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Structural and catalytic properties of Pt/$ZnAl_2O_4$ as catalyst for VOC total oxidation

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ABSTRACT

Spinel type zinc aluminates prepared through the methods of microwave-assisted solvothermal and non-conventional coprecipitation were used as platinum catalyst supports in this study. Structure of the catalysts containing 0.5, 1 and 3 wt.% Pt was characterized by means of XRD, EDS, HRTEM, N_2 adsorption–desorption at −196 °C and H_2 chemisorption. Catalytic activity was tested in the reaction of *iso*-butane total oxidation. Prepared samples possessed desired properties for application as platinum support for catalytic combustion of VOC. All samples exhibited nanocrystallinity with well defined spinel structure, high surface area ($S_{BET} > 100\,m^2/g$) and mesoporosity, very good metal dispersion (up to 96%) and good catalytic activity in *iso*-butane combustion with thermal stability. VOCs being one of the main pollutants of the air are an environmental problem so their destroying by using effective catalytic combustion is very attractive.

1. Introduction

Volatile organic compounds (VOCs), originated mainly from emissions of industrial processes and automobile exhausts, are recognized as major contributors to air pollution because of their toxicity to human health and their contribution to the formation of photochemical smog, depletion of stratospheric ozone and the production of ground-level ozone [1]. Several alternative VOCs removal technologies are available but catalytic combustion seems to be one of the most effective and economically feasible [2]. Noble metal-based catalysts, such as supported platinum, show good activity at low temperatures for the complete oxidation of VOCs and are being widely used for many years. Nevertheless, researchers are still looking to improve their catalytic properties, among others by using new support materials or new/modified methods of their preparation [3–5].

A lot of works concerning methods of nanomaterials synthesis have appeared in the recent years. Well known are: sol–gel, coprecipitation, combustion and solvothermal methods. The broad group of methods based on solvothermal synthesis is very interesting because of the great possibility of influencing the properties of obtained materials [6]. Various parameters play important role in this kind of process, e.g. temperature, pressure, reaction medium, methods of autoclave heating, etc. [7]. As a result, materials suitable for catalytic applications may be obtained in this way.

The aim of this work was to study the structural and catalytic properties for diluted *iso*-butane total oxidation of zinc aluminate with spinel structure $ZnAl_2O_4$ obtained by solvothermal and non-conventional coprecipitation method. Spinel materials, including aluminates, have recently gained considerable interest in the field of catalysis since they might be used as supports for noble metals to substitute the more traditional materials, such as γ-alumina [8]. *Iso*-butane being short chain alkane with high vapour pressure is characterized by long lifetime in air and temperature of non-catalytic combustion ∼700 °C then seems to be suitable as a VOC probe molecule. Studying its complete destroying at low concentrations and searching for efficient catalysts is essential since mixture of propane and butanes (as LPG) is increasingly used as a substitute for gasoline and diesel in transport vehicles. Moreover, light hydrocarbons, recognized as the most difficult to destroy, are emitted from a range of stationary sources and their treatment is a priority.

2. Experimental

Zinc acetate and aluminum isopropoxide (with molar ratio 1:2) suspended in 1,4-butanediol were used as starting materials for solvothermal synthesis, which was provided in the reactor with microwave heating (MW, Ertec 02-02) through 0.5 h at 200 °C, under pressure up to 25 bar. For non-conventional coprecipitation method (Cp), water solutions of zinc and aluminum nitrates were used (cooled down below 10 °C and precipitated with NH_3aq to pH 11). Synthesized materials were washed, extruded, air-dried, calcined at 550 °C, impregnated with water solution of H_2PtCl_6 to obtain 0.5, 1 and 3 wt.% of Pt loading. Finally, after drying at 110 °C,

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all samples were heated at 550 °C for 3 h in air, washed with boiling water to remove chlorine ions and next reduced in H_2 flow at 500 °C. Some of the catalysts were additionally heated at 800 °C in air and reduced at 500 °C to examine their thermal resistance. The catalysts were denoted as follows: e.g. 3Pt_MW_550 means the catalyst sample with 3 wt.% Pt supported on solvothermally prepared $ZnAl_2O_4$, after heating at 550 °C. The Pt loading in all catalysts was determined by the inductively coupled plasma ICP-AES method.

