DRY REFORMING OF METHANE OVER PrO_x-Al_2O_3 SUPPORTED Pt CATALYSTS

I. Tankov[1], S. Andonova[1], K. Arishtirova[1], B. Pawelec[2], J. L. G. Fierro[2], S. Damyanova[1]

[1] Institute of Catalysis, Bulgarian Academy of Sciences
[2] Instituto de Catalisis y Petroleoquimica, Madrid, Spain

Hydrogen – the fuel of the future

Presently, the energy policy of industrially developed countries and worldwide research efforts are focusing on the development of effective clean-up technologies and search for alternative fuels, whose utilization does not give rise to toxic and harmful emissions.

Hydrogen is considered an alternative fuel and non-polluting, efficient and cost-attractive energy carrier for the future.

95% of the hydrogen produced in the USA and 48% globally come from natural gas by applying steam reforming of methane.

Methane reforming processes

Steam reforming of methane:

$CH_4 + H_2O \rightarrow 3H_2 + CO$ $\Delta H^o_{298} = 206$ kJ/mol

Dry reforming of methane:

$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ $\Delta H^o_{298} = 247$ kJ/mol

Partial oxidation of methane:

$CH_4 + 0.5O_2 \rightarrow 2H_2 + CO$ $\Delta H^o_{298} = -38$ kJ/mol

Autothermal reforming of methane:

$CH_4 + CO_2 + 0.5O_2 \rightarrow H_2 + 2CO + H_2O$ $\Delta H^o_{298} = 211$ kJ/mol

Catalysts for methane reforming processes

1. Supported Pt, Pd, Rh, Ru catalysts

2. Supported Ni catalysts

3. Supports:

- ❖ metal oxides: Al_2O_3, ZrO_2, CaO, TiO_2, SiO_2
- ❖ mixed oxides: CeO_2-Al_2O_3, CeO_2-ZrO_2
- ❖ zeolites and mesoporous materials: ZSM-5, MCM-41.

Aims

- Preparation of active and stable Pt catalysts supported on Al_2O_3 modified with praseodymium oxide for dry reforming of methane.
- Characterization of the catalysts: X-ray diffraction analysis, X-ray photoelectron spectroscopy, temperature-programmed reduction with hydrogen, temperature-programmed desorption of CO_2, and catalytic activity measurements.
- Investigation of the effect of different amounts of PrO_2 on the catalytic behavior of Pt/PrO_2-Al_2O_3 catalysts in the reaction of dry reforming of methane.

Preparation of Pt/PrO_2-Al_2O_3 catalysts

❖ Preparation of PrO_2-Al_2O_3 supports

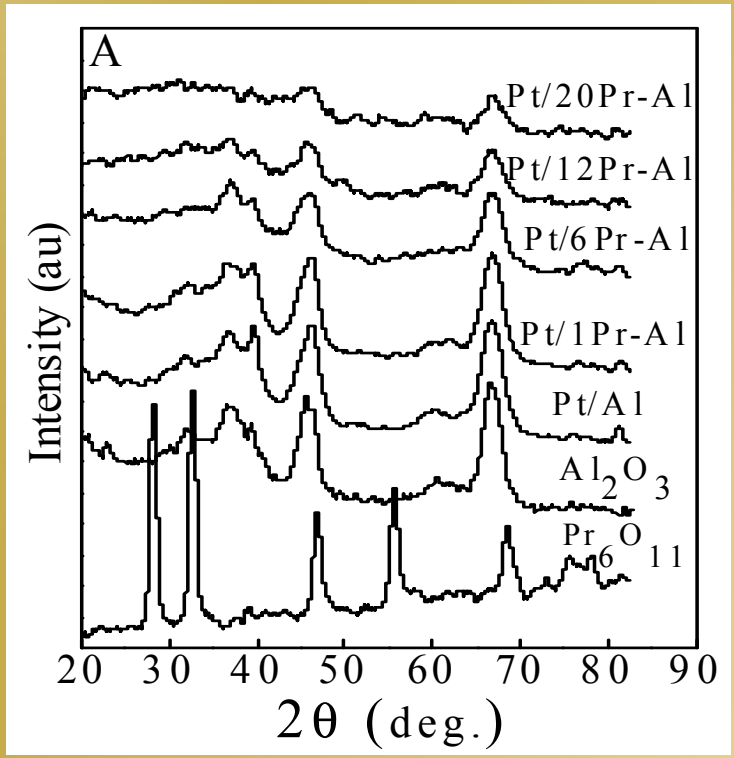
PrO_2-Al_2O_3 supports with different amount (1, 6, 12, and 20 wt.%) of PrO_2 were prepared by impregnation of Al_2O_3 with aqueous solutions of $Pr(NO_3)_3.6H_2O$. The samples were dried at 383 K for 12 h and calcined at 823 K for 2 h.

