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Specific surface area – key factor determining the catalytic activity of Pd/SnO_2 catalyst in nitrate hydrogenation

M. KOVACEVIC, A. R. ZARUBICA, G. BOSKOVIC*
University of Novi Sad, Faculty of Technology, Cara Lazara 1, 21000 Novi Sad, Serbia

Mesoporous nanocrystalline SnO_2 supports were synthesized by modified sol gel method in different pH environment (pH=2 and pH=8) both starting from $SnCl_2·2H_2O$ and citric acid. Equal amount of palladium was introduced via wet impregnation of obtained supports using $PdCl_2$ solution as active phase precursor. Lower pH value during the support synthesis results in final material characterized with more developed porosity and higher surface area. Corresponding catalyst samples showed affirmative activity in nitrate removal reaction from water, performed in semi-batch conditions under hydrogen flow. The mild basic conditions of SnO_2 support synthesis result in unfavorable material by means of very low surface area and corresponding catalyst samples with equally low activity regardless of their other characteristics. Presented activity results speak in favor of nitrate hydrogenation as a specific structure sensitive reaction performing a maximum activity for an optimal SnO_2 crystalline size.

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1. Introduction

Denitration of potable water is an environmental issue of extreme importance. Excessive nitrate content in air, soil and water resources is a consequence of increased NO_x emission, combustion processes, exaggerates fertilizer usage, as well as industrial waste water impact. Conventional physico-chemical and biological methods of nitrate removal are currently considered to be exchanged by catalytic approach. This is due to significant drawbacks of conventional methods, provoking either secondary contaminations, or requiring additional disinfections, respectively. The problem of catalytic denitration is acute and efforts to find an efficient catalyst to reach EU standard of 25 ppm of NO_3^- (5.65 ppm calculated by N/l) are still under progress [1].

To solve the problem of nitrate removal usage of monometallic Pd/SnO_2 catalysts seems promising, particularly in terms of satisfying low content of ammonia produced during the course of reaction, i.e. catalysts selectivity demand [2, 3]. Nevertheless, the surface science of SnO_2 is still relatively unexplored, and field of SnO_2 application as support/catalyst for denitration reaction in the presence of hydrogen is a challenge.

From the catalytic point of view tin oxide is interesting in the respect that tin possesses a dual valency, with preferably attaining an oxidation state of 2+ or 4+ [4]. Co-precipitation, sol–gel, spraypyrolysis, hydrothermal routes [5-7] and the other methods are commonly used to prepare nanonocristallyne SnO_2 powder. On the other hand, sol-gel method based on organic precursor becomes more popular in preparation of broad spectrum of materials with advantageous properties. The benefits are emphasized through valuable pore structure, which can be tailored due to well organized particles of nano-size [8-11]. Traditional methods of synthesis based on inorganic salts are claimed to be easier for handling and less sensitive to environment [12].

Modified sol-gel method involves mixing of cheap metal precursor ($SnCl_2·2H_2O$) and an organic polyfunctional acid having at least one hydroxyl and one carboxylic group, e. g. citric acid. Citric acid has the role of tuning the rate of hydrolysis and condensation step during the process. Further low temperature solvent evaporation leads to the formation of highly viscous homogenous polymeric glassy state of tin nanopowders at atomic level. Calcinaton of achieved amorphous glassy material allows its quick conversion to the tin oxide [13].

In this paper modified sol-gel method in acidic as well as basic condition was applied in Pd/SnO_2 synthesis and influence of preparation conditions on samples performances including activity in nitrate hydrogenation reaction was discussed.

