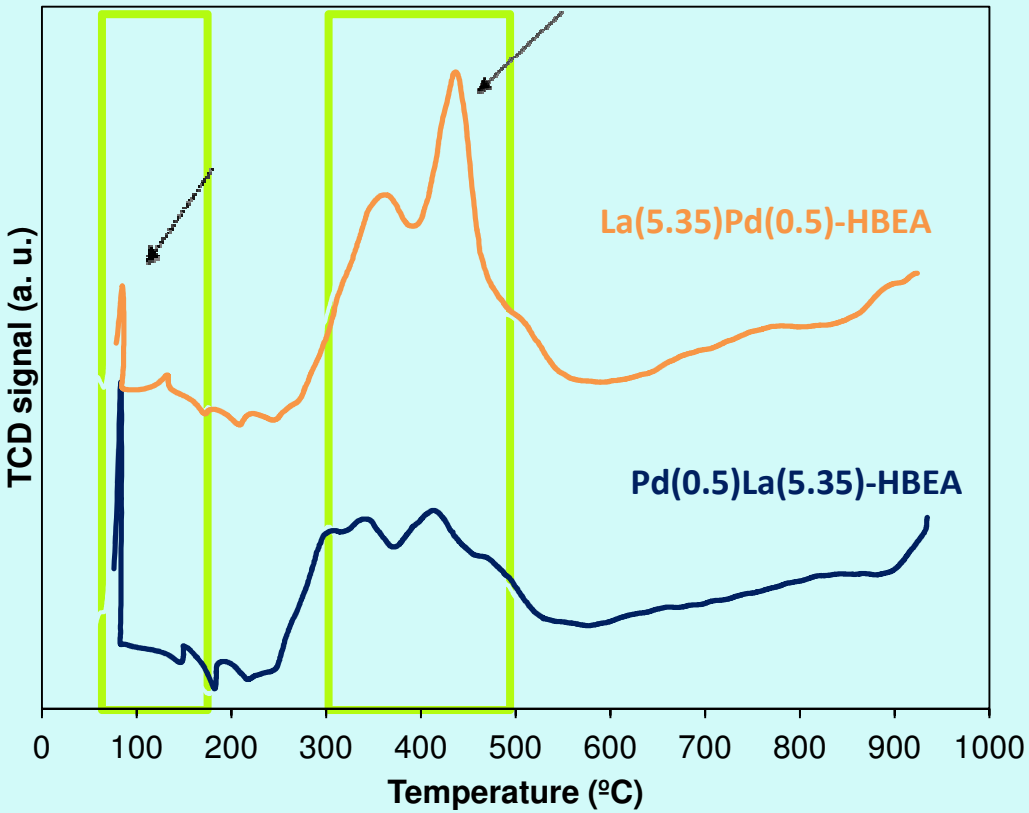
- Presented catalysts did not recover the initial activity after water test,
- During 2nd isothermal test, monometallic La catalyst had the best catalytic behavior, as well as for the reaction of NO_x reduction.

PdLa-HBEA



- ✓ Different order of exchanged metals,
- ✓ Different method of Pd ions introduction.

H_2-TPR profiles of bi-metallic PdLa –HBEA catalysts

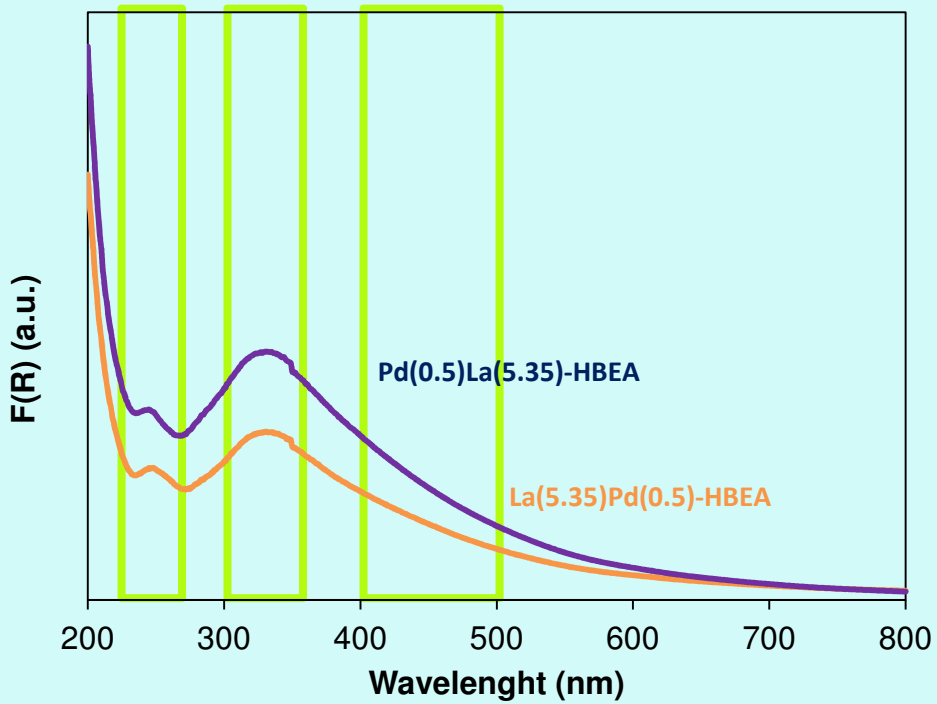


- 100°C → reduction of PdO species in the main channel of the zeolite structure,
- 300 to 500°C → reduction of PdO species on ion exchanged positions [9, 10].

