Water Denitrification by Hydrogenation over Ru-Sn Catalyst

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Hydrogenation of nitrates from water was performed on 0.5% Ru-Sn/γ- Al_2O_3 catalyst, using a fixed bed catalytic reactor, in continuous systems. The catalyst was characterized by determining the distribution of the acid strength, Langmuir isotherm and textural characteristics. The reaction mixture was analyzed spectrophotometric and by measuring of pH. Conversion of nitrate decrease with increasing of volume hourly space velocities of water with a similar slope and increases *with increasing of temperature. The pH of the nitrate solution processed at 85°C was basic.*

Keywords : water denitrification, hydrogenation, catalyst, Ru-Sn/γ- Al_2O_3

According to EPA the nitrates content of soil in areas where man has not intervened is between 0 - 2.5 mg / L. The pollution of soil with nitrate is caused by human factor. Thus the major source of water pollution in Europe is agricultural use of nitrates in organic fertilizers.

Reduction of nitrates in water can be performed on bimetallic catalysts, obtained mainly through redox techniques. The parent metal is generally a noble metal (Rh, Pd, Pt), while the promoter is most particularly a non-noble metal (Ge, Sn, Cu ...) whose oxidation state plays a important role in the hydrogenation. In order to reduce nitrate, the second metal affects essentially the first step of the process (the conversion of nitrate to nitrite) and the selectivity of the overall (limiting the NH_3 formation) may be considerably improved by adjusting of the ratio base metal – additive, but should not be disregarded the reaction conditions (temperature, pressure, influence of water *p*H) [1].

In other work [2] It is shown the role of the interaction between Pt and Cu in the catalytic reduction of nitrate in water using Pt catalyst supported on mixed oxides of CuMgAl. They achieved three concentrations of Pt obtaining different specific areas, confirmed by BET, TPR, HRTEM, XRD and FTIR spectroscopy. In all cases they were detected low concentrations of ammonium, and the nitrate concentrations have fulfilled the requirements of EU legislation on maximum permissible concentration. The presence of particles of the Pt-Cu alloy has resulted in an increase in selectivity to nitrogen, by enhancing the reduction of nitrites. In order to maximize the conversion of nitrate is necessary to be obtained Pt particles that interact with Cu and Pt-Cu alloy [2].

Pd-Cu catalysts supported on activated carbon (Pd-Cu / ACC) prepared by selective depositing, presented a high activity (92% conversion) and a good selectivity (about 93%) in liquid phase hydrogenation of nitrates to nitrogen. For this study, data were obtained about the composition of Cu-Pd / AC bimetallic catalyst surface and their influence on the catalytic nitrate hydrogenation process. By combining CO chemisorption and HRSEM was evidenced Cu metal deposition in Pd crystallites core, probably forming Pd-Cu bimetallic clusters and Pd atoms free [3].

By combination of Al_2O_3 and SiO_2 supports the catalytic properties of Pd and in the nitrates hydrogenation process are improved to increase nitrate conversion and reduce the ammonia concentration. Mechanical mixture of monometallic catalysts treated with hydrogen at 450 °C are efficient catalysts if Pd is supported on Al_2O_3 and In on SiO_2. Thus mixture of 75 wt.% Pd /Al_2O_3 and 25 wt%. In/ SiO_2 shows a considerable activity and a high selectivity to nitrogen. When these monometallic catalysts are reduced separately and then mixed in-situ in a batch reactor, is obtained a moderate activity of nitrate reduction, suggesting some migration of In or Pd [4].

The Pt, In, and Pd,catalysts supported on alumina or silica are active for nitrate reducing r to N_2 using H_2 as the reducing agent. Presence of In determine a change in bands of CO species adsorbed on Pd and Pt, suggesting the formation of intermetallic particles. These results indicate the metal particles agglomeration during the reaction, being in accordance with the TEM results. The increase of In content from 0.25 to 0.5 wt%. cause a moderate decrease in the nitrates conversion for all catalysts, which may be associated with a decrease in Pd isolated centers which are responsible for the hydrogen dissociation [5].