2. Experimental

$SnCl_2·2H_2O$ (99%,Centrochem, Serbia) and citric acid (99%, Alkaloid, Macedonia) were dissolved in de-ionized water separately and obtained solutions were quickly mixed adjusting tin/citric acid moles ratio 3:5 [13], while at the same time pH=2 was determined. A modified procedure was repeated by means of keeping moderately basic conditions (pH=8) by addition of NH_4OH. In both cases resulted Sn-citrate complexes (“A” and “B”, denoting the acidic and basic conditions of synthesis, respectively) become highly viscous during the following slow solvent evaporation at 80˚C and finally turned into a transparent glass. Glassy state samples differing in pH environment were than calcined in a static condition of air at 300, 500 and 700˚C for 6, 2 and 1/2h, respectively. The calcination time was chosen in a way to satisfy elimination of residual carbonaceous deposits of citrate origin, which was proved by a bright color of obtained powder. Calcination procedure leads to gel combustion, highly exothermic process allowing fast SnO_2 production [13]. The described procedure resulted in catalyst support samples 1-3 (series A, pH=2) and samples 4-6 (series B, pH=8), differing within a single series in applied calcination temperature (300, 500 or 700 ^oC).

The noble metal was introduced by wet impregnation of described SnO_2 supports with $PdCl_2$ solution (99%, Sigma-Aldrich) to get the nominal loading of 6% mass. palladium. Next to impregnation catalyst samples were dried at 105˚C overnight and calcined at 400 °C for two hours in static condition of air.

Textural characteristics were investigated by means of surface area determined by BET, as well as mean pore diameter and pore volume both determined using desorption isotherms. Corresponding data were obtained by dynamic low temperature nitrogen adsorption/desorption (LTNA) using He as carrier gas on Micromeritics ASAP 2010. The crystal structure was resolved by means of X-ray diffraction analysis (XRD) using Philips APD-1700 diffractometer with Cu-anticathode and monochromator, at 40 kV and 55 mA. The crystallite size was estimated from the full width at half-maximum using Scherrer's equation. The surface morphology of catalysts samples was investigated by scanning electron microscope (SEM) JEOL JSM-6460LV at accelerating voltage of 25 kV. Solid samples previously were coated with gold in order to achieve their conductivity.

Catalysts' testing was performed in a slurry semi-batch reactor made out of pyrex at reaction conditions which are listed in Table 1. Hydrogen and CO_2 were co-feed for the purpose of keeping acidic environment (pH=5.4) of the water model system. Catalyst samples were reduced ex situ in a flow of pure H_2 for 2h at 25 ^oC prior to the reaction. In the course of the reaction that lasted for 3.5h several liquid samples in desired time intervals were taken for analysis. Nitrate and ammonium ions content were analyzed using corresponding Cole-Palmer Ion Electrodes, while pH was controlled continuously, both on pH/ION 510 Oakton meter.

Table 1. Reaction conditions

Reaction temperature (K)	298
Operating pressure (bar)	1.0
Initial nitrate concentration (ppm)	100
Catalyst weight (mg)	40
Liquid phase volume (ml)	70
Hydrogen flow rate (ml/min)	60
H_2 / CO_2	1:8
pH	5.4
Stirring rate (min^{-1})	350

3. Results and discussion

Residual nitrate content presenting catalyst samples activities with time-on-stream, and amounts of produced ammonium ions (undesired product) as selectivities at the end of reaction, are given in Figures 1, and 2, respectively. Structural as well as textural characteristics of catalysts are listed in Table 2. The data presented speak in favor of structural, textural and consequently catalytic properties, which are strongly dependent on samples preparation mode (pH condition of a support synthesis and its calcination temperature).

Activity results (Fig. 1) point out to significant differences among investigated samples and detrimental impact of higher pH value (pH=8) during Sn-citrate (support precursor) synthesis on catalysts efficiency in nitrate hydrogenation reaction. Namely, only catalysts sample 2, prepared in the acidic condition (series A), reach an accepted level of residual nitrates in the nitrate-in-water model system (25 ppm NO_3^- by EPA), while the same results proved extremely bad catalytic performance of samples 4-6 prepared in the basic condition (series B). While difference in calcination temperature has a significant impact on samples catalytic activity of series A, it is of no effect in the case of catalyst samples prepared in the basic conditions (Fig.1). This fact reveals that the pH level in synthesis of SnO_2 support is a crucial factor affecting catalytic properties of Pd/SnO_2 catalyst in nitrate hydrogenation reaction.

