THERMAL ANALYSIS APPLIED TO CHARACTERIZATION OF COPPER AND NICKEL CATALYSTS

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A series of mono- and bimetallic catalysts of copper and nickel supported on silica were synthesized by the wet impregnation method. The obtained materials were characterized by X-ray diffraction (XRD) and thermal analysis (TG/DTG). From TG curves and applying the Vyazovkin model-free kinetics, the apparent activation energy (E_a) related to the decomposition of Cu and Ni nitrates on the silica surface were determined. The obtained values were correlated to the catalytic activity of the materials on the reaction of nitrate degradation in water. The catalytic processes were carried out in a batch slurry reactor under continuous flow of hydrogen in the aqueous solution containing 200 ppm of nitrate. It was verified that the catalysts with lower activation energy presented higher catalytic activity.

Keywords: copper and nickel catalysts, nitrate degradation, thermal analysis

Introduction

The increase of nitrate concentration in ground water is a permanent problem for many cities because nitrate causes a serious risk of health [1–7]. The concentration of nitrate in drinking water exceeds the maximum admissible level in many European countries, in the United States and in many others coutries, worldwide [8, 9]. Currently, the process of removing nitrates from these water is difficult and very expensive. Therefore, the water plant companies decrease this problem by diluting the water with uncontaminated water or disabling the well [10]. In this pioneer work in Brazil, nitrate degradation in drinking water by catalytic hydrogenation using mono- and bimetallic catalyst of copper and nickel supported on silica was developed. The selection of the metals depended on the hydrogenation power and their expenses.

This paper deals with the synthesis, characterization and catalytic application of copper and nickel catalysts supported on silica. A study of the catalytic and thermal properties on the obtained materials was used for understanding the catalytic activity for nitrate degradation in water. From TG analysis and applying the Vyazovkin model-free kinetics [11–13], the apparent activation energy (E_a) relative to copper and nickel salts decomposition on the silica surface was determined. The E_a values were correlated with the catalytic activity of the materials on the nitrate degradation process.

Experimental

The copper and nickel catalysts supported by silica were prepared by conventional method of wet impregnation [14]. Silica was provided from Merck. The precursors salts were copper nitrate ($Cu(NO_3)_2 \cdot 6H_2O$, Lafan) and nickel nitrate ($Ni(NO_3)_2 \cdot 3H_2O$, Riedel-de-Haen) and the supported metal catalysts were prepared in order to obtain mono- and bimetallic configurations: AM1=6.0 mass% Ni; AM2=3.0 mass% Cu and 3.0 mass% Ni; AM3=6.0 mass% Cu.

The obtained materials were calcined at 400°C for 4 h in air atmosphere, and then characterized by X-ray diffraction (XRD) and thermogravimetry and differential thermogravimetry (TG/DTG). XRD measurement were carried out on a Shimadzu (XRD 6000) X-ray equipment using CuK$_\alpha$ radiation in the 2θ angle of 5 to 80 with a step of 0.02º. For this analysis ca. 100 mg of each synthesized material was used. TG/DTG measurements for uncalcined samples were carried out in air atmosphere using a TGA/SDTA 851 apparatus in the temperature range of 30 to 900°C at a heating rates of 5, 10 and 20°C min^{-1} under dynamic air flow at a rate of 25 mL min^{-1}. TG analyses were used to determine the kinetics properties of uncalcined material, in the decomposition stage of the precursor salts of copper and nickel on silica support. The Vyazovkin model-free kinetic method was used [11–13] to evaluate the kinetics parameters, as activation energy, conversion rate and degradation time of salts as function of temperature [15, 16].