❖ Preparation of Pt/PrO_2-Al_2O_3 catalysts

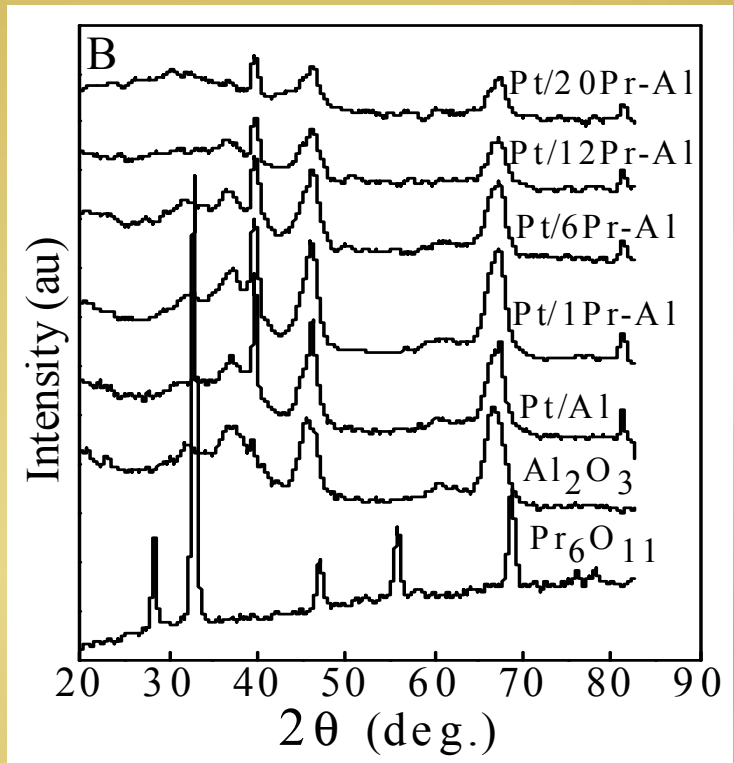
Pt/PrO_2-Al_2O_3 catalysts were prepared by impregnation of the supports by $H_2PtCl_6.6H_2O$ in ethanol. The amount of Pt was 1 wt.%. The catalysts were dried at 383 K for 12 h and calcined at 823 and 1023 K for 2 h.