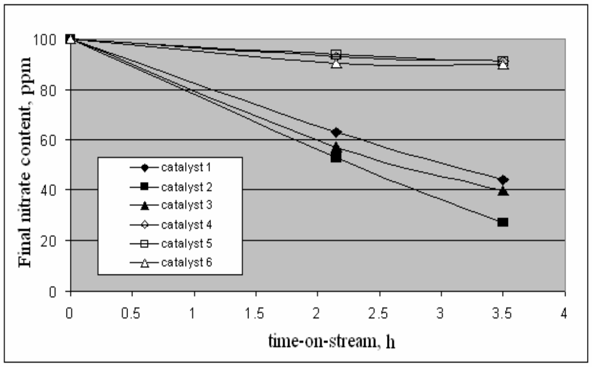

Fig.1. Catalysts activities with time-on-stream.

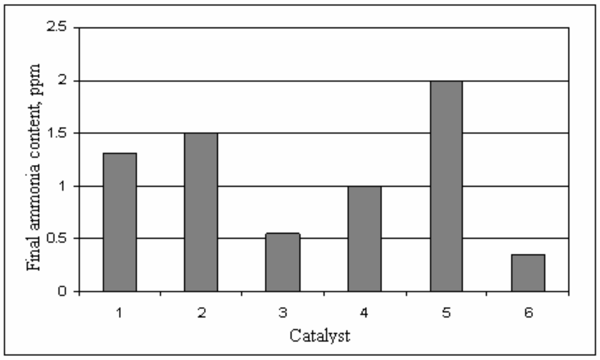

Fig. 2. Catalysts selectivities.

Table 2. Structural and textural properties of catalysts.

Catalyst and calc. T applied		pH	S_{BET}, m^2/g	Mean pore diam., nm	Total vol. of pores, cm^3/g	Crystall. size of SnO_2, nm
1	300	2	42.6	8.3	0.090	26.8
2	500		29.3	11.9	0.087	33.5
3	700		11.0	17.6	0.068	44.8
4	300	8	2.1	15.8	0.012	32.0
5	500		3.2	2.1	0.001	67.0
6	700		3.1	8.7	0.006	67.1

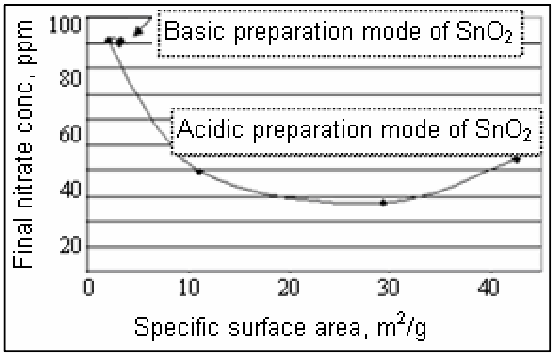

Fig. 3. Catalysts activities vs. specific surface area for samples of series A and B.

Variation in pH environment of catalyst support synthesis is also reflected in notably different textural properties of obtained samples (Table 2). For catalysts which precursors experienced the acidic condition specific surface areas range from 43-11 m^2/g while mean pore diameters are in mesopores range. In contrast, for samples of series B obtained in the basic environment, surface area drops drastically to the value of 3 m^2/g and lower. Again, calcination temperature has an impact on surface area of only those catalysts originating from an advanced support material obtained in the acidic environment; as expected calcination temperature increase leads to specific surface area decrease, following with expansion of mean pore diameters. As seen from Figure 1 and Table 2 for series A samples there is no obvious dependence of activity on surface area as there is an optimal specific surface area (achieved after calcination at 500 ^oC) when the maximal activity was reached. Positive influence of surface area decrease on catalytic activity of Pd/SnO_2 catalyst have been noticed before in the specific surface area narrow of 60-11 m^2/g, followed by average pore diameter increase from 7-37 nm [2]. This is only to a certain extent in line with findings of this work, showing first specific surface area/residual nitrate relation having a minimum for series A samples, but also fundamentally loss of catalytic activity with farther extended decrease of surface area for those samples having the basic history of their synthesis (Fig.3).