[9] Zhang Z., Xu L., Wang Z., Xu Y., Chen Y., Journal of Natural Gas Chemistry, 19 (2010), 417–421.
[10] Park Y.K., Lee J.W., Lee C.W., Park S.E., Journal of Molecular Catalysis A: Chemical Vol. 158, (2000), 173–179.

Diffuse reflectance UV-vis spectra at room temperature for bi-metallic PdLa-HBEA catalysts

PdLa-HBEA catalysts

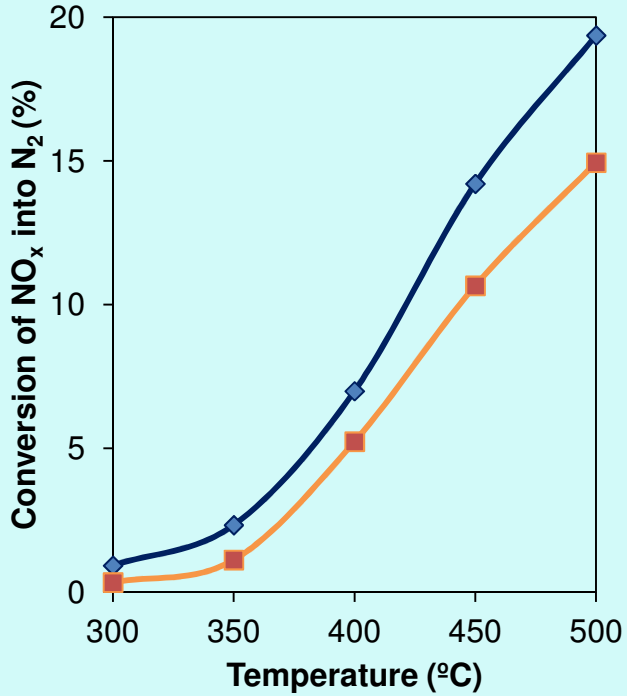


- 240nm →formation of palladium clusters,
- 340nm → formation of palladium chlorides in the surface of the support,
- 400 - 500nm → presence of palladium oxides [7].

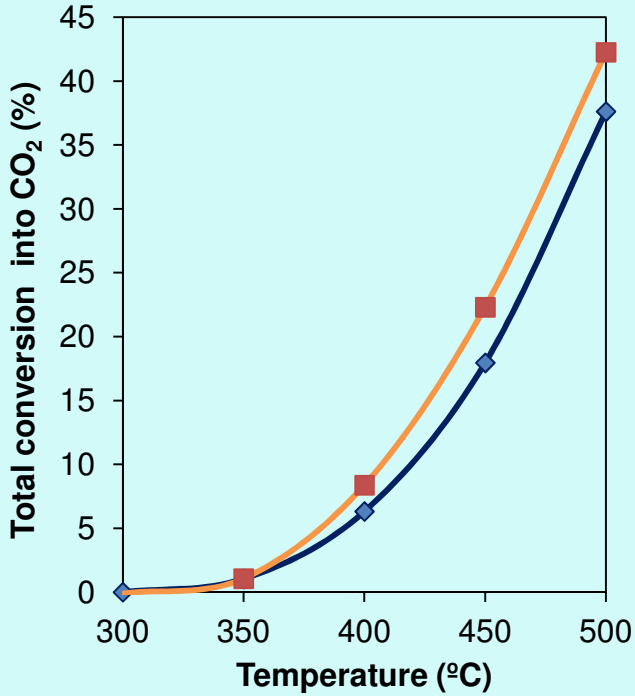
[7] Park Y.K., Lee J.W., Lee C.W., Park S.E., Journal of Molecular Catalysis A: Chemical Vol. 158, (2000), 173–179.

