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Thermal Stability of Platinum Supported Zinc Aluminate Combustion Catalysts

by W. Miśta[1], M. Zawadzki[1], J. Wrzyszcz[1], H. Grabowska[1] and J. Trawczyński[2]

[1] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences,*
P.O. Box 1410, 50-950 Wrocław 2, Poland
[2] *Institute of Chemistry and Technology of Petroleum and Coal, Wrocław University of Technology,*
50-344 Wrocław, Gdańska St. 7/9, Poland

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Mesoporous, nanocrystalline zinc aluminate supports for high-temperature catalysts were synthesized by hydrothermal method. $ZnAl_2O_4$ support was impregnated by an incipient wetness technique using aqueous solution of H_2PtCl_6 to obtain platinum contents up to 1wt.%. The possible application of platinum supported on $ZnAl_2O_4$ for high-temperature combustion was evaluated by comparison with traditional Pt/Al_2O_3 catalyst in combustion of *iso*-butene after high temperature treatment up to 1200°C. The prepared materials were additionally characterized by XRD and textural studies (specific surface area and pore size distribution).

Key words: catalytic combustion, $Pt/ZnAl_2O_4$, thermal stability

The properties of materials with spinel type structures make them interesting as catalyst and carriers for noble metals to substitute the more traditional alumina systems. The main characteristics of those solids, among them zinc aluminate, are a high thermal stability, no phase transition at high temperatures, a high mechanical resistance, and a low surface acidity [1–8]. Because the sintering resistance and the chemical stability of catalytic active phase are playing a crucial role in the high-temperature processes, zinc aluminate with spinel structure ($ZnAl_2O_4$) may be a promising material for the catalytic combustion of hydrocarbons, especially methane [9]. Well known conventional methods for the preparation of multicomponent powders using solid-state reactions with the mechanically mixed starting oxides, generally involve the high temperature calcination for many hours to homogenize the sample [10]. However, such a method gives materials with a very low surface area and pore volume. The samples obtained *via* coprecipitation techniques often yield compositional inhomogenities and surface area always below 100 m^2/g [11–13]. Traditional alumina catalytic carriers, which meet the demands of industrial users, must demonstrate a surface area within the range of 100–300 m^2/g and pore volume of 0.3–1.0 cm^3/g. Wrzyszcz and Zawadzki [14–15] report a new method for the preparation of zinc aluminate spinel with high surface area. The proposed method is based on the hydrothermal treatment of basic aluminium salts and zinc compounds at a relatively low temperature.

This paper presents results of our work including preparation and characterization of platinum, supported on high surface area zinc aluminate, prepared by hydrothermal method [16]. The influence of the gel synthesis technique on the porous structure of zinc aluminate and its evolution during heat treatment up to 1200°C was analyzed by XRD and nitrogen adsorption method. The catalytic activity was tested for the combustion of *iso*-butene in a gradientless, circular-flow reactor.

EXPERIMENTAL

Samples preparation: Three zinc aluminate samples prepared from different precursors were selected as support materials. The aluminium precursors were aluminium hydroxide or basic aluminium salts with the empirical formula $Al_2(OH)_{6-x}(Y)_x$, where Y = (NO_3) or Cl and x were close to 1. Basic aluminium salts were obtained by hydrolysis of powdered aluminium metal in aqueous solution of aluminium nitrate or chloride at elevated temperatures (preferably from 60–70°C). Aluminium hydroxide was produced through hydrolysis of solid aluminium isopropoxide in water excess heated at 70°C. Sample **A**, with $ZnO{:}Al_2O_3 = 1{:}1$, was prepared by the reflux boiling at 100°C for 10 days a water solution of hydrated zinc acetate and basic aluminium chloride. The resulting slurry was completely precipitated by adding urea solution to reach pH 7.5. The precipitate obtained was washed several times until the solution was free of chloride ions and the paste prepared was extruded. Sample **B** with $ZnO{:}Al_2O_3 = 1{:}2$ and **C** with $ZnO{:}Al_2O_3 = 1{:}1$ was prepared by heating in autoclave the water solution of zinc acetate and basic aluminium nitrate (sample **B**) or aluminium hydroxide (sample **C**) at 190°C for 3 h. After quenching the autoclave in cold water, the obtained sols were concentrated by evaporating, drained off and water washed. The resulting gels were then extruded. The solids **A**, **B** and **C** were dried up and calcined in airflow at 600°C for 6 h. Additionally the samples were heat treated between 600–1200°C to study the evolution of textural properties and phase changes. The Pt catalysts were prepared by the incipient wetness impregnation of zinc aluminate supports calcined at 600°C (sample **A**, **B**, **C**) and γ-Al_2O_3 support from Pechiney with an aqueous solution of H_2PtCl_6. The Pt loading was 1% by weight. The catalysts (1%Pt/**A**, 1%Pt/**B**, 1%Pt/**C**, 1%Pt/Al_2O_3) were dried at 120°C, calcined at 500°C and reduced in H_2 at 450°C.

