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METAL-SUPPORT INTERACTION - THE KEY FACTOR GOVERNING ACTIVITY OF Pd/SnO_2 CATALYST FOR DENITRATION OF GROUND WATER

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Two mesoporous nanocristalline Pd/SnO_2 catalysts were prepared by modified sol-gel technique differing in the pH conditions (pH = 2 and 9.5) of the synthesis of their supports. Samples achieved different activity and selectivity in water denitration reaction using hydrogen. XPS results of reduced samples indicate a strong interaction between the Pd and the Sn possibly as a result of electron shift from Sn to Pd. The solid solution of Pd^{2+} and SnO_2 is formed by taking O from the surface of the support. In such a way some SnO_{2-X} species may stay onto the surface and be responsible for its pronounced activity.

KEYWORDS: Nanosized Pd/SnO_2 catalyst, SMSI of Pd and SnO_2, SnO_{2-X} active site, water denitration

INTRODUCTION

Because of the excessive use of fertilizers and other sources of nitrogen-containing pollutants contamination of groundwater by nitrates has become a serious problem. Efforts to remove high-toxic nitrates in the process of water production recently have been turned from classical physico-chemical and biological technologies to more promising catalytic processes. Nevertheless, commercial catalytic denitration is still in its infancy, and looking for efficient catalysts to reach EU standard is still under progress.

It is believed that on a bimetallic Cu-Pd catalyst using traditional supports the reaction proceeds through consecutive steps: a) nitrates to nitrites transformation and b) further hydrogenation of intermediate nitrites to either N_2 or NH_4^+, the last being an undesirable product (1). Recent literature data speak in favor of monometallic Pd catalysts on SnO_2 or TiO_2 supports (2-5).

„Soft chemistry“ based on alkoxide precursor has become rather popular in preparation of broad spectrum of different catalysts with advantageous properties determined by

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nano-scaled particles. The benefits are emphasized through valuable pore structure, particularly by advantageous mesoporous materials, which can be tailored due to well-organized particles of nano-size (6-8). On the other hand, traditional methods of catalyst synthesis based on inorganic salts are easier for handling and less sensitive to environment, although very dependent on the type of the precursor used (9).

A modified sol-gel method, avoiding the use of costly alkoxide, involving cheap metal precursors and strong chelating agents instead, has proved as an appropriate technique in the case of SnO_2 preparation as a catalyst support (10). Two Pd/SnO_2 catalyst samples based on differently prepared support exhibited rather different catalytic behavior, which has been explained by the differences in textural properties (10). In this paper, further investigation of the same catalysts has been performed and discussed in terms of metal(s) oxidation state, and its likely additional influence on the catalyst performances in nitrate hydrogenation reaction.

EXPERIMENTAL

Two Pd/SnO_2 catalyst samples were prepared by wet impregnation of SnO_2 supports with $PdCl_2$ to get the nominal loading of 2 mass% of Pd. Conditions for the preparation of two different SnO_2 supports, as well as further Pd introduction and catalysts thermal treatment have been given earlier (10). The final loading of palladium, as well as the amount of Cl^--ions as impurity, was verified by Energy Dispersive Spectroscopy (EDX) on a scanning electron microscope (SEM) JEOL JSM-6460LV.

X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB 220iXL with AlKα radiation (1486.6 eV). The electron binding energy was referenced to the C 1s peak at 284.8 eV. The peaks were fitted by Gaussian-Lorentzian profiles after a Shirley background subtraction. For quantitative analysis, the peak area was divided by the element-specific Scofield factors and the transmission function of the analyzer. The residual pressure in the chamber was lower than 10^{-7} Pa. The oxidation state of Sn and Pd was investigated in both unreduced and reduced (50 ^{o}C in hydrogen flow) samples.

RESULTS AND DISCUSSION

Catalysts activities, as well as samples' structural and textural characteristics, all presented earlier (10), support the hypothesis of the precursor memory effect, governing the catalyst properties, following different preparation procedures (11). Table 1 gives the Pd loading together with the amount of Cl^- ions present as impurity for both catalyst samples.