NO_x SCR steady-state catalytic test results, over bi-metallic Pd(0.5)La(5.35)-HBEA and La(5.35)Pd(0.5)-HBEA catalysts

NO_x conversion into N_2



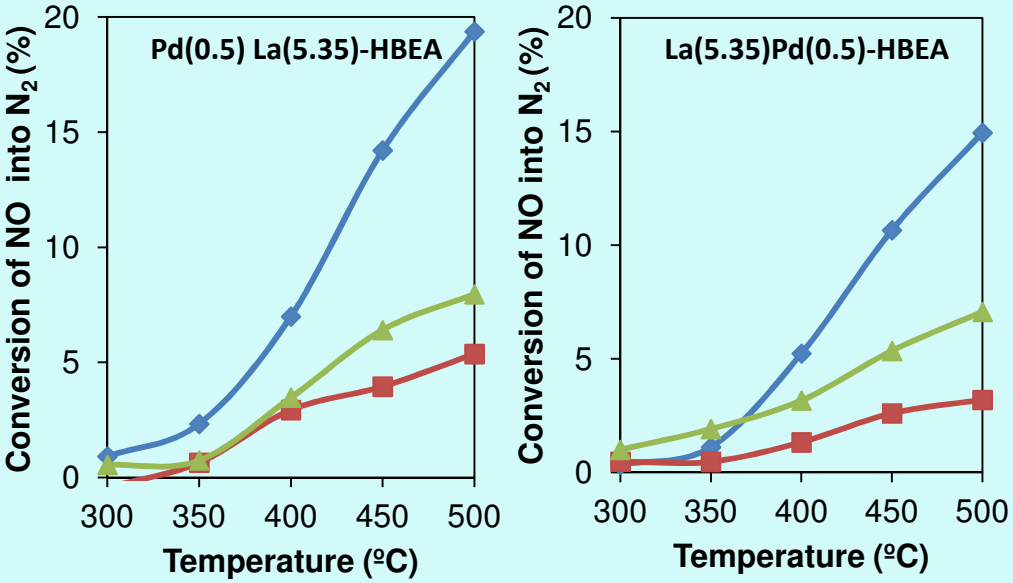
CH_4 conversion into CO_2



- Catalyst prepared by introducing La before Pd ions (blue line), showed better catalytic performance during NO_x reduction.

Conversions during the whole catalytic cycle, obtained over PdLa-HBEA catalyst

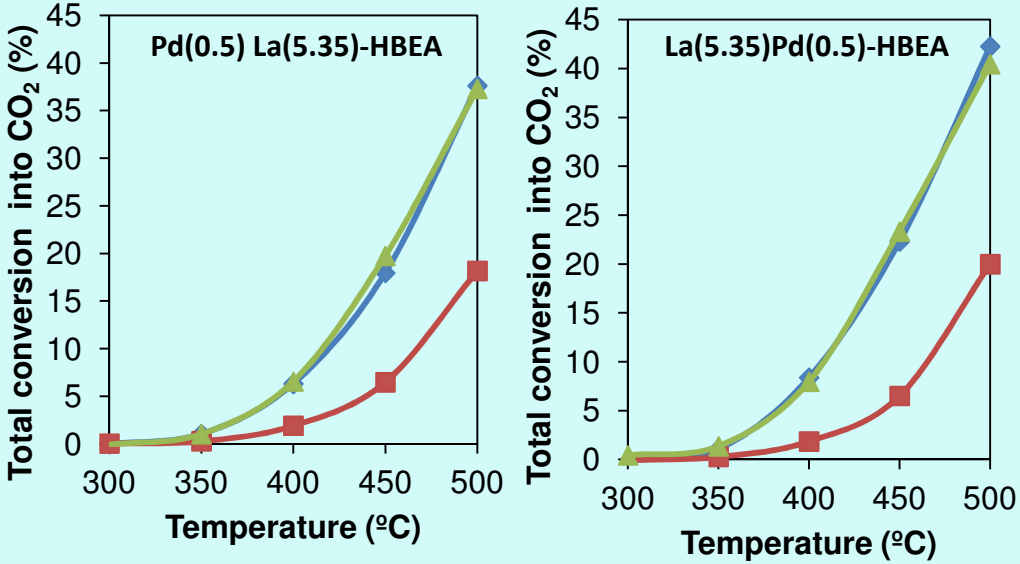
Isothermal, Isothermal wet , Isothermal 2nd dry



- Catalytic activity for PdLa-HBEA catalysts was restored only for the reaction of methane combustion.

NO_x conversion into N_2

CH_4 conversion into CO_2



Conclusions

- The catalytic activities observed in all BEA catalysts were relatively low, in fact, the conversion for NO into N_2 were below 20% and the total CH_4 combustion reaches maximum values around 40%,

- All of the samples exhibit a greatly decreased in the catalytic activity during the test under water conditions, which clearly shows the negative impact of water in gas stream,

- Only three catalysts had recovered their initial activity after contacting with water in gas stream and it may be attributed to the modification in the location of the ions or to a change in the strength of available acid sites,

Conclusions

- Most of the prepared catalysts had no acid sites after the last exchange and this might be contributing for the impossibility of catalysts to recover from the contact with water,

- Concerning the stability of the catalysts Ce appears to play an important role when it is present in bi-metallic catalysts.

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