The obtained samples were characterized through the use of various methods. The crystal structure was determined by X-ray diffraction (XRD, X'Pert Pro Panalytical diffractometer) using Cu Kα radiation. The crystallite size was calculated based on the Scherrer equation. Energy dispersive spectroscopy (SEM equipped with EDAX, Philips SEM515) was used for chemical analysis. The morphology and microstructure were studied by a transmission electron microscopy (HRTEM and SAED, Philips CM20 Super Twin). Textural properties (surface area and porosity) were determined from nitrogen adsorption–desorption data obtained in a volumetric system (Autosorb-1 Quantochrome Instruments apparatus). The dispersion of Pt catalysts was determined by the volumetric H_2 chemisorption method at 100 °C using home-made apparatus. The mean Pt particle size was estimated from H_2 uptake using the relation $d_{Pt}(nm) = 1.13/(H/Pt_{total})$. The catalytic tests were performed in a fixed-bed flow reactor placed in a programmable furnace, by passing a diluted *iso*-butane (2000 vppm in air) over 1.1 g catalyst. Temperature in the reactor was controlled by PID Temperature Controller connected with the thermocouple placed exactly at the top of the catalyst bed. Before the test, each catalyst was first pressed and compacted, and then crushed and sieved to the desired size. The catalysts were packed to a constant volume (~1 cm^3) to give gas hourly space velocity GHSV of 21,000 h^{-1}. The combustion products were analyzed on-line using a gas chromatograph (Chromatron GCHF 18.3) with FID detector. Activity measurements were obtained once steady state was attained and the data were an average of at least 3 consistent analyses.

3. Results and discussion

XRD analysis has confirmed spinel structure of $ZnAl_2O_4$ for all catalyst samples. XRD patterns of 1Pt_MW catalyst heated at 550 and 800 °C in comparison to the as-prepared metal-free support material are presented in Fig. 1 as an example. Very broad diffraction peaks for the as-prepared support, become more intense and sharper after heat treatment indicating subsequent increase in the degree of crystallinity. It could be noticed that pattern of catalyst sample heated at 550 °C does not show any diffraction peaks characteristic for Pt. Two board and weak peaks at $2\theta = 39.8°$ and 46.2°, which could be assigned to (1 1 1) and (2 0 0) lattice plane of Pt (JCPD 04-0802), appear only after heat treatment of the catalysts at 800 °C and reduction at 500 °C. XRD measurements indicate nanocrystalline structure of $ZnAl_2O_4$ without impurities. Average crystallite sizes of ~5 and ~7 nm after heating at 550 °C and 800 °C, respectively, are dependent only on the temperature of heat treatment. It indicates good support thermal stability irrespective of its preparation method.

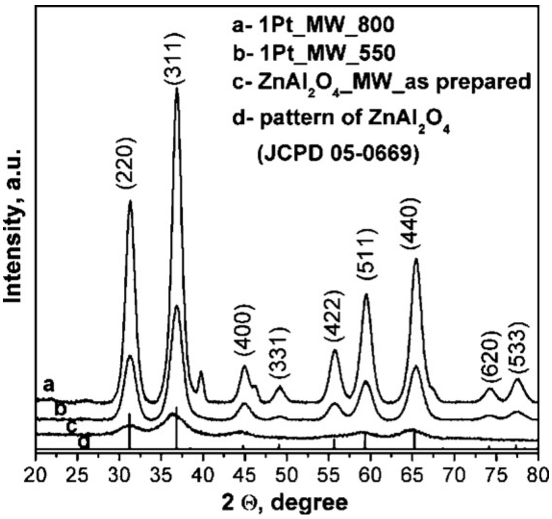

Fig. 1. Diffractograms of $ZnAl_2O_4$ samples.

EDS analysis has confirmed platinum presence and spinel stoichiometry (Al:Zn = 2:1). Moreover, Cl atoms are detected: the highest (~2.53 at.%) concentration for samples with 3% Pt and the lowest (~0.4 at.%) for samples with Pt concentration amounted to 0.5 wt.%.

HRTEM and SAED analysis are in good agreement with XRD results. Apart from $ZnAl_2O_4$ crystallites only small dark spots without lattice fringes are visible on the recorded micrographs. SAED patterns of samples heated at 550 °C cannot prove the Pt presence, only diffraction rings characteristic for zinc aluminate with spinel structure are present. HRTEM images of 3Pt_MW_550 and 3Pt_MW_800 (Fig. 2) show higher crystallites sizes as well $ZnAl_2O_4$ as Pt, which is visible as dark spots or crystals with characteristic