The catalysts containing 1wt%. Pt and 0.25 wt.% In had a high initial activity which decreased with reaction time. EXAFS characterization showed that fresh solid consists of mixture of bimetallic particles of Pt / In and of monometallic Pt particles. After the reaction, the bimetallic particles amount decreased and the non-alloyed Pt amount increased considerably, which led to a catalyst partial deactivation [6].

In a study of the nitrate reduction to nitrogen on Pt-In and Pd-In bimetallic catalysts, deposited on alumina or silica, was used hydrogen as the reducing agent. The results indicate that the main surface species present in catalysts are bimetallic particles with surface enriched in In, Pt or Pd metalic crystals, Pt or Pd oxides and In_2O_3. Requirements specified as limit values for water are 50 ppm NO^{3-}, 0.1 ppm NO^{2-} and 0.5 ppm NH_4^+. They studied more catalysts based on Pt, Pd and In. The reaction rate is strongly influenced either by the ratio Pt: In or Pd: In ratio, the optimum being a low In content. Among all catalysts studied the most active is Pd (1 wt.%) In (0.25 wt.%) / Al_2O_3, but has a high selectivity to ammonia when the nitrate conversion is lower than 100%. Also Pt (1.0%) - In (0.25%) / Al_2O_3 present a high initial activity, but is

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deactivated quickly during the reaction time. In general, Pd-In catalysts are more active for converting nitrate than Pt-In and alumina is a better support than silica [7].

Bimetallic Pd-Cu catalysts supported on Dowex cationic resin and on γ-Al_2O_3 were prepared by ion exchange and by impregnation method. These catalysts were tested for hydrogenation of nitrates in the liquid phase. Various methods were used to reduce metal precursors. Pd-Cu catalysts have been prepared by liquid phase reduction the palladium (II) and copper (II) chloride deposited in a resin. Pd-Cu catalysts supported on γ-Al_2O_3 exhibited a high activity to nitrate removal. Pd-Cu catalysts on resin favor the formation of other products than nitrite and ammonia better than alumina-based catalysts. [8] The use of various reducing agents such as sodium borohydride in ethanol or water affect catalyst activity [9].

The reduction of nitrates has been studied on bimetallic Pd-Cu catalysts supported on a TiO_2 [10, 11]. Bimetallic Pd catalysts deposited on TiO_2 and promoted with Mg and Nb were very active for catalytic hydrogenation of nitrates, but the ammonium selectivity was great. Promoting with Nb decreases the activity of nitrates reducing and promoting with Mg improves this activity [10]. Basic medium favor the hydrogenation of the nitrate to nitrite, while the acidic conditions favor the hydrogenation of nitrites to nitrogen [11].

They were tested Pd-Cu metal catalysts supported on activated carbon to reduce nitrates in the water. The method of preparation affects the activity of the Pd-Cu catalysts to nitrate reducing, but the effect on selectivity for ammonia is negligible. The atomic ratio Cu / Pd, and the total content of metal affects both the activity and selectivity of catalysts prepared by chemical reduction [12].

Ru-based catalysts have been used in various chemical processes [13, 14]. This paper aims to study the possibility of eliminating nitrates from water by reduction on Ru-Sn/ γ-Al_2O_3.

Experimental part

The raw materials used in experiments were ruthenium(III) chloride hydrate p.a.(Sigma-Aldrich), tin(II) chloride dehydrate puriss p.a.(Sigma-Aldrich), sodium nitrate ACS reagent (Sigma-Aldrich), γ-alumina granulated and electrolytic hydrogen purity from Linde Company.

The synthesis of catalysts where achieved by successive impregnation of ã-alumina with aqueous solutions of tin(II) chloride and ruthenium(III) chloride, applying the method of filling the pores. Chemical composition of catalyst used in the experimental program was determined by atomic absorption (Varian AA240FS). Thus, the metal concentration of catalyst was 1% for Ru and 2% for Sn. Conditioning of the catalyst between impregnations was achieved by drying at 160°C for 4 h. The final conditioning was performed by drying at 160°C for 6 h, calcination at 450°C for 6 h and two-stage reduction by treatment with sodium borohydride in aqueous solution at a temperature of 80°C, followed by activation in a stream of hydrogen at 450°C for 6 h[13].