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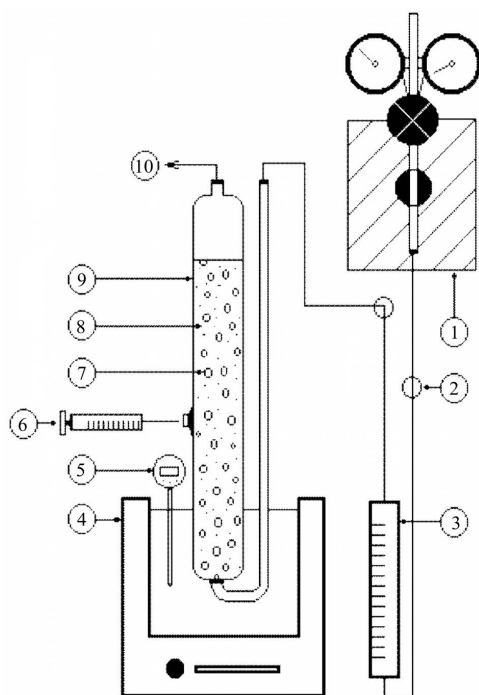
Fig. 1 Bath slurry reactor used in the catalytic process, where
1 – hydrogen pressure valve, 2 – adjusting valve,
3 – flow meter, 4 – heating system, 5 – thermometer,
6 – syringe, 7 – hydrogen bubbles, 8 – nitrate solution
with catalyst, 9 – tubular mud reactor, 10 – effluents exit

The catalytic evaluation was carried out in a batch slurry reactor under continuous hydrogen flow through in the aqueous solution containing nitrate at atmospheric pressure, as can be seen in Fig. 1. In a typical test was used placing ca. 150 mg of catalyst into 20 mL of aqueous solution containing 200 ppm of nitrate. Prior to the tests, in order to obtain the active catalysts, the copper and nickel oxides were reduced to obtain their respective metal form (Cu° and Ni°). The catalytic materials were designed using the following compositions: AM1: 6% Ni/SiO$_2$; AM2: 3% Cu, 3% Ni/SiO$_2$ and AM3: 6% Cu/SiO$_2$. Then, the reduced catalysts were submitted to the catalytic tests and the degree of conversion *vs.* time was monitored. The reaction took place at 60°C under a continouos hydrogen flow (flow rate: 80 mL min^{-1}).

Results and discussion

Figure 2 shows the XPRD patterns of the synthesized samples of copper and nickel supported on silica at several compositions. For the sake of comparison, the XPRD profiles for pure copper and nickel oxides are given in Fig. 2. As it can be seen, AM1 sample showed the presence of pure NiO phase with main peaks around 2θ=37.27°, 43.30° and 62.90°. The AM3 presented characteristic peaks of CuO in 2θ=35.50°, 38.74° and 48.66°

and the AM2 sample presented characteristic peaks corresponding to the CuO and NiO mixture, evidencing that under the synthesis conditions the formation of mixed oxides type NiCuO$_x$ by the simultaneous copper and nickel salts decomposition was not verified. A broad peak observed at ca. 22° is related to the silica supporter.
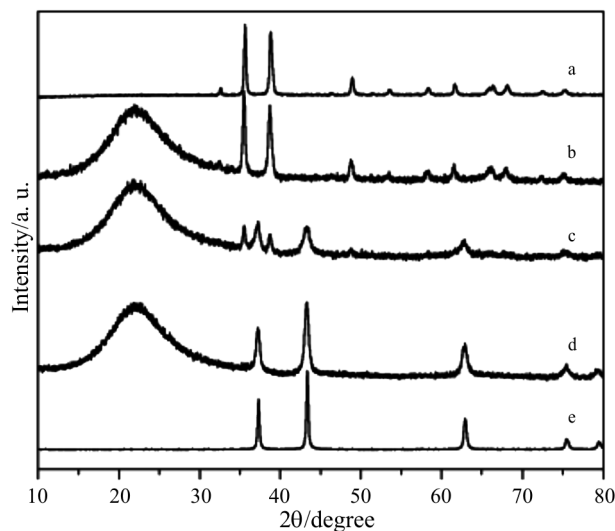

