

REGENERATION OF NO_x CATALYSTS USING SUPERCRITICAL AND SUBCRITICAL WATER

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ABSTRACT:

SCR-NO_x has been described as a method to remove NO_x from natural-gas-fueled engines, such as lean-burn gas engines in cogeneration systems. One of the main problems of this kind of catalysts is the fast deactivation at industrial level due to the presence of SO_x. A technique for reduction of the operation costs is remove the retain substances. With this method catalysts can be reused. Within the possible techniques for the full regeneration of catalysts emphasize the use of sub and supercritical fluids. The advantages of this technology are mainly economics and environmental. In this work, we studied the regeneration of catalysts used in Selective Catalytic Reduction of NO_x using supercritical water.

KEYWORDS: Regeneration, catalysts, supercritical.

INTRODUCTION

Much research related to the selective catalytic reduction of NO_x by hydrocarbons was undertaken and reported in the literature due to its potential for the effective control of NO emission in oxidant environment [1-7]. This reaction has been described as a method to remove NO_x from natural-gas-fueled engines, such as lean-burn gas engines in cogeneration systems [8] and lean-burn gasoline and diesel engines where the noble-metal three ways catalysts are not effective in the presence of excess oxygen [9]. Hydrocarbons would be the preferred reducing agents over NH₃ because of the practical problems associated with its use: handling and slippage through the reactor.

One of the main problems of this kind of catalysts is the fast deactivation at industrial level due to the presence of SO_x [10-13] that normally come along with the NO_x, as well as the coquization of the catalysts in presence of hydrocarbons [14-17]. Because of that is necessary the substitution of the catalyst in the installation with the environmental problem, due to the presence in the catalyst of heavy metals such as cobalt, copper, nickel, palladium, platinum, manganese, etc. Also, the increase of lifetime of the catalysts is very interesting from an economical point of view. The cost of the catalysts in a short lifetime is high and unjustified.

A technique for reduction of the operation costs is remove the retain substances. With this method catalysts can be reused.

Deactivation and regeneration of catalysts has been studied from the point of view of the coke deposits in the catalytic centres (acids and metallics) using temperature program oxidation or similar techniques [18, 19]. Although these studies have contributed to the better grasp of the basic principles of decoquization, is necessary expand the study to the full regeneration of the catalysts, namely both coke elimination and sulphates present at the poisoned catalyst.

Within the possible techniques for the full regeneration of catalysts emphasize the use of sub and supercritical fluids [20-22]. The advantages of this technology are mainly economics and environmental. On the one hand the generation of residues dangerous for the environment. On the other hand a double economic action: increase the lifespan of the catalysts, saving in the acquisition of fresh catalyst, normally of high value and decrease cost of residue treatment.

In this work, we studied the regeneration of catalysts used in Selective Catalytic Reduction of NO_x using supercritical water.

EXPERIMENTAL

Catalysts preparation.

Zeolite mordenite was supplied in the sodium form by PQ Corp. with an atomic ratio Si/Al = 7.5 and cristallinity = 100%. The acid form of the zeolite was obtained by exchanging the Na⁺ with 25 ml/g of 0.6 N HCl under agitation at room temperature for 2 h. Next, the suspension was filtered and thoroughly washed with deionized water in order to completely remove the acid, and the solid was then air dried at 120 °C for 14 h. Metal was introduced by conventional ion exchange using 25 mL of 0.1 M metal aqueous solution per gram of zeolite. Co(CH₃COO)₂•4 H₂O and AgNO₃ were used. The mixture was kept under agitation at 30 °C for 14 h. Next, the suspension was filtered and thoroughly washed with deionized water in order to completely remove the occluded salt, and the solid was then air dried at 120 °C for 14 h. This procedure was repeated in the case of catalysts with two metals. Finally, the samples were air-calcined at 550 °C for 4 h. Table 1 summarizes the catalysts here prepared. These catalysts were referred to as a function of proton or sodium form and the metal content. For instance, Na-Ag1.2-Co2.3-MOR corresponds to a catalyst in sodium form exchange firstly with silver (1.2 % wt.) and secondly with cobalt (2.3 % wt.). The ion exchange levels included in Table 1 were determined taking as a reference the number of aluminium atoms contained in the structure.