Table 1. Pd loading and amount of Cl^- impurity

Catalyst	Pd (mass %)	Cl^- (mass %)
1	1.4	0.33
2	1.9	-

Lower metal loading than intended in the case of catalyst sample 1 reflects the difficulties in Pd incorporation in the case of SnO_2 experiencing lower pH conditions in the sol-gel syntheses. The insufficient Pd-loading may speak of SnO_2 iso-electric point and/or Pd^{2+} precipitate conditions as limiting factors in the preparation of SnO-based catalysts (12). Considering the difference in noble metal loading for two samples the result of their activities is not in line with the expected behavior. Namely, the higher palladium content of catalyst 2 should be more promising in achieving an optimal surface density of reducing agent as a result of the emphasized hydrogen spill-over effect. Accordingly, both stages of reaction, i.e. nitrate to nitrite conversion on Pd sites and further nitrite reduction to nitrogen or ammonia on bimetallic Pd–SnO_2 sites, are both controlled by Pd-loading. The last is responsible for both turn-over-frequency, as well as the “regeneration” of active sites on the support, providing the surface hydrogen accessibility which is essential for catalytic activity. Still, catalyst 1 attained an accepted level of residual nitrates already after three hours from the beginning of the reaction, while the test reaction proved extremely bad catalytic performances of catalyst 2 (10).

The observed behavior can be explained by appropriate textural properties of catalyst 1, i.e. its mesoporous structure, in contrast to significantly lower pores in the case of catalyst 2 (10). Namely, if the movement of produced OH^- ions takes place, the active site will be blocked and the result will be the production of unfavorable NH_4^+. This means that textural properties, i.e. surface area and porosity are crucial for good catalytic performances of the Pd/SnO_2 (10).

Another aspect of catalyst samples properties which has to be considered here is the presence of Cl^- as impurity and its possible influence on the activity performance. These ions originate from chloride precursors used for both support and metal used for the catalyst preparation, i.e. $SnCl_2·2H_2O$ and $PdCl_2$. A significant amount of Cl^--impurities present in the very active catalyst sample 1 seems not very logical. This is due to the well known fact that residual Cl^- in catalyst may cause agglomeration (13), or may perform as n-dopant to the base material (14). However, undesirable oxygenation function of residual Cl^- ions, i.e. up to 0.33 mass% in the catalyst sample 1 (Table 1), seems to have no important role in the catalysts activity, although some selectivity implications may be speculated on. In principle, residual Cl^- ions might act as geometric promoters towards noble metal active centers, influencing thus their redispersion (15,16). As the result there might be a lower number of active centers closed together that are necessary for proximity of N-containing adsorbed species leading to N_2 formation. The scenario is pictured by the surface with more isolated active centers responsible for overhydrogenation of adsorbed nitrate species, finally leading to the undesired NH_4^+ and insufficient selectivity of catalyst sample 1 in terms of absolute ammonia amount produced (10).

The XPS results of calcined and reduced samples are presented in Fig. 1 and in terms of their Pd and Sn of 3d-serie electron binding energies in Table 2. Hydrogen reduces the Pd in all cases, however, different number of Pd states can be observed. On the other hand, for the sample with a higher Pd amount (sample 2) there are two Pd states, i.e. before and after hydrogen treatment, for sample 1 double Pd oxidation state is seen only in the calcined sample. The reducibility of the Pd seems to be different depending on support preparation and amount of Pd; palladium in sample 1 is reduced more strongly than its counterpart having support obtained at pH 9.5 and higher Pd loading (17).

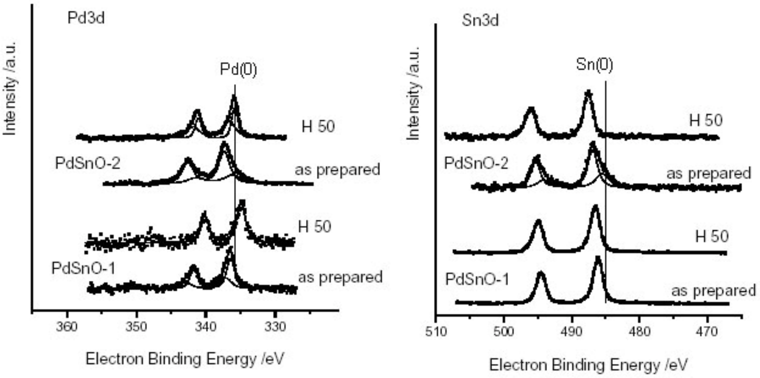

Figure 1. XPS spectra of Pd 3d and Sn 3d states of catalyst samples 1 and 2 before and after reduction in H_2 at 50 °C