Characterization: The XRD diffractograms and lattice parameters were measured using CuK_α radiation on a DRON-3 powder diffractometer. The WinFit software [17] was used to determine the peak position, by fitting entire peak profiles. The mean crystallite diameters were estimated based on the Scherrer's equation for the X-ray diffraction (XRD) patterns. The width of the Pt(111) peak at half-maximum was corrected for K_α doublet and instrumental broadening.

The BET specific surface area and porosity were determined by nitrogen adsorption at –196°C using an automatic volumetric apparatus (FISONS Sorptomatic 1900). Samples were previously degassed for 5 h at 250°C and 10^{-3} Torr. The pore size distribution was analyzed following the Dollimore-Heal method [18], which was applied to the desorption branch of each isotherm. The catalytic activity was measured in a gradientless, circular-flow reactor as reported previously [16,19]. Catalyst (2.5 g; cylindrical extrusions with diameter 1 mm) was loaded into a stainless-steel reactor in the stream of mixture of 0.05 vol.% *iso*-butene with air at the space velocity of 10^3 h^{-1}. It was checked that the reaction was not diffusion controlled and the heat-transfer limitations were negligible. The unreacted *iso*-butene was analyzed in a gas chromatograph with FID detector.

The thermal stability of the Pt catalysts was measured after an ageing test performed at 1200°C in air for 5 h. Comparison of the catalysts was performed by measuring the T_{50} temperature, defined as the temperature corresponding to 50% of hydrocarbon conversion.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the dried samples (**A**, **B**, **C**) are presented in Fig. 1. The phase compositions of the gels following the drying process depended mainly on hydrothermal conditions. Sample **A**, formed from the mixed solutions of parent metal salts by mild hydrothermal treatment at 100°C for 10 days, was found to be semi-amorphous, as shown in Fig. 1a. However, a small amount of microcrystalline pseudoboehmite $AlO(OH)\cdot xH_2O$ together with ultra-fine $ZnAl_2O_4$ spinel {broad spinel peaks $(111)_s$ and $(311)_s$}, were visible. The samples **B** and **C** hydrolyzed in hydrothermal conditions at 190°C appeared to be a nanocrystalline single-phase material with the spinel-type structure. The XRD diagram for sample **B** (Fig. 1b) with smaller $ZnO:Al_2O_3$ ratio provides strong evidence for the nanocrystalline Al_2O_3-$ZnAl_2O_4$ solid solution formation during the hydrothermal hydrolysis of zinc acetate and basic aluminium nitrate [20]. The sample **C** was composed of the well-crystallized fine $ZnAl_2O_4$ spinel (Fig. 1c). The first precipitate formed during hydrothermal synthesis is a amorphous aluminium hydroxide gel, which then continuously transforms to stoichiometric spinel $ZnAl_2O_4$ particles by continuous diffusion of the Zn^{+2} ions to the surface of alumina hydroxide according to the solution and precipitation mechanism proposed by Hirano *et al.* [21]. After the heat treatment of dry precursor samples (**A**, **B** and **C**) at 600°C, X-ray patterns show only $ZnAl_2O_4$ spinel peaks. As-prepared materials were used as support for platinum catalysts.

After the high-temperature heat treatment of catalyst samples at 1200°C, the formation of well crystallized mixture of α-Al_2O_3 and $ZnAl_2O_4$ spinel was observed for catalyst 1%Pt/**B**, which confirmed a smaller $ZnO:Al_2O_3$ ratio (Fig. 2b). The $ZnAl_2O_4$ spinel was in fact the main phase in two other catalysts 1%Pt/**A** and 1%Pt/**C** (Fig. 2a and 2c). On all the catalysts samples, XRD showed that aging in air at 1200°C led to an excessive sintering of the platinum particles, similar on all the catalysts. The platinum average crystallite size for all catalysts calcined at 1200°C, calculated from the broadening of X-ray (111) Pt line, were *ca.* 600 Å. The lattice parameter of the synthe-