Catalyst characterization.

The X-ray diffraction (XRD) patterns were measured with a Philips model PW 1710 diffractometer with Ni-filtered Cu-K α radiation.

The metallic content (wt. %) of the prepared catalysts was determined by atomic absorption measurements by using a SPECTRAA 220FS analyzer. The samples were previously dissolved in hydrofluoric acid and diluted to the interval of measurement. In all cases, calibrations from the corresponding patron solutions were performed.

Total acid-site density and acid-strength distribution of each of the catalysts were measured by temperature-programmed desorption (TPD) of ammonia, using a Micromeritics TPD/TPR 2900 analyzer. The samples were housed in a quartz tubular reactor and pretreated in a flow of helium while heating at 15 °C/min up to the calcination temperature of the sample. After a period of 30 minutes at this temperature, the samples were cooled to 180 °C and saturated for 15 min in a stream of ammonia. The catalyst was then allowed to equilibrate in a helium flow at 180 °C for 1 h. The ammonia was then desorbed by using a linear heating rate of 15 °C/min up to 900 °C. Temperature and detector signals were simultaneously recorded. Total acidity is defined as the total acid site density, which is obtained by integration of the area under the curve. To obtain the strength distribution, the desorption profiles were fitted using two peaks, the maximum and width of these peaks being held as constant as possible while fitting each profile. Weak and strong acidities are defined as the concentration of weak and strong acid sites, respectively, obtained by integration of the area under the peaks at the lowest and highest temperatures, respectively. These peaks were not assigned to a specific acid site (Brönsted or Lewis), but it was a convenient way to categorize the acid strength distribution obtained by this method.

TPR measurements were carried out with the same apparatus described above. After loading, the sample was outgassed by heating at 15 °C/min in an argon flow up to the calcination temperature of the sample and kept constant at this temperature for 30 min. Next, it was cooled to room temperature and stabilized under an argon/hydrogen flow ($\geq 99.9990\%$ purity, 83/17 volumetric ratio). The temperature and detector signals were then continuously recorded while heating at 15 °C/min up to 900 °C. The liquids formed during the reduction process were retained by a cooling trap placed between the sample and the detector.

Catalyst activity measurements.

The experiments were carried out at atmospheric pressure in a flow-type apparatus designed for continuous operation. This set-up consisted of a gas feed system for each component with individual control by mass flow meters, a fixed-bed down flow reactor and an exit gas flow meter. The reactor, a stainless steel tube with an internal diameter of 4 mm, was filled with the catalyst sample (0.25 g). A temperature programmer was used with a K-type thermocouple installed in

contact with the catalyst bed. The products were analysed simultaneously by chemiluminescence (NO-NO₂-NO_x ECO PHYSICS analyser) and by a FT-IR analyser (PERKIN ELMER Spectrum GX) capable of measuring continuously and simultaneously the following species: NO, NO₂, N₂O, CO₂ and C₃H₈.

The catalysts were brought to identical reaction conditions for each test (1000 ppm C₃H₆, 1000 ppm NO, 5% O₂, and the balance He; space velocity (GHSV) of 15000 h⁻¹ and a flow rate of 125 ml/min). Before the reaction was started, the catalysts were preconditioned at 550 °C for 60 min by flowing helium over the sample (125 ml/min). After this, the temperature was down to 200 °C. The feeding gases were mixed and preheated prior to entering the reactor.

The reaction products were analysed after 30, 60, 90 and 120 minutes from the beginning of the experiment. Conversion of NO_x to N₂ shown in all tables is the arithmetic mean of these four analyses, the differences between them being always less than 2%.

RESULTS AND DISCUSSION

In a previous work [23], we reported the high activity of Co ion-exchanged mordenite in the presence of excess of oxygen for SCR of NO_x. Zeolite form (H vs. Na) is known to have influence on the catalytic performance as far as SCR by hydrocarbons is concerned [24], so that both acid and sodium zeolite forms were also studied. In this work we report the effect of regeneration of these catalysts after use in presence of SO_x. [25, 26].

Catalyst characterization.

Table 1 list the ion exchange level and both the weak and strong acid sites density.

Table 1. Composition and characterization of zeolite-based catalysts. (Temperatures corresponding with the maximum of the desorption peak are included in bracket together with the acid sites density value).