An additional difference between Pd/SnO_2 catalyst samples owing to their preparation pH conditions and subsequent calcination temperature is their pore size distribution, as shown in Fig. 4. Namely, all catalyst samples originating from precursor obtained in the acidic condition are attributed with monomodal pore size distribution. Besides, maxima indicating pores of prevailing size are shifted to higher diameters following calcination temperature increase, which coincide with decrease of specific surface area (Table 1). The observed monomodal pore distribution is quite opposite to an earlier finding with some other semiconductor materials, like ZrO_2, synthesized by means of standard sol-gel method. Using an organic precursor as a starting material and basic environment conditions these materials after calcination ended up with bimodal pore distribution [10, 11]. As shown on the right hand side of Fig. 4, the moderate basic preparation condition applied in this work for series B seems to induce a similar scenario. However, in line with very low specific surface area obtained, the samples porosity is also extremely low. Namely, all samples of series B express several maxima as indication of diameters of dominant pores fractions; however, absolute values of their absorption capacities are particularly low. An almost complete absence of hysteresis loops in adsorption/desorption diagrams of the same samples presented on the right hand side of Fig. 5 indicates nonporous adsorbents [14].

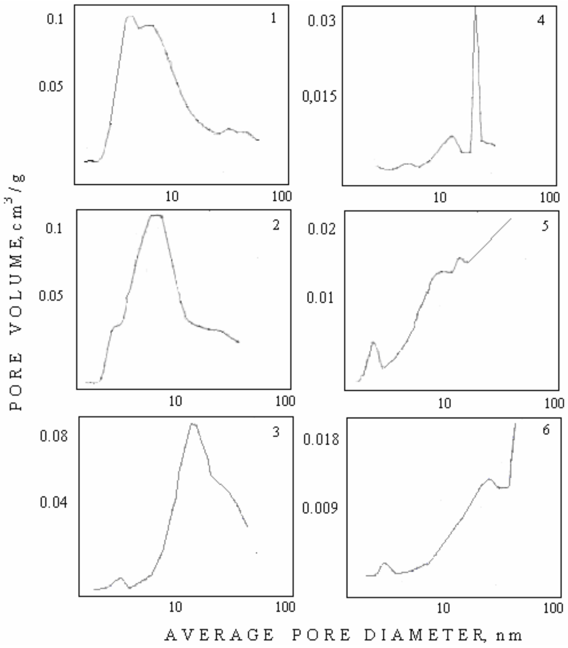

Fig. 4. Pore size distributions of catalysts 1-3 (left), 4-6 (right).