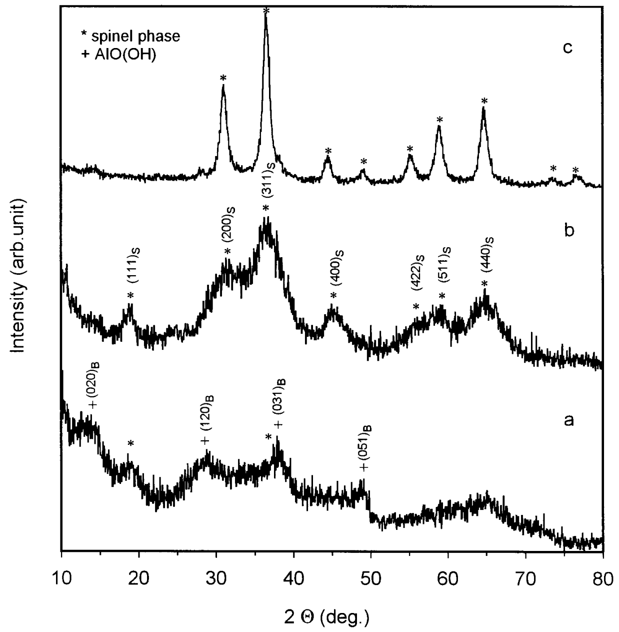

Figure 1. X-ray diffraction powder patterns of microcrystalline precursor samples dried at 120°C: a) sample **A**; b) sample **B** (indexing corresponding to spinel-type phase); c) sample **C**.

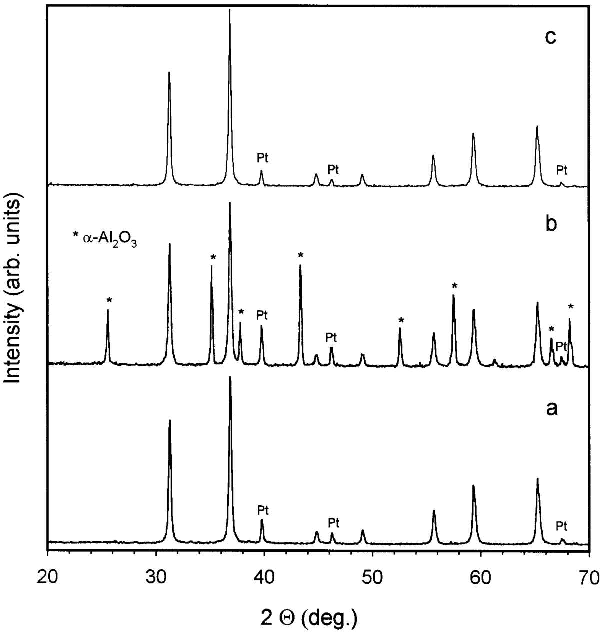

Figure 2. X-ray diffraction powder patterns for Pt catalyst powders calcined at 1200°C for 5 h: a) catalyst 1%Pt/**A**; b) catalyst 1%Pt/**B**; c) catalyst 1%Pt/**C**.

sized $ZnAl_2O_4$ spinels at 1200°C approached the reported value for the stoichiometric composition (a = 8.0848 Å, JCPDS Card 5-669) and reached a = 8.085 Å. The nitrogen adsorption-desorption isotherms, together with the pore size distribution of supports after the heat-treatment at 600°C, are reported in Fig. 3. All samples give nitrogen adsorption isotherms of type IV with closed hysteresis loops described as type H1 in the IUPAC classification [22], which suggested the presence of mesopores. These types of hysteresis loops are characteristic for solids consisting of particles crossed by nearly cylindrical channels or made by aggregates or agglomerates of spheroidal particles. The pore size distribution analysis (Fig. 3b) showed monomodal pore radius centred at about 2.5, 4.5 and 7 nm for samples **B**, **A** and **C**, respectively. The surface areas and pore volumes for a series of samples after the heat-treatment in air up to 1200°C are collected in Table 1. Clearly visible is the strong decrease in surface area of the Al_2O_3-$ZnAl_2O_4$ solid solution (sample **B**) between 1000°C and 1100°C, related to the partial transition to the stable α-Al_2O_3 phase. This is also confirmed by the X-ray results of the 1%Pt/B catalyst, given in Fig. 2b. The continued decrease at higher temperatures is due to crystal growth and densification. The $ZnAl_2O_4$ support materials (sample **A** and **C**) with close to stoichiometric $ZnO:Al_2O_3$ = 1:1 ratio had a lower surface area after heat-treatment at 600°C than sample **B** with a smaller $ZnO:Al_2O_3$ ratio. There is a general trend to increase the surface area on increasing the alumina contents of the ZnO-Al_2O_3 mixed metal oxides [20]. However, after high temperature ageing at 1200°C stoichiometric spinel samples (**A** and **C**) had a much higher surface area, (18 m^2/g and 14 m^2/g, respectively) than sample **B** (Table 1).