X-ray diffraction analysis

Calcined at 823 K

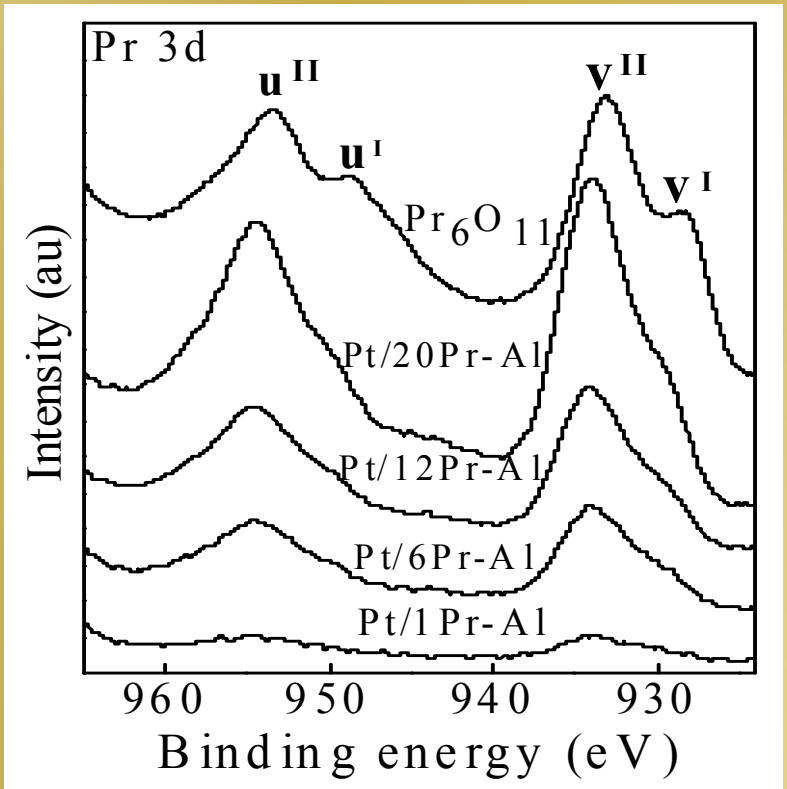


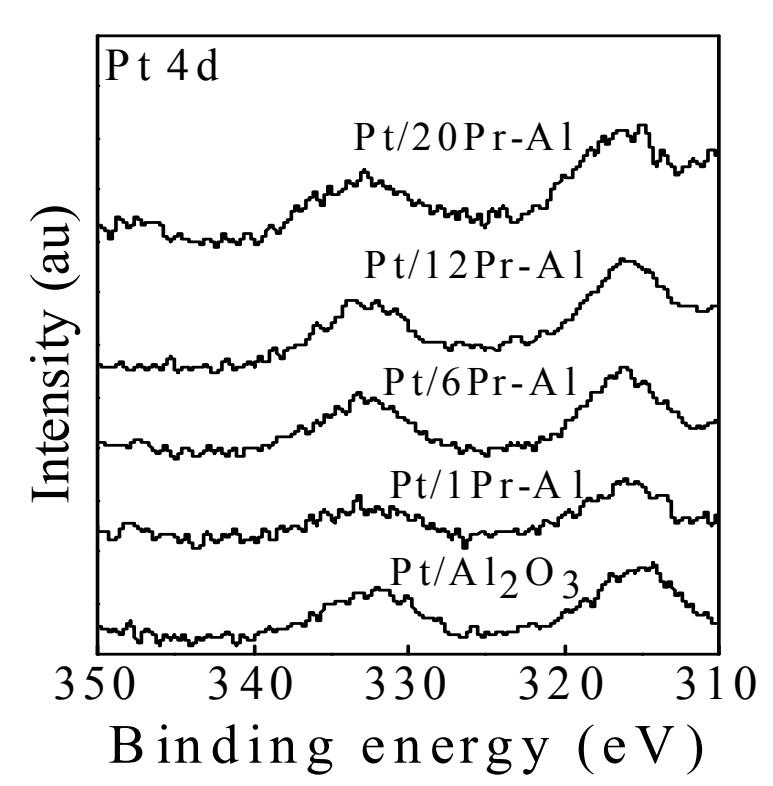
Calcined at 1023 K



- ❖ Presence of well dispersed Pr oxide species at both temperatures of calcination
- ❖ Strong agglomeration of Pt species after calcination at the higher temperature (1023 K)
- ❖ Formation of Pt species of smaller average size on increasing the PrO_2 content