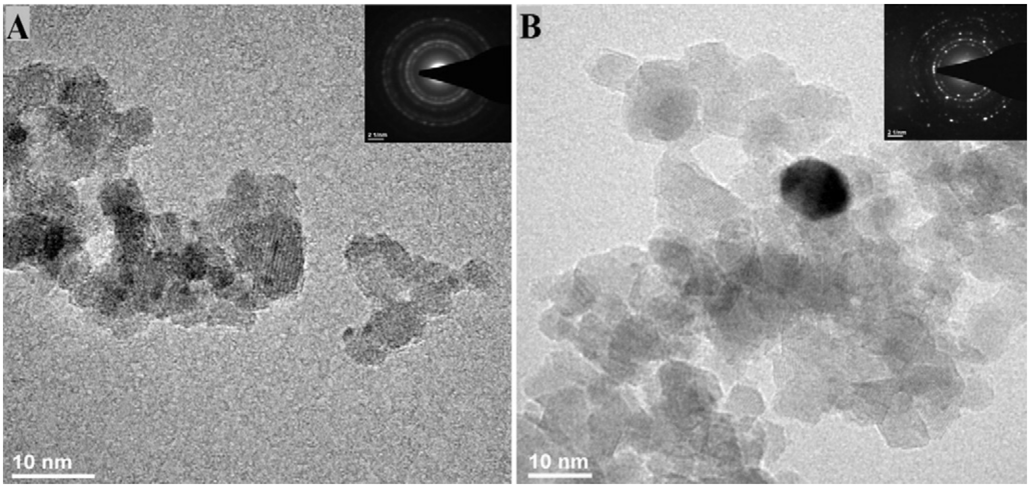

Fig. 2. HRTEM images of 3Pt_MW_550 (A) and 3Pt_MW_800 (B) with SAED patterns as an *inset*.

Table 1
Textural and catalytic properties of studied samples.

	0.5Pt MW 550	0.5Pt Cp 550	1Pt MW 550	1Pt Cp 550	3Pt MW 550	3Pt Cp 550	1Pt MW 800	3Pt MW 800
Specific surface area, S_{BET} [m^2/g]	98	126	102	136	130	135	87	79
Average pore diameter, d_{BJH} [nm]	6.5	7.7	5.6	6.5	4.3	5.6	6.5	6.6
Total pore volume, V_{tot} [cm^3/g]	0.2	0.4	0.2	0.4	0.2	0.3	0.2	0.2
Pt dispersion, D_{H2}	0.96	0.85	0.88	0.88	0.56	0.52	0.31	0.22
Pt crystals size, d_{Pt} [nm]	1.2	1.3	1.3	1.3	2	2.2	3.6	4.8
Iso-butane conversion, T_{50} [%]	322	339	280	285	333	340	358	365

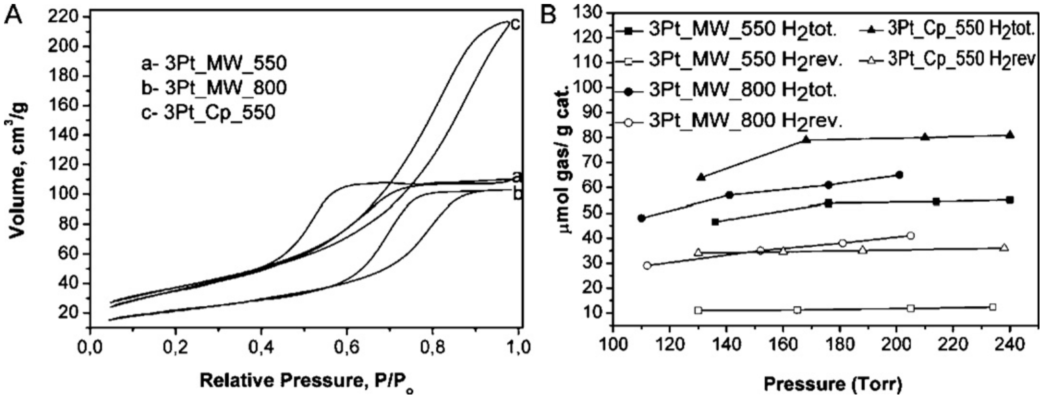

Fig. 3. N_2 adsorption–desorption isotherms (A) and results of H_2 chemisorption measurements (B).

lattice fringes. Pt presence has confirmed also corresponding SAED patterns (as *insets* in Fig. 2).

N_2 adsorption–desorption measurements have shown that Pt catalysts supported on $ZnAl_2O_4$ obtained both under solvothermal conditions and by coprecipitation method have high specific surface area ($S_{BET} > 100\,m^2/g$) and mesoporous structure. However, independent on Pt loading, all catalysts possess somewhat lower S_{BET} than that of bare supports, suggesting that $ZnAl_2O_4$ undergoes further textural changes upon deposition of the platinum metal and the reduction treatment in hydrogen. Textural results are presented in Table 1 and adsorption–desorption isotherms in Fig. 3A.