Fig. 2 XPRD pattern of copper and nickel silica supported catalysts: a – pure NiO, b – AM1, c – AM2, d – AM3 and e – pure CuO

TG analysis of copper and nickel supported on silica provides information on the mass loss steps of the uncalcined samples. The mass loss steps occurred in the following temperature ranges: *i*) between 30–200°C the evaporation of the physically adsorbed water takes place *ii*) between 200–350°C the decomposition of the nickel and copper salts can be seen. TG curves (Fig. 3) were used to obtain information about the optimum temperature of calcination of the samples as well as the activation energy of the nickel and copper salts decomposition by the Vyazovkin model free kinetic method [9–11].

In a typical experiment, to obtain the activation energy is necessary to repeat the TG runs at least with three different heating rates (β) and the respective conversion curves (Fig. 4) are evaluated from the measured TG curves. For each conversion (α), ln(β / T_α^2) is plotted *vs.* 1/T_α, gives a straight line with a slope –E_α/R, therefore the activation energy (Fig. 5) is obtained as function of the conversion. The values of apparent activation energies are presented in Table 1.

The catalytic tests indicated that the activity for nitrate degradation can be related to the activation energy relative to the decomposition of the Cu and Ni precursor salts. The catalyst that presented the higher activation energy values showed lower catalytic ac-

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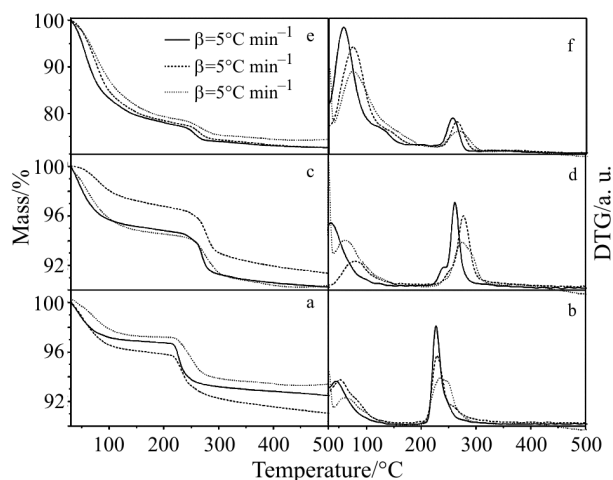
Fig. 3 TG and DTG curves for uncalcined copper and silica
supported catalysts at different heating rates:
a, b – AM1, c, d – AM2 and e, f – AM3
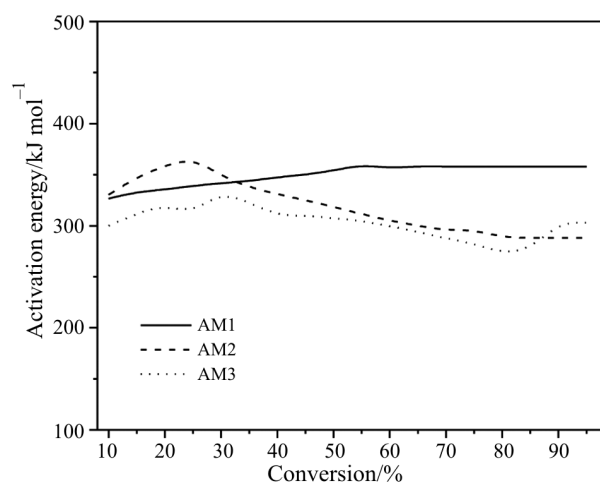
Fig. 4 Activation energy *vs*. conversion related to degradation
of the copper and nickel salts
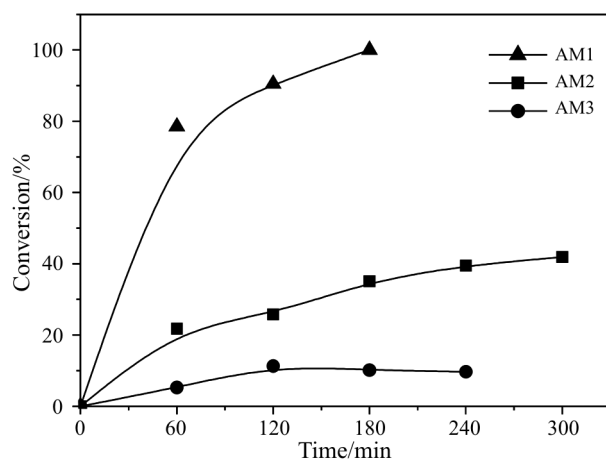
Fig. 5 Conversion of nitrate as a function of the reaction time
of the catalysts