X-ray photoelectron spectroscopy

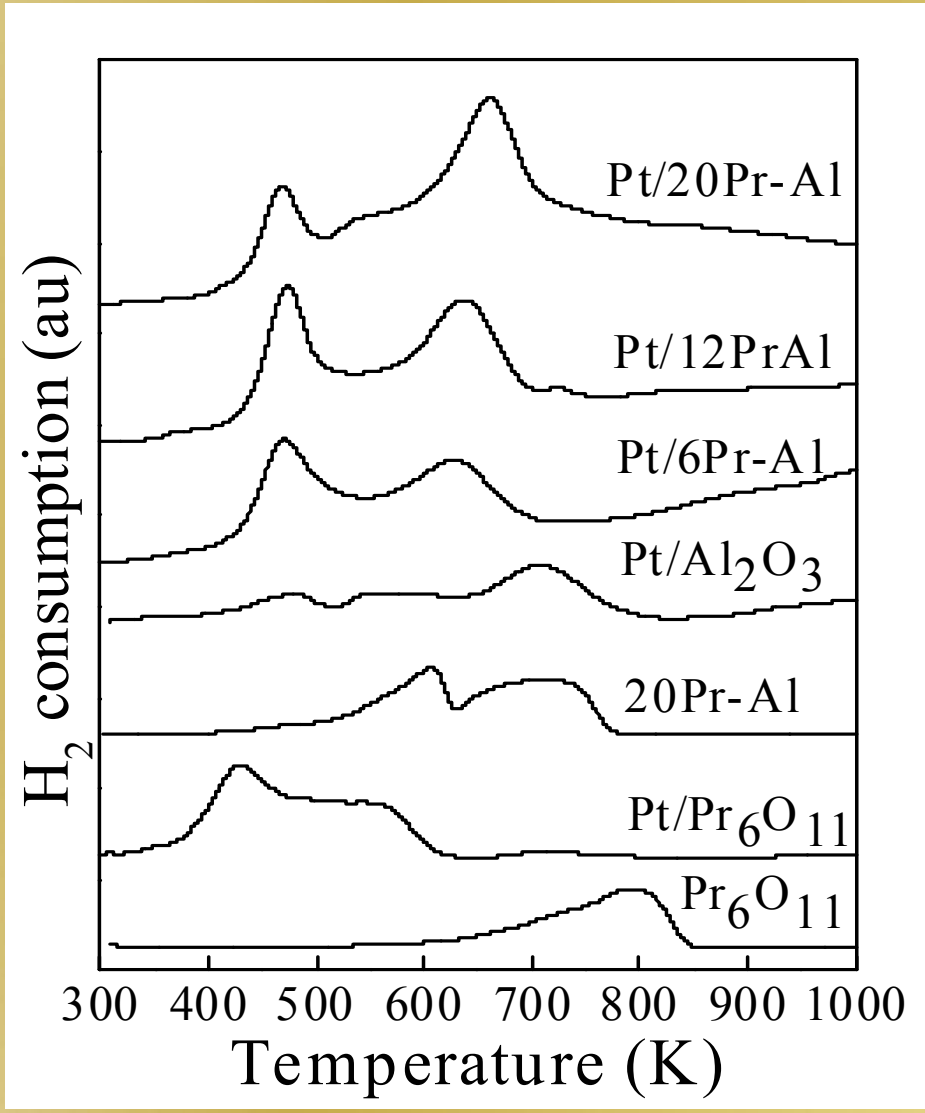




❖ The binding energy of Pr 3d level increases from 933.0 (for Pr_6O_{11}) to 934.0 eV for supported Pr oxide samples: formation of Pr-O-Al bond due to strong interaction between Pr oxide and alumina.

❖ The increasing PrO_2 loading leads to an increase of the binding energy of the Pt 4d core electron level from 314.8 (Pt/Al_2O_3) to 316.4 (Pt/20Pr-Al) due to close contact between Pt and Pr.

