BENEFITS OF MESOPORES IN NANOCHRISTALLINE Pd/SnO₂ CATALYSTS FOR NITRATE HYDROGENATION

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Mesoporous nanocrystalline SnO₂ supports were synthesized by a modified sol-gel method starting from SnCl₂·2H₂O and citric acid at pH 2.0 and 9.5. Noble metal was introduced via wet impregnation using PdCl₂ as active phase precursor. Catalysts activities in water denitration were correlated with their textural, structural and morphological properties using LTNA (BET), XRD and SEM/EDS analysis. Lower pH value during the catalyst synthesis resulted in a final material characterized with more developed porosity and higher surface area. Although both catalysts turned out to be tailored from nano-scale crystallites, higher pore fraction of mesopores resulting from the synthesis in acidic conditions, was found to be responsible for superior catalytic behaviour.

KEYWORDS: Nanostructured Pd/SnO₂, mesopores, water denitration

INTRODUCTION

Denitration of potable water is an environmental issue of extreme importance. The presence of nitrate in groundwater is due to both exaggerate usage of fertilizers and contamination from domestic or industrial waste effluents. Conventional physico-chemical and biological methods of nitrate removal are currently considered to be replaced by a catalytic approach. This is due to significant drawbacks of conventional methods, provoking either secondary contaminations, or requiring additional disinfections. The problem of catalytic denitration is acute and efforts to find an efficient catalyst to reach EU standard of 25 ppm of NO₃⁻ (5.65 ppm calculated by N/l) are still under progress (1). Current literature advocates the usage of monometallic Pd/SnO₂ catalyst, particularly in terms of its selectivity, i.e. reasonable low content of secondary pollutant, ammonia, produced during the course of the reaction (2,3). It is believed that superior catalytic properties of Pd/SnO₂ comes from dual valence of its support, with preferably attaining an oxidation state of 2+ or 4+ (4). On the other hand, the surface science of SnO₂ is still relatively unexplored, and its application as support/catalyst for nitrate hydrogenation (denitration) reaction is a challenge.
Among various methods for preparation of nano-sized catalysts (5-7), sol-gel method based on organic precursor becomes more popular thanks to advantageous properties of the resulting materials. The benefits are emphasized through valuable pore structure, which can be tailored due to well organized nano-sized particles. On the other hand, traditional methods of synthesis based on inorganic salts are claimed to be easier for handling and less sensitive to the environment (8).

Modified sol-gel methods avoid usage of expensive alkoxides and involve mixing of a cheap metal precursor and an organic polyfunctional acid having at least one hydroxyl and one carboxylic group, as citric acid, e.g. Subsequent low temperature solvent evaporation leads to the formation of highly viscous homogenous polymeric glassy state of tin nano-powder at atomic level. Further calcination of achieved amorphous glassy material allows its quick conversion to the tin oxide (9).

In this work, a modified sol-gel method in an acidic, as well as basic condition, was applied in the Pd/SnO₂ synthesis and resulting physico-chemical properties were correlated to the catalytic performances in nitrate hydrogenation reaction.

EXPERIMENTAL

SnCl₂·2H₂O (p.a., Centrohem) and citric acid (99%, Alkaloid) were dissolved in de-ionized water separately and obtained solutions were quickly mixed adjusting tin/citric acid mole ratio 3:5. The pH 2.0 of the solution was kept without modification (support 1), or was modified by adding of NH₄OH to pH=9.5 (support 2). In both cases the resulting complex became highly viscous during the slow solvent evaporation at 80°C and finally turned into a transparent glass. Glassy state samples were then calcined under static conditions of air at 700°C for ½ h. Gel combustion, a highly exothermic process, allowed fast SnO₂ production (9).

The noble metal was introduced by wet impregnation of SnO₂ supports with PdCl₂ (99%, Sigma-Aldrich) to get the nominal loading of 2 mass% of Pd. After the impregnation catalyst samples were dried at 105°C overnight and calcined at 400°C for two hours. The final loading of the metal was confirmed by Energy Dispersive Spectroscopy (EDS) on a scanning electron microscope (SEM) JEOL JSM-6460LV. The same device was used to check the morphology of the supports preceding their impregnation with palladium.

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 a carrier gas on a Micromeritics ASAP 2010. The crystal structure was resolved by means of X-ray diffraction analysis (XRD) using a 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. Catalysts’ testing was performed in a slurry semi-batch reactor (Fig. 1) at 25 °C, atmospheric pressure, using stirring rate of 350 rpm, and under H₂ and CO₂ flows of 60 ml/min and 480 ml/min, respectively. The flow of CO₂ was chosen to keep pH 5.4, as was confirmed by pH-meter. Fresh catalyst samples amounting to 40 mg, previously reduced ex situ in a flow of pure H₂ for 2 h at 25 °C, were charged into 70 ml of nitrate-in-water model system initially containing 100 ppm of NO₃⁻. Liquid phase
samples were taken in desired time intervals, and nitrate, as well as ammonium, contents were analyzed using Cole-Palmer nitrate and ammonia ion electrodes and an ION 510 Oakton Meter. Formation of intermediate nitrites was followed on a Vis-spectrophotometer Jenway 6300 at \( \lambda = 538 \) nm, using standard method (10). The reaction consecutive steps are: a) nitrates to nitrites transformation and b) further hydrogenation of intermediate nitrites to either \( \text{N}_2 \) or \( \text{NH}_4^+ \). The ratio of the alternative products, \( \text{N}_2 \) and \( \text{NH}_4^+ \) (undesirable), determines catalyst selectivity.