One can see that such prepared catalysts maintain significant value of S_{BET} after heat treatment at 800 °C confirming their good thermal stability. It should be noticed that coprecipitation method used in this work was provided in non-conventional way what had significant influence on crystallinity and texture properties of the samples. Spinel materials produced by traditional coprecipitation method have usually low surface area and porosity [9].

Results of H_2 chemisorption measurements, shown in Fig. 3B and in Table 1, indicate that $ZnAl_2O_4$ forms material with a high capacity to achieve high dispersion of the metallic phase. The low loaded catalysts have a very high dispersion close to 1 and with rise the metal loading to 3 wt.% it decreases to about 0.6. Much lower Pt dispersion can be obtained only for catalysts after additional heat treatment at 800 °C. The average Pt particle size increases from about 1.2 to 2.2 nm by rise the metal loading from 0.5 to 3 wt.%. There are no significant differences in the Pt dispersion and in mean Pt size for the catalysts with the same Pt loading, in which the support is prepared by the solvothermal or co-precipitation method. Good correspondence of the mean particle sizes calculated from H_2 chemisorption and TEM can be observed for higher loaded catalysts.

Preliminary catalytic tests reveal that there is no significant effect of $ZnAl_2O_4$ support and virtually no *iso*-butane conversion in the empty reactor below 500 °C. Light-off curves for the oxidation of *iso*-butane on metal-free zinc aluminate show that conversion starts at ~400 °C, i.e. at temperature up to 300 °C higher than that corresponding to *iso*-butane oxidation over Pt supported on $ZnAl_2O_4$. The studied catalysts exhibit similar catalytic activity in *iso*-butane combustion. Observed differences in light-off curve performances should be connected with Pt dispersion and poisoning effect of chlorine. The characteristic temperatures (T_{50}) at which 50% conversion is achieved (collected in Table 1) indicate higher activity of samples synthesized by solvothermal method. Sample with 1% of Pt loading exhibits the best activity, probably because of lower Cl concentration than in the sample with 3% of Pt. Fig. 4 shows the *iso*-butane conversion over the 0.5Pt_MW and 0.5Pt_Cp catalysts heated at 550 and 800 °C as a function of reaction temperature. It is clearly seen that heat treatment at 800 °C leads to some decrease of catalytic activity: T_{50} is about 40 °C higher and complete *iso*-butane oxidation to CO_2 also occurs at higher temperature. Similar changes in activity are found for other metal loadings what suggests that thermal stability of Pt catalysts supported on such prepared $ZnAl_2O_4$ is promising. Butane light-off performances which have already been reported in the literature for other sup-

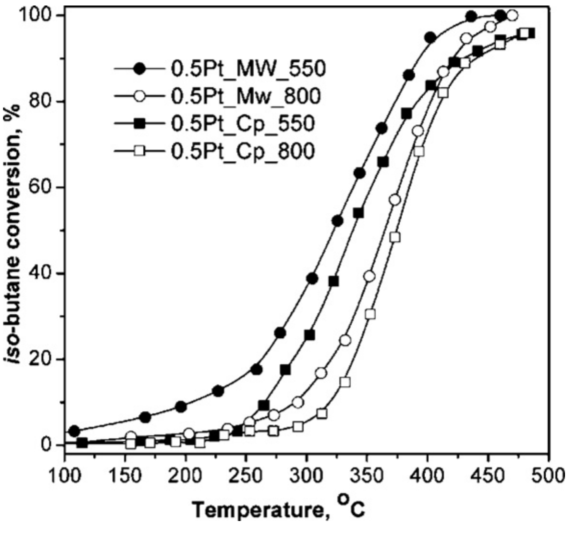

Fig. 4. *Iso*-butane conversion as a function of temperature.

ported platinum catalysts are comparable to presented now, and $T_{50\%} = 370\,^{\circ}\mathrm{C}$ [10] or 280–290 °C [11,12] have been found for Pt/MgO and Pt/Al_2O_3, respectively, while the enhanced activity is observed for Pt supported on zeolites ($T_{50\%} < 200\,^{\circ}\mathrm{C}$) [10]. The evolution of the catalytic activity as a function of time on stream (at constant reaction temperature) are also measured (results not shown) and it is clear that irrespective of Pt catalysts, *iso*-butane conversion has not changed after 6 h time on line indicating high stability of all catalysts under used reaction conditions.

4. Conclusions

This work shows that zinc aluminate spinel prepared by either solvothermal or non-conventional coprecipitation way is characterized by desired properties for application as support of VOC combustion catalysts, i.e. high surface area and mesoporous structure, high capacity to achieve high platinum dispersion and good thermal resistance. It was found that irrespective of the preparation method, Pt catalysts supported on them exhibited good catalytic activity in combustion of *iso*-butane, which as linear short chain alkane is one of the most difficult to destroy.

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