The experimental program was performed in a continuous system and fixed bed catalytic reactor. The process was carried out in isothermal conditions. The temperature was regulated with an automatic system coupled with two thermocouples fixed, placed in the reactor jacket.A metallic jacket for the mobile thermocouple was also placed in the axis of the reactor in order to measure the reaction temperature of the catalyst bed.

Reaction conditions for catalysts were:

-pressure: 5 atm.;

-temperature: 50 -85^{0}C ;

-volume hourly space velocities of water (VHSV): 1.5 – 3.0 h^{-1};

-molar ratio hydrogen/ water: 2/1.

Characterization of reaction products was determined with standardized methods. Thus, the content of nitrate in the reaction mixture was performed by UV-VIS spectrometry (*SR* ISO 7890-3:2000) with a spectrometer UV-VIS JENWAY. The *p*H of the reaction mixture was determined with a pH-meter TOLEDO (SR ISO 10523 - 2012). The aqueous solution used in the experiment had a sodium nitrate content of 60 mg / L.

Acid strength distribution of the catalyst was determined by termodesorption of diethyl amine in the temperature range 20-700°C. Thermal analyzes (ATG, DSC) was performed on a DuPont Instruments' Thermal Analyst 2000/ 2100 coupled with a module 951 Thermogravimetric Analizer.

Textural characteristics of the catalysts, specific surface area, pore volume, average pore diameter, and respectively pore size distribution, were determined by automatic recording and processing of the isotherms of adsorption / desorption of nitrogen on the instrument Autosorb 1 Quantacrome.

Results and discussions

Thermodesorption curve of diethylamine for the Ru - Sn/γ-Al_2O_3 catalyst is shown in figure 1 (A-thermodesorption from centers with weakly acidic, B-thermodesorption from centers with medium acidity, C-thermodesorption from centers with high acidity). Based on thermal desorption curves of diethylamine it was determined the concentration of acidic centers of different acidities (table 1).

The concentration of strong acidic centers is lower with 70% than the concentration of medium acidic centers and the concentration of weak acidic centers is higher with 280% than medium acidity centers.

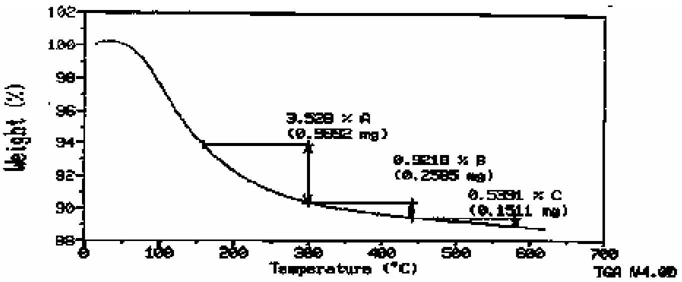

Fig.1. Diethylamine thermodesorption curve for Ru - Sn/ γ-Al_2O_3 catalyst [13]

Table 1

THE DISTRIBUTION OF ACIDITY STRENGTH OF Ru - Sn /γ-Al_2O_3 [13]

The type of the acidic centers	The acidity strength, meq./G
Weak acids centers	0.4824
Medium acids centers	0.1260
Strong acids centers	0.0737
Totally	0.6821