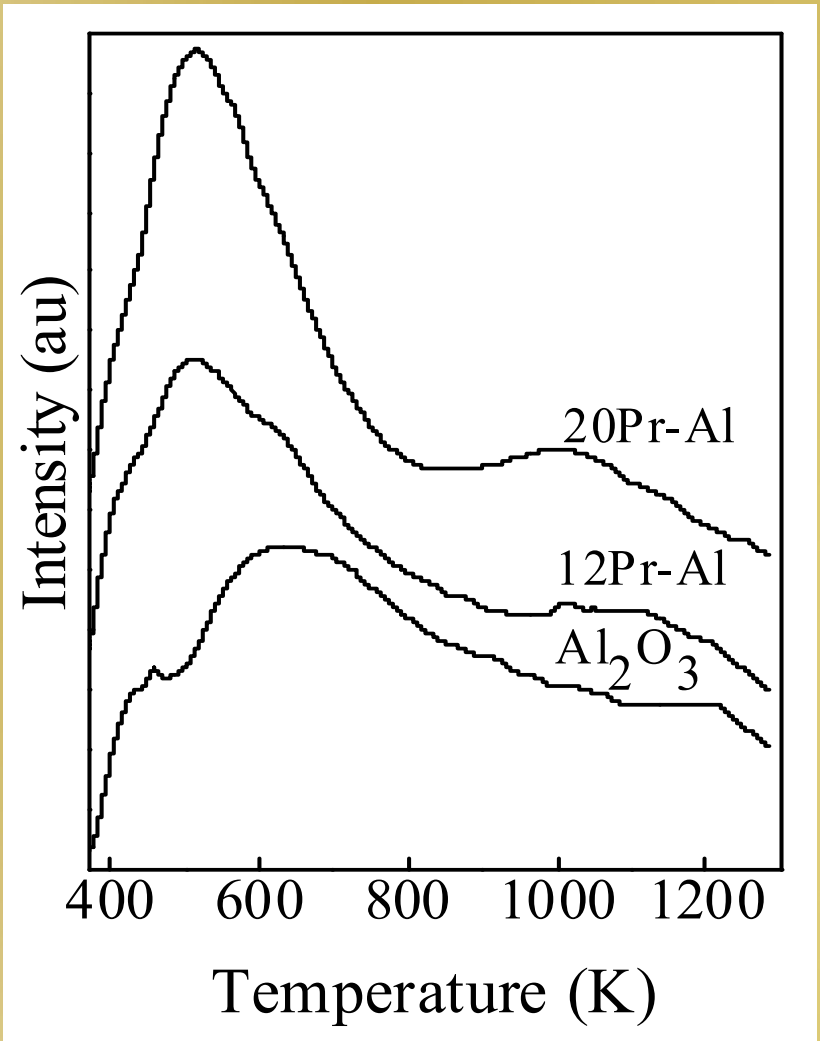
Temperature-programmed reduction



❖ The presence of platinum facilitates the reduction of the Pr oxide species.

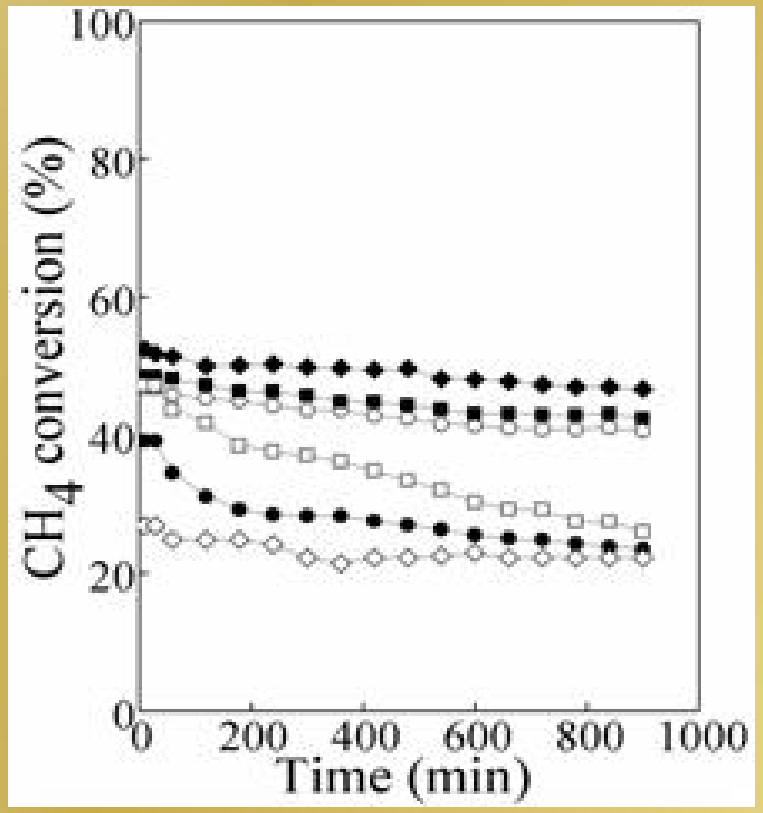
❖ Modification of Pt/Al_2O_3 by praseodymium oxide enhances the reducibility of the platinum oxide species. The latter is assigned to attenuation of the Pt-alumina interaction due to a strong interaction between Pr oxide and alumina.