RESULTS AND DISCUSSION

Catalysts activities in terms of residual nitrate content with time-on-stream, as well as samples’ structural and textural characteristics are presented in Figure 2 and Table 1, respectively. The data presented support the hypothesis of precursor memory effect on structural, textural and activity properties of catalyst samples following different preparation procedures (11,12).

Fig. 1. Schematic diagram of the reaction apparatus: gas outlet (1), thermometer (2), reaction vessel (3), magnetic stirrer (4), motor stirrer (5), contact thermometer (6), bath (7), heater (8)

Fig. 2. Steady-state catalysts activities (light) and selectivities (dark) in nitrate hydrogenation after three hours from the beginning of the reaction.
Catalytic performances of samples 1 and 2 in hydrogenation of nitrates show large discrepancy reflecting the difference in the preparation conditions. Catalyst 1 reached an accepted level of residual nitrates already after three hours from the beginning of the reaction, while test reaction proved extremely bad catalytic performances of Catalyst 2. Considering the difference in noble metal loading (Table 1) the observed results are not in line with the predicted behaviour. Namely, the palladium content of Catalyst 2, close to its nominal level, should be a guaranty of optimal surface density of reducing agent as a result of emphasized hydrogen spill-over effect. According to traditionally accepted mechanism, nitrate hydrogenation reaction precedes through two consecutive steps: nitrate to nitrite conversion, on Pd sites, and further nitrite reduction to nitrogen or ammonia, on bimetallic Pd–support entities or, according to the new literature data referring to noble metal/titania catalyst, on some low-coordinated metal-site from the support (Ti in this particular case) (13). In both stages of the reaction the noble metal loading controls turn-over-frequency (TOF), as well as the „regeneration” of active sites on the support, providing the surface hydrogen accessibility which is essential for the catalyst activity.

The mentioned samples catalytic activities are in line with considerable differences of the corresponding textural properties (Table 1) and catalytic behaviour should be discussed from that viewpoint. According to the data presented in Table 1, a real reason for the extremely bad performance of Catalyst 2 has to be assigned to its small mean pore diameter. Although both catalysts are characterized by mean pore dimensions within a meso-range, significantly smaller pores in the case of Catalyst 2 may indicate constrains imposed by diffusion restrictions as predominant reason for such a low activity. In addition, pore volume of Catalyst 1 is even one order of magnitude larger compared to that of catalyst 2. A consequence of this is a more developed porosity and surface area, arising from an effective pH control in the vicinity of active sites. Namely, the reaction proceeds through a stoichiometric OH⁻ formation:

$$2\text{NO}_3^- + 5\text{H}_2\text{-catalyst} \rightarrow \text{N}_2 + 2\text{OH}^- + 4\text{H}_2\text{O}$$

or

$$\text{NO}_3^- + 4\text{H}_2\text{-catalyst} \rightarrow \text{NH}_4^+ + 2\text{OH}^- + \text{H}_2\text{O}$$

If the pH-gradient induced during the course of the reaction is lasting inside a catalyst particle, the produced OH⁻ ions block active sites and diminish catalyst’s activities. This means that textural properties, i.e. surface area and porosity, are crucial for good catalytic performances of the Pd/SnO₂ system. Tin, as presented in (14), is known to have a very strong metal-oxygen bond; this means that oxygenated species (OH⁻, O²⁻) are the dominant adsorbates at higher pH values that hinder its reduction (15) and further re-oxidation.
in its activity cycle. Catalyst 2, having experienced inappropriate method of synthesis in terms of a higher pH, has significantly lower values of surface area and total pore volume compared to Catalyst 1. In contrast, catalysts 1 prepared by modified sol-gel technique conducted in a highly acidic medium has textural properties that are beneficial for its high activity, i.e. low final nitrate content.

X-ray diffraction patterns (not presented), on the other hand, indicate nano-scale dimensions of SnO₂ crystallites as a single phase of rutile structure (tetragonal system) for both samples regardless of preparation route (Table 1). The nano-dimension particles can be proved by SEM patterns (Figure 3) although their obvious difference in morphology confirm previous statement about the precursor memory effect on the properties of catalyst samples following different preparation procedures (11,12).

![Fig. 3. SEM images of SnO₂ supports resulting from acidic (a) and basic (b) conditions of modified sol-gel synthesis](image)

CONCLUSION

Presented results illustrate a strong impact of pH condition upon SnO₂ (catalyst’s supports) synthesis on textural and structural properties of obtained materials. Lower pH conditions used in liquid mixing technique is a guaranty of sample’s developed porosity, probably more important than active metal loading, morphology and nano-size of crystallites.

ACKNOWLEDGEMENT

Financial support of the Serbian Ministry of Science (Project ON 142024 „To Green Chemistry via Catalysis“) is highly appreciated.

REFERENCES


POZITIVAN UTUČAJ MEZOPORA U NANOKRISTALNOM Pd/SnO$_2$
KATALIZATORU ZA UKLAĐANJE NITRATA

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Мезопорозни нанокристални SnO$_2$ носачи катализатора синтетисани су модификованом сол-гел методом полазећи од SnCl$_2$·2H$_2$O и лимунске киселине при различитим pH условима (pH 2,0 и pH 9,5). Племенити метал унет је влажном импрегнацијом користећи PdCl$_2$ као прекурсор активне фазе. Активности катализатора у тест реакцији денитрације воде корелисане су са њиховим текстуралијним, структуралним и морфолошким особинама користећи LTNA(BET), XRD и SEM/EDS анализе. Нижа вредност pH приликом припреме катализатора резултира развијенијом порозношћу, као и више специфичном површином добијеног материјала. Мада су честице оба узора нано-димензија, супериорно каталитичко понашише приписује се више уделу мезопоре катализатора синтетисаног у киселој средини.

Received 11 June 2007
Accepted 5 September 2007