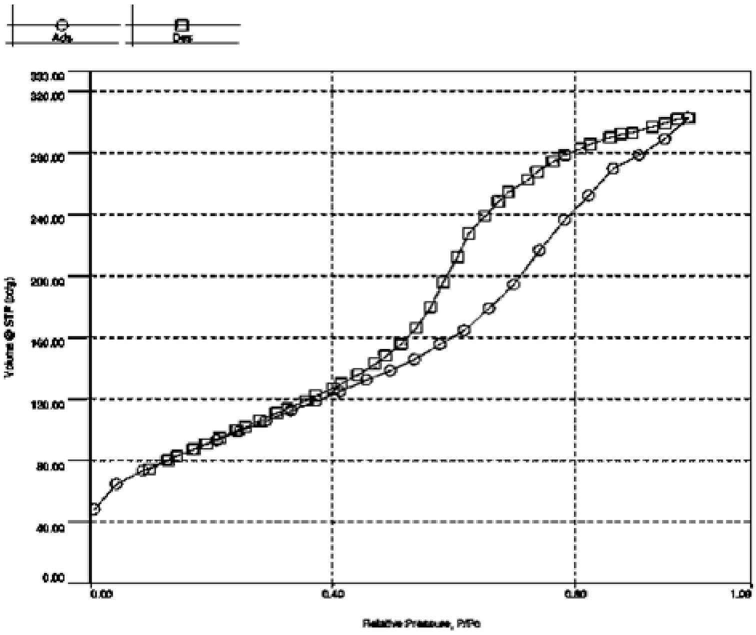

Fig. 2. Langmuir isotherm for Ru-Sn/γ-Al_2O_3 catalyst

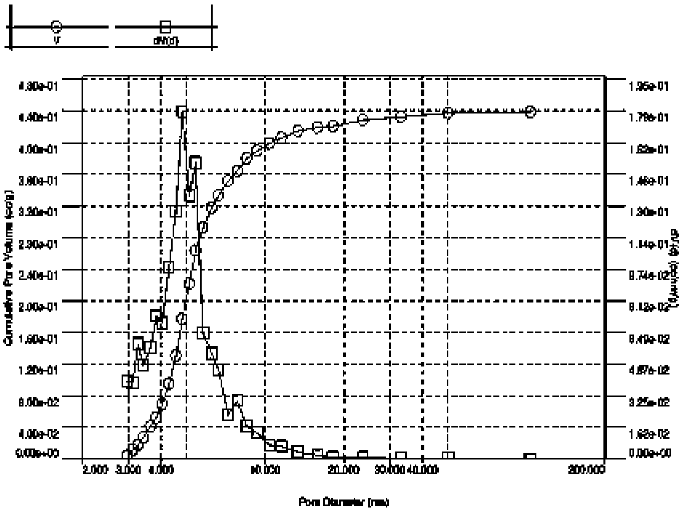

Fig. 3. The pore size distribution of the Ru-Sn/γ-Al_2O_3 catalyst

Langmuir isotherm for Ru-Sn/γ-Al_2O_3 catalyst is shown in figure 2. The isotherm is type IV with H2 loop hysteresis, specific for networks pores or interconnected pores.

Textural characteristics of the catalyst were determined by the BET method:

- surface area: 322.416 m² / g;
- pore volume: 0.438 cm^3 / g;
- average pore diameter: 4.832 nm.

Pore size distribution of the catalyst Ru-Sn/γ-Al_2O_3, determined by the BJH desorption method is presented in figure 3.

This figure shows a higher concentration of pore with diameter of approx. 4.8 nm. The catalyst falls into the category of mesoporous materials.

Influence of reaction times on the content of nitrates is shown in figures 4. The slope variation of water nitrate content, with reaction time, shows a higher value at lower reaction times.

The influence of temperature on the conversion of nitrates and on the *p*H is shown in figures 5 and 6. Figure 6 shows an increasing of nitrates conversion with temperature, the increased being nearly linear for the volume hourly space velocities tested. The conversion increases with a slope whose value is greater at lower volume hourly space velocities.

*p*H variation of nitrate solution with temperature arises after a nearly linear slope for higher values of volume hourly space velocities and after an exponential curve for lower values of volume hourly space velocities. Differences between pH of nitrate solution after reduction with the those two values of volume hourly space velocities is probably due to the stripping of ammonia at higher flow of hydrogen.