Table 1 Apparent activation energy related the copper and
nickel salts decomposition on silica supported cata-
lysts and the respective nitrate conversion values

Sample	E_a/kJ mol^{-1}	Conversion/%	
		NO$_3^-$	NO$_2^-$
AM1	293.6±10.4%	100.0	0.0
AM2	332.7±10.8%	41.9	46.9
AM3	352.3±10.1%	9.7	0.0

tivity. These results can be justified through the inter-
action of the Cu and Ni metallic particles with the
support [17] as it is shown schematically in Fig. 6. For
a strong interaction of the metal with silica, it is nec-
essary to apply more energy to the system. When the
metal is distributed the internal layers on the sup-
porter, the activation energy is high and consequently
less active metal sites are available. These analogies
are observed through the results presented in Table 1
and Figs 4 and 5.

Figure 6 shows a schematic representation of the
possible metal-support interaction. The cases a–c rep-
resent a small, medium and larger metal-support in-
teraction, respectively. Case a represents the nickel
supported catalyst (AM1), case b represents the bime-
tallic copper-nickel (AM2) supported catalyst while
case c represents the copper based catalyst (AM3).
This assumption was based on the values of the appar-
ent activation energies obtained by using the
Vyazovkin model-free kinetic method as it is indi-
cated in Table 1 compared to the catalytic activity.
High values of the apparent activation energy are as-
sociated to difficulty of the decomposition of precur-
sors on the silica surface. This evidences that a poor
metallic dispersion of the oxide particles on the silica
supports occurred according the following order of
E_a: AM3>AM2>AM1. Sample AM1 presented lower
activation energy and high catalytic activity for the
nitrate degradation reaction.
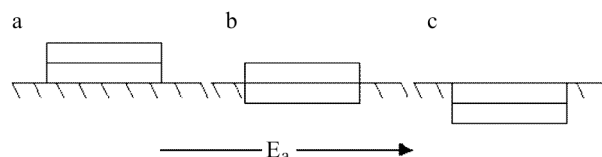
Fig. 6 Schematic representation of interaction of the oxide
particles onto silica support after salt decomposition
indicating the tendency of activation energy tendency.
a – AM1 (6% Ni/SiO$_2$), b – AM2 (3% Ni, 3% Cu/SiO$_2$)
and c – AM3 (6% Cu/SiO$_2$)

Conclusions

From TG/DTG analysis it was observed that the decomposition of the copper and nickel nitrates occurred in the range of 200–400°C, evidencing that the materials can be calcined at 400°C. From XPRD analysis, after the decomposition of the precursor salts the formation of copper and nickel oxides on the supports were observed, while Cu–Ni mixed oxide phase was not verified. The catalytic activities of the catalysts were in relation to the type of oxide species obtained after the metal decomposition onto silica and also with the metallic particle dispersion obtained after the reduction. Concerning the catalytic activity, the materials that presented lower activation energies relative to salt decomposition resulted in a substance with higher activity for the reaction of nitrate decomposition in aqueous solution with total conversion after 3 h of reaction. The high values of activation energy can be associated to a low metal-support interaction, and, consequently to low catalytic activity. Thus, the nickel supported on silica exhibited presented the lower activation energy, being the more easily reduced material with a better metallic dispersion, showing higher catalytic activity.

Acknowledgements

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