Catalyst	II _{Ag} (%) ^a	II _{Co} (%) ^b	Weak acid sites density (mmol NH ₃ /g)	Strong acid sites density (mmol NH ₃ /g)
Na-Co3.0-MOR	-	55	0,785 (273°C)	0,300 (638°C)
H-Co3.2-MOR	-	58	0,415 (278°C)	0,739 (658°C)
Na-Ag1.2-Co2.3-MOR	6	42	0,600 (303°C)	1,492 (469°C)
H-Ag1.4-Co2.6-MOR	7	48	0,387 (308°C)	1,763 (494°C)

(a) II_{Ag}: Ion exchange level of silver in the catalyst.

(b) II_{Co}: Ion exchange level of cobalt in the catalyst.

Figure 1 show the TPR profile for cobalt-silver catalysts. The lower overlapping peaks at about 100 °C and 120 C are ascribed to the two dispersed Ag₂O phase [27]. On the basis of the result in [28, 29], the peak at about 700 °C is ascribed to Co²⁺. In the cobalt-silver catalysts the peaks at 300 °C and 500 °C are ascribed to the cobalt oxides, which show a lower reduction temperature than Co-MOR, due to the presence of silver at the catalyst. According with Luo et al. [27], silver oxide is first reduced to form silver atoms at lower temperature and then H₂ is dissociated over these silver atoms and hydrogen atoms spillover to the surface of cobalt oxides. Thus the reduction temperature of cobalt oxides by H₂ can be decreased.

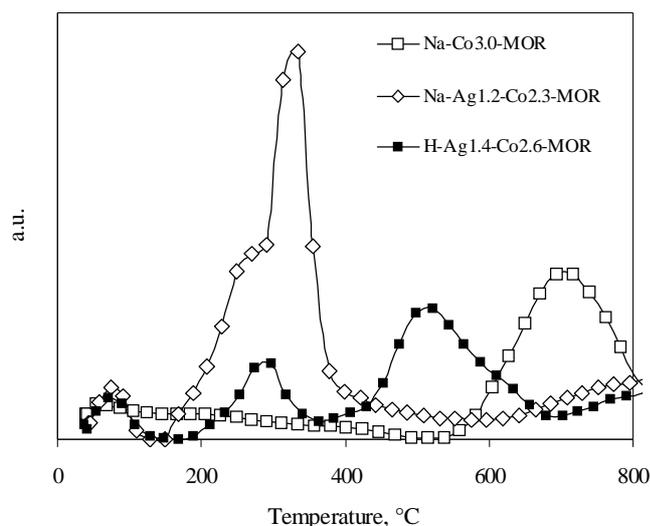


Figure 1. TPR profile of cobalt-silver-based catalysts.

Catalytic activity.

Table 2 shows, the NO_x conversion to N_2 vs. the reaction temperature. Maximum values of NO_x conversion for each of catalysts are indicated in bold.

Table 2. NO_x conversion to N_2 for the zeolite-based catalysts. (No N_2O detected).

Catalyst	NO_x conversion to N_2 (%)											
	T_R (°C) ^a	200	250	300	325	350	375	400	425	450	475	500
Na-MOR		4,6	3,7	6,2	5,8	6,1	7,7	8,3	4,2	8,1	8,5	6,9
H-MOR		9,3	10,0	12,5	15,2	19,5	20,5	22,0	21,4	19,0	17,0	13,8
Na-Co3.0-MOR		8,9	12,2	21,6	35,1	65,1	77,7	79,9	78,0	73,3	68,7	60,1
H-Co3.2-MOR		8,9	10,5	15,7	22,9	32,4	42,4	43,3	40,5	35,7	31,0	26,7
Na-Ag1.2-Co2.3-MOR		9,2	9,9	14,5	32,8	56,4	60,3	37,4	46,6	46,6	47,3	49,6
H-Ag1.4-Co2.6-MOR		9,3	12,0	14,0	17,1	18,7	22,7	70,2	71,8	67,5	63,3	59,6

Figures 2 and 3 shows, the NO_x conversion to N_2 vs. the reaction temperature after use in SO_2 presence and after regeneration using water at 400 °C and 230 atm for Na-Ag1.2-Co2.3-MOR and H-Ag1.4-Co2.6-MOR.