Table 2. Electron binding energies of Pd and Sn of catalyst samples 1 and 2 before and after reduction in H_2 at 50 °C

Sample		Electron binding energy, eV							
		Pd 3d $_{5/2}$		Pd 3d $_{3/2}$		Sn 3d $_{5/2}$		Sn 3d $_{3/2}$	
1	calcined	336.4	337.1	341.7	343.0	486.1		494.5	
	reduced	334.9		340.2		486.5		495.0	
2	calcined	336.1	337.4	341.4	342.6	485.6	486.9	494.4	495.4
	reduced	335.8	336.6	341.0	341.8	487.6		496.1	

Oxidation state of tin in the case of calcined samples differs depending on support preparation conditions; there is one Sn state for the calcined sample 1, but two for the calcined sample 2. After the hydrogen treatment a change of Sn oxidation states takes place, resulting in only one valence state in all samples. However, the hydrogen treatment leads to a bit higher electron binding energies in the case of sample 2, indicating that part of the Sn stays in its oxidation form (17).

These results indicate a strong interaction between the Pd and the Sn (17). It could be postulated that Pd is not only reduced by the hydrogen, but in addition there is an electron shift from Sn to Pd. The hydrogen treatment leads to decrease of the Pd amount on the surface of all samples; however this decrease is the smallest in the case of sample 2. The extremely low Pd fraction on the surface of sample 1 obtained after the reduction (Fig. 2) might be explained by metal segregation from the surface to the bulk. Subsequently, the existence of some interaction of Pd entities and SnO_2 may be considered as a cause for an activity rise in the particular case.

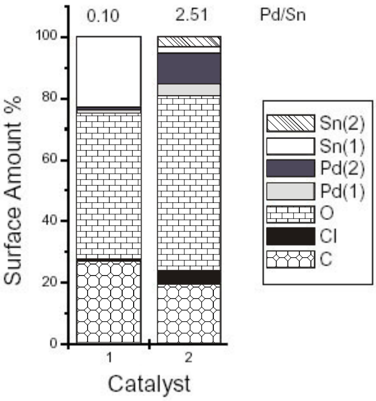

Figure 2. Fraction of elements determined by XPS on the surface of reduced catalyst samples 1 and 2

The low Pd fraction over the sample 1 surface might be the result of a partial dissolution of Pd species into the SnO_2 lattice, resulting in a number of defects. As mentioned before, novel literature suggests the monometallic mechanism that includes low-coordinated SnO_2-site as an active center (2). This SnO_{2-X} active phase originates as a consequence of Pd and SnO_2 interaction (2). The absence of nitrites as intermediate in both of catalytic runs performed in this investigation speaks against the traditionally accepted mechanism. Therefore, the lack of Pd on the surface may be a result of the highly disordered solid solution imposed by strong metal support interactions (SMSI) of Pd^{2+} and SnO_2, occurring by taking up the O from the surface of the support. In such a way some SnO_{2-X} species may stay onto the surface of catalyst 1, which might be responsible for its pronounced activity.

CONCLUSION

Textural properties of Pd/SnO_2 catalyst, although being important, are not crucial for denitration catalytic activity. It seems that Pd reducibility and the degree of metal support interactions between Pd and SnO_2 in a way that Pd^{2+} is dissolved in SnO_2 matrix govern additionally catalytic activity. Taking up of O from the surface of the support it makes possible formation of some SnO_{2-X} active sites. From that perspective the bifunctional mechanism does not seem possible, at least in the case of sample 1 lacking the Pd active sites.

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ИНТЕРАКЦИЈА МЕТАЛ-НОСАЧ – КЉУЧНИ ФАКТОР АКТИВНОСТИ Pd/SnO_2 КАТАЛИЗАТОРА У РЕАКЦИЈИ ДЕНИТРАЦИЈЕ ВОДЕ

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Извршена је синтеза два мезопорозна наноструктурна Pd/SnO_2 катализатора модификованом сол-гел методом при различитим pH вредностима синтезе носача. Узорци катализатора показали су различиту активност и селективност у реакцији денитрације воде у присуству водоника. XPS резултати указују на јаку интеракцију између Pd и Sn, што је вероватно резултат електронског прелаза са Sn на Pd. Чврст раствор Pd^{2+} и SnO_2 се формира по отпуштању O са површине носача. На овај начин неке SnO_{2-x} врсте могу остати на површини катализатора и бити одговорне за његову повећану активност.

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