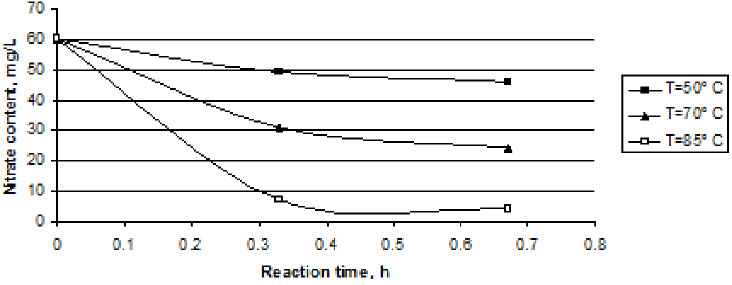

Fig. 4. Nitrates conversion with reaction time at different temperature

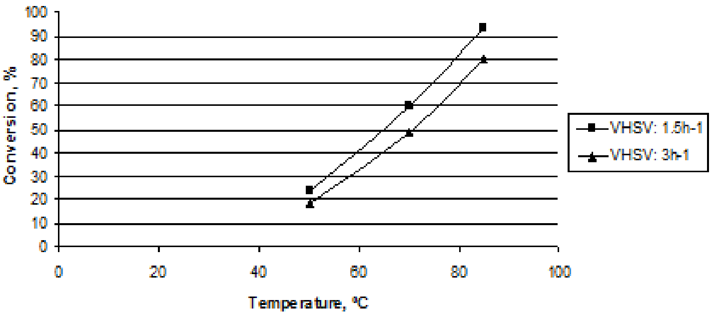

Fig. 5. Variation of nitrates conversion with temperature at different volume hourly space velocities

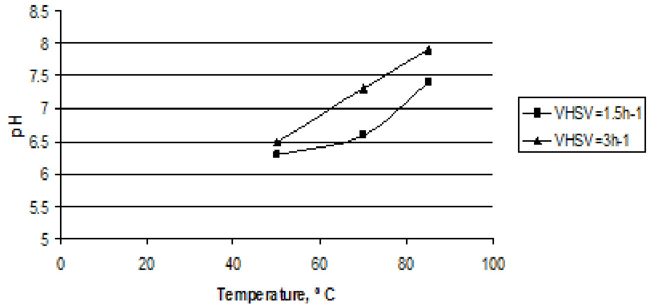

Fig. 6. Variation of *p*H with temperature at different volume hourly space velocities

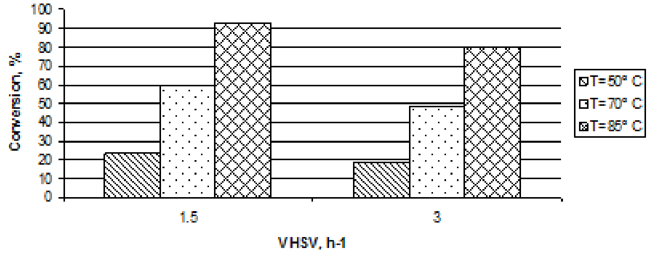

Fig. 7. Conversion of nitrate with volume hourly space velocities of water at different temperatures

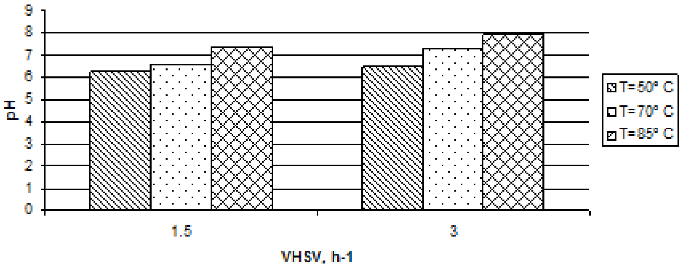

Fig. 8. Variation of the *p*H with volume hourly space velocities of water at different temperatures

Influence of volume hourly space velocities on the conversion of nitrates and on *p*H is shown in figures 7 and 8.

It shows a decrease in conversion of nitrate with increasing of volume hourly space velocities of water for all three temperatures. The conversion increase of nitrates with temperature is more pronounced at lower values of volume hourly space velocities.

The variation of the *p*H of the nitrate solution with volume hourly space velocities of water is reduced, the *p*H of the nitrate solution processed at 85 °C for both volume hourly space velocities and at 70°C for volume hourly space velocities of $3h^{-1}$ being basic.

Conclusions

Hydrogenation of nitrates from water was performed on Ru - Sn/ γ-Al_2O_3 catalyst, using a fixed bed catalytic reactor in continuous systems.

The reaction mixture was analyzed by determining nitrate content and by measuring of *p*H.

The catalyst was characterized by determining the acidity and textural characteristics.

Pore size distribution of the catalyst Ru-Sn/γ-Al_2O_3 was determined by the BJH desorption method.

Conversion of nitrate decrease with increasing of volume hourly space velocities of water and increase with temperature.

The variation of the *p*H of the nitrate solution with volume hourly space velocities of water is reduced, the *p*H of the nitrate solution processed at higher temperatures being basic.

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