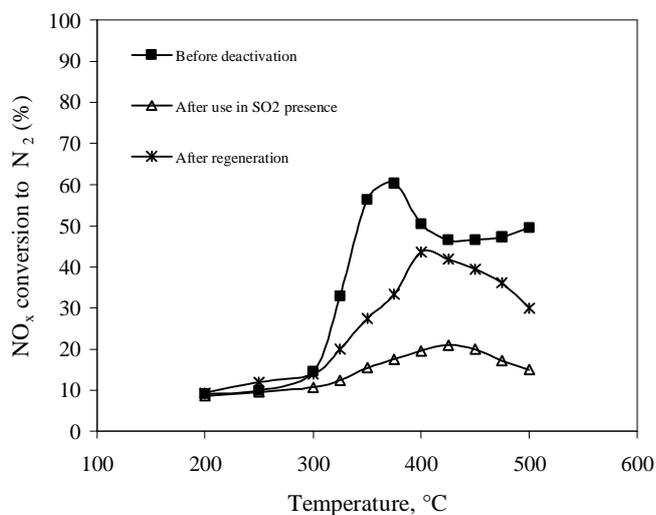


Figure 2. NO_x conversion to N_2 for Na-Ag1.2-Co2.3-MOR.

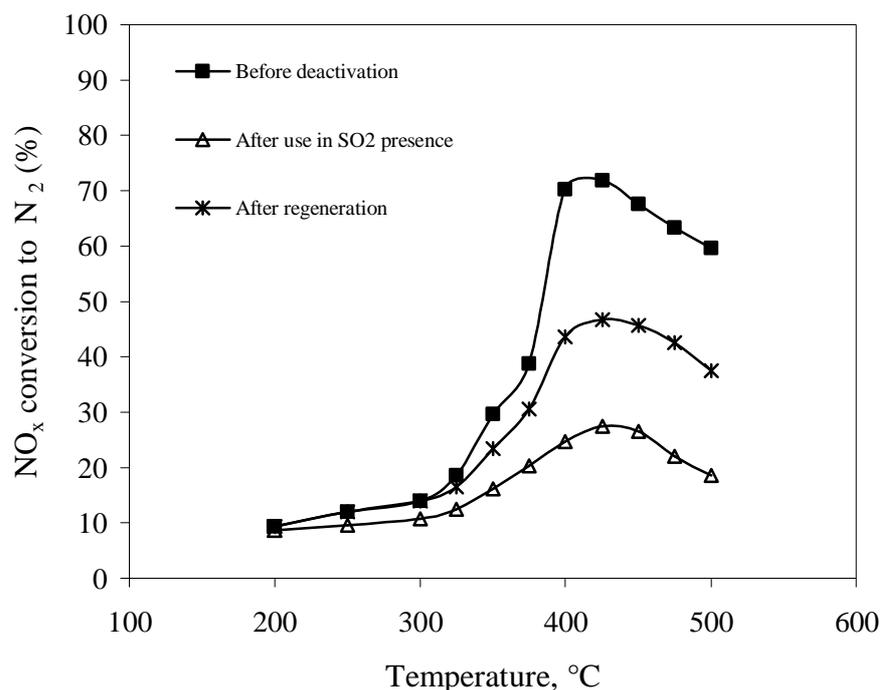


Figure 3. NO_x conversion to N₂ for H-Ag1.4-Co2.6-MOR.

CONCLUSIONS

Selective catalytic reduction of NO by propene was investigated on Co ion-exchanged mordenite in the presence of excess of oxygen studying the effects of parent zeolite (H vs. Na) and the presence of silver on the performance of catalysts.

H₂-TPR results showed that for cobalt, metal was mainly present in the form of Co²⁺. All the catalysts exchanged with silver showed lower activity than the former catalysts, using cobalt. Conversely, the kind of former zeolite (Na⁺ or H⁺) have different influence to the activity of the catalysts. When silver was used as cocation, an increase of the catalytic activity has been observed from sodium to proton former zeolite.

After use in SO₂ presence an important loss of activity have been observed. The catalysts were regenerated using supercritical water, recovering part of its activity.

Regeneration using supercritical fluids is a promising method to recover catalyst activity.

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