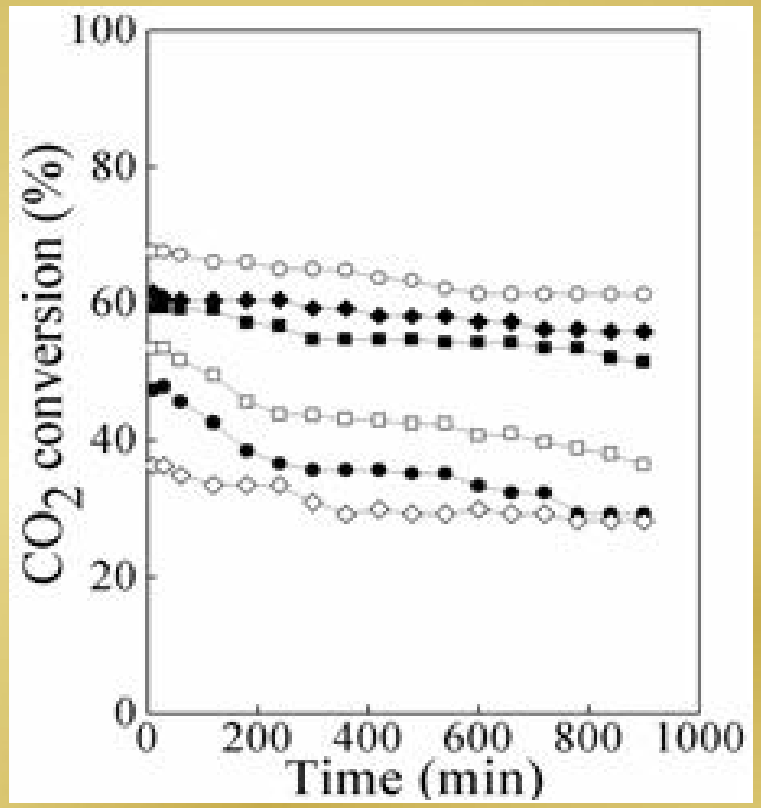
Temperature-programmed desorption of CO_2



❖ The increase of Pr oxide content leads to an increase of the quantity of desorbed CO_2, corresponding to the amount of surface basic sites. The presence of a higher number of basic sites on praseodymium-modified alumina supports is correlated with an increase in basicity of the samples and with a corresponding decrease in acidity of the systems.

Catalytic behavior of Pt/PrO_2-Al_2O_3 catalysts in dry reforming of methane





❖ High activity and stability of Pt/PrO_2-Al_2O_3 catalysts with PrO_2 content ≥ 6 wt.%.

Conclusions

❖ The presence of Pr oxide species in the Pt/PrO_2-Al_2O_3 catalysts leads to formation of well dispersed Pt particles. An improved Pt dispersion of the Pr-containing catalysts was suggested to originate mostly from interaction between the noble metal species and the Pr-modified alumina support.

❖ Addition of PrO_2 facilitates the reduction process of the Pt oxide species owing to attenuation of the Pt-alumina interaction caused by close contact between Pt and Pr.

❖ An increased basicity of the Pr-promoted supports was observed which was assumed to reflect to significant extent on the stability of the Pt/PrO_2-Al_2O_3 catalysts. Catalytic activity results displayed that the addition of Pr improves the performance of the Pt/Al_2O_3 catalyst in the reaction of dry reforming of methane. The high activity and stability of the Pt/PrO_2-Al_2O_3 catalysts with Pr content ≥6 wt.% were correlated with acceleration of the carbon gasification caused by a close contact between the Pt and Pr oxide species.

Acknowledgements

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Thank you for your attention!