X-ray diffraction lines (Fig. 6) of Pd/SnO_2 catalyst samples point out the presence of exclusively rutile phase of SnO_2, indicating very well dispersed palladium. Having in mind dual character of SnO_2 being at the same time the catalyst support but also an active phase, like SnO_X unstoichiometric irregularities [2], size of SnO_2 crystallites for all samples are calculated and presented in Table 2. For the series A catalyst samples there is an expecting trend of SnO$_2$ crystalline size increase following calcination temperature rise (Table 2), pointing out to the partly occurrence of process of sintering of the support. Yet the catalytic activity dependence on crystalline size is a twofold, as it follows a profile having a minimum similar to the one showing specific area-activity relation given in Fig. 3. Such a relation indicates rather complicated structure sensitivity behavior of denitration reaction, neither sympathetic nor anti-sympathetic, but structure sensitivity showing maximum activity for crystallites of a certain size [15] (note that curve minimum observed at Fig. 3 means maximum activity!). On the other hand, in a case of samples originating form the base condition crystalline size of SnO$_2$ has not any impact on catalytic behavior, although the sample 4 is characterized with a crystallite of similar size to that one from the series A pronouncing maximal activity (sample 2). This unexpectedly low particle size obtained at such a depleted surface area could be understood in terms of its surrounding by carbonaceous deposits segregated at grain boundaries in the synthesis procedure. These carbon deposits were not eliminated during the synthesis procedure, which was proved by a grey color of the sample hold off even after the thermal treatment. It has to be mentioned, however, that Scherrer's equation used for grain size calculation is valid only for spherical particles. Therefore one must consider a possible error obtained in calculation of particles size of samples of series B (see Fig. 7, e.g.).

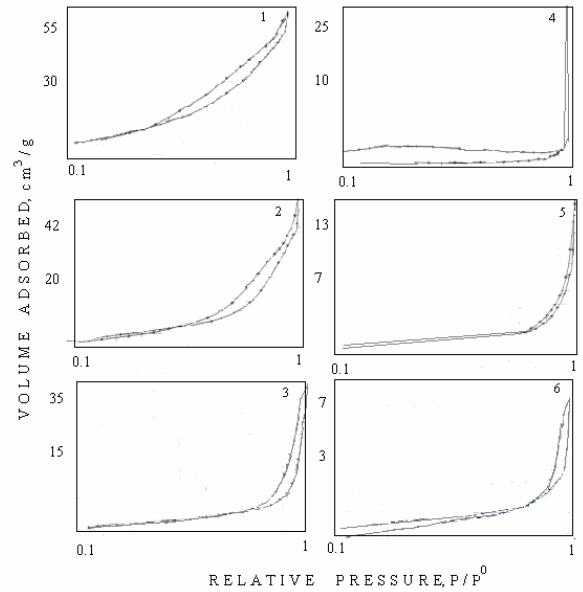

Fig. 5. Adsorption/desorption isotherm hysteresis loops of catalysts 1-3 (left) and 4-6 (right).

The surprising ambiguous influence of SnO$_2$ crystalline size on catalyst activity points to either a synergistic effect of optimal porosity and optimal structure (grain size) of catalytic material on its efficiency in denitration reaction, or opposite: speak in favor of some solely property being the most important in determining the catalytic behavior. Indeed, a detailed look into data of Table 2 and curves in Fig. 1 advocates specific surface area as a key factor determining catalytic behavior. Although samples 2 and 4 have similar grain size and probably consequently similar concentration of active Lewis SnO$_x$ sites [16], as well as comparable average pore diameters indicating similar constrains imposed by potential diffusion restrictions [17, 18], activity results strongly address the importance of specific surface area on catalytic behavior.

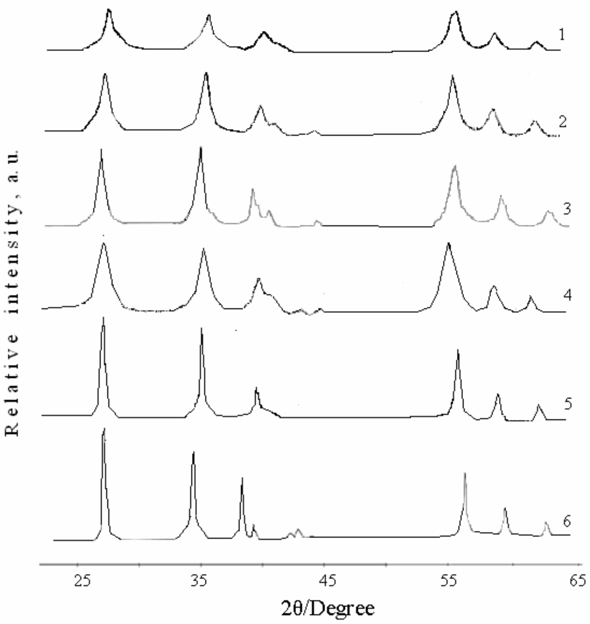

Fig. 6. XR difractograms of catalyst samples 1-6.