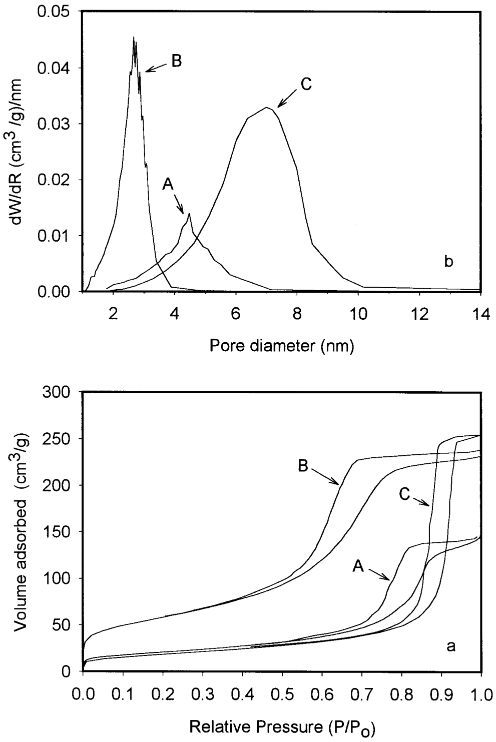

Figure 3. Textural properties of zinc aluminate supports calcined at 600°C for 5 h: a) nitrogen adsorption-desorption isotherms for samples **A**, **B** and **C**; b) pore size distributions for samples **A**, **B** and **C**, based on the Dollimore-Heal method.

Table 1. Textural properties of samples after heat treatment in air for 5 h.

Sample/treatment	Surface area [m^2/g]	V_p [cm^3/g]
A/600°C	74	0.217
A/1100°C	26.9	0.17
A/1200°C	18	0.11
B/600°C	173	0.23
B/1000°C	67	0.2
B/1100°C	16	0.046
B/1200°C	8	0.028
C/600°C	66	0.389
C/1100°C	19.6	0.167
C/1200°C	14.2	0.11
Al_2O_3/600°C	266	0.38
Al_2O_3/1100°C	20	0.05
Al_2O_3 /1200°C	5	0.018

The *iso*-butene conversion curves obtained for Pt/$ZnAl_2O_4$ catalysts, calcined at 1200°C for 5 h depending on the reaction temperature, are shown in Fig. 4. By comparison of temperatures at which the conversion of *iso*-butene reaches 50%, it can be concluded that all Pt/$ZnAl_2O_4$ catalysts sintered at 1200°C have a higher activity in comparison with that supported on traditional γ-Al_2O_3. The modification of catalytic activity of catalysts can be related with the difference with textural properties of aged supports that are collected in Table 1. Additionally the nitrogen adsorption-desorption isotherms for the reference 1%Pt/Al_2O_3 catalyst and the most active catalysts (1%Pt/**A**) calcined at 1200°C are shown in Fig. 5. All accessible pore volume (V_p = 0.11 cm^3/g) for platinum supported on zinc aluminate is in the mesoporous range, what is an evidence of type IV adsorption isotherm with well visible closed hysteresis loop. Nitrogen adsorption isotherm for platinum supported on alumina is of type II, which is characteristic to nonporous solids. The use of zinc aluminate support causes, therefore, a significant improvement of the thermal stabilization of the Pt catalysts. Similar results were obtained by Labalme *et al.* [23]. They studied the resistance of platinum deposited onto alumina and barium modified alumina towards ageing at 1200°C using the catalytic combustion of *n*-butane as a test reaction. Despite the good thermal behaviour of the Ba-loaded support (S_{BET} = 53–65 m^2/g aged at 1200°C for 5 h), the dispersion of platinum is very low and hardly measurable (<1%). Surprisingly, the activity of aged Pt/Ba-Al_2O_3 catalyst is much higher than for reference Pt/Al_2O_3 catalyst. They come to the conclusion that the catalytic activity in total combustion of hydrocarbons cannot be directly connected with the metal dispersion. Some authors found [24] that the total hydrocarbon oxidation was a structure sensitive reaction, since a change in the turn-over frequency (TOF) with the Pt particle size was observed. However, the effect of influence of the Pt particle size on the catalytic combustion of different hydrocarbons is problematic, probably because the correlation between catalytic activity and metallic dispersion depends on the type of hydrocarbon [25]. Additionally, platinum catalysts are sensitive to other factors as chlorine [26]. Our catalysts contain small quantities of chlorine, because of usage of metallic precursor (H_2PtCl_6) and in the case of support **A** also chlorine from the basic aluminium chloride, which was used as a substrate. The presence of chlorides favoured the agglomeration of small Pt cluster under a reducing environment during activation of catalysts [27].

