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Towards a New Oxidation Process Using Ozone to Regenerate Coked Catalysts

Romain Richard , Carine Julcour, and Marie-Hélène Manero

Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, 31432 Toulouse, France

ABSTRACT

This work focuses on the regeneration of a zeolite catalyst from industry deactivated by fouling with coke. To replace high temperature combustion, a common and energy intensive process, an oxidation process under milder conditions (50 °C–200 °C) has been investigated using ozone. Coked zeolite has been oxidized by an ozone stream in a fixed bed reactor, and regeneration kinetics was followed by analyzing carbon content of the particles and ozone concentration at