SEM images of support samples preceding formation of corresponding catalysts point out to explicit differences in morphology among samples prepared in various pH conditions (Fig. 7). Support samples synthesized in the acid environment are of spherical shape, while these having experienced the moderate base environment result in lamellar morphology with plate-lake particles shape. Particles of samples from both series are in nano-range, with their size increasing following the calcination temperature rise. It seems, however, that temperature treatment increase has an additional effect next to the particles grow. Namely, for the support samples of series B (right-hand side of Fig.7) there is a “smoothing effect”, manifested as particle morphology change from original pyramidal form, i.e. 3D-nano size (sample 4 support), to a kind of lamellar shape, ie. 2D-nano size (sample 6 support). Again, this likely morphology change is unimportant from the catalytic activity point of view, pointing out again the specific surface area as a key feature for Pd/SnO$_2$ catalysts in hydrodenitration reaction.

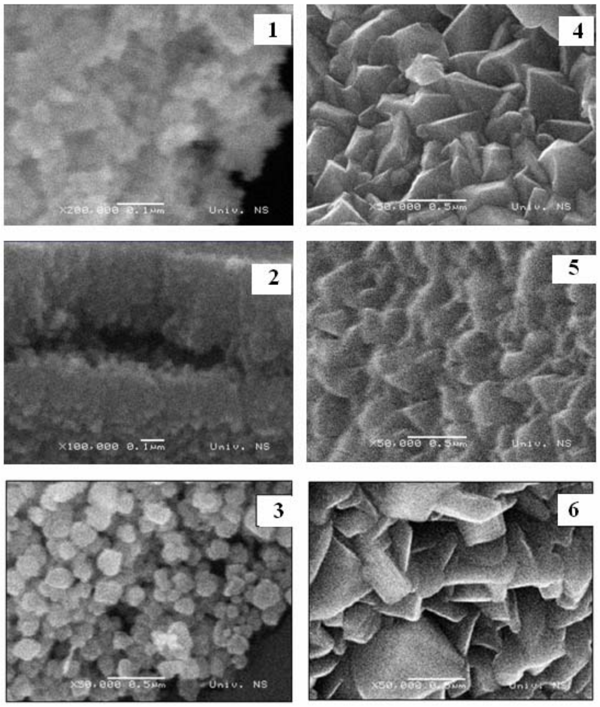

Fig. 7. SEM images of supports preceding catalysts samples: 1-3 (left) and 4-6 (right) (notice a difference in magnification).

4. Conclusions

State of pH in liquid mixing technique is the key factor determining morphological, textural and structural properties of SnO_2 support as precursor for Pd/SnO_2 catalyst for nitrate removal from water. Support samples synthesized in the acid environment are of spherical shape, while these obtained in the moderate base environment result in lamellar morphology with plate-lake particles shape. Strong acidic condition (pH=2) of precursor synthesis lead to catalysts with broad range of surface area, mean pore and crystalline size, with varieties imposed by further calcination at different temperatures. Such a catalyst is characterized with optimal values of specific surface area, SnO_2 crystalline size and mean pore diameter in meso-range, all together providing the best activity. The mild basic condition (pH=8), however, brings support material with such inferior surface area, which is unaffected by further difference in calcination temperature. Even though other characteristics (crystalline size and mean pore diameter) of at least one catalyst sample from this series are comparable with the same from the previous, corresponding catalytic activity is unequally inferior. This speaks of specific surface area as major factor determining activity of Pd/SnO_2 catalyst for nitrate removal from water.

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[*] Corresponding author: boskovic@uns.ns.ac.yu