It is well known that sintering of highly dispersed metals is controlled by a combination of atomic diffusion (surface and bulk), and also by vapour transport under high-temperature conditions [28]. At 1200°C, the size and aggregation texture of nanocrystals possibly retarded the occurrence of a meaningful densification. The spinel surface has none or very few hydroxyl groups, irrespective of surface area. Interaction of the spinel surface with large Pt particles is therefore very limited. It is probably beneficial for a stable dispersion of the active noble metals to have a crystalline support with a relatively inactive surface. However, precise explanation of such enhanced catalytic activity of large Pt particles in Pt/$ZnAl_2O_3$ catalysts will need the use of more sensitive methods to study these catalysts.

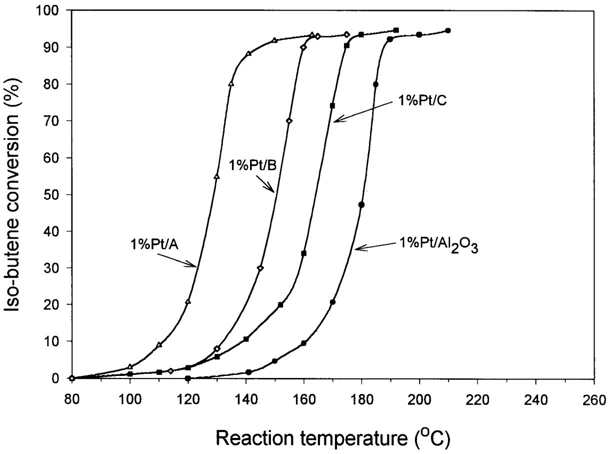

Figure 4. Effect of temperature on *iso*-butene conversion for 1%Pt supported on zinc aluminate (sample **A**, **B**, **C**) and Al_2O_3 support. All catalysts samples were calcined at 1200°C for 5 h.

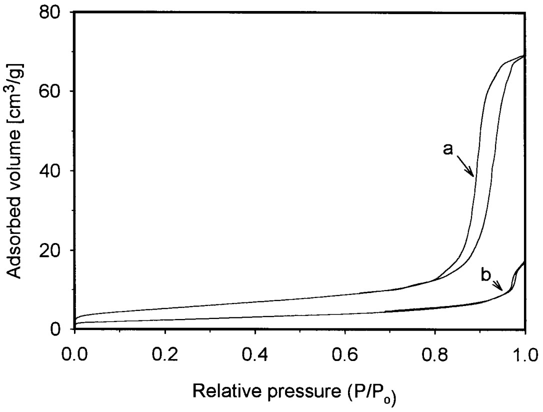

Figure 5. Nitrogen adsorption-desorption isotherms for catalysts after calcinations at 1200°C for 5 h: a) 1%Pt/A and b) 1%Pt/Al_2O_3.

CONCLUSIONS

A series of Pt/$ZnAl_2O_4$ catalysts were compared as to their suitability in combustion application. We find that all Pt/$ZnAl_2O_4$ catalysts are much better thermal stable in comparison with traditional Pt/Al_2O_3 catalysts after high temperature heat-treatment at 1200°C. Despite the difference of catalytic activity, the dispersion of Pt is very low, as evidenced by the formation of very large particles (*ca* 600 Å) in all catalysts calcined at 1200°C in air. Spinel-type oxides show a better resistance to sintering than aluminas. Our nanocrystalline $ZnAl_2O_4$ materials could find a practical application in high temperature catalytic combustion of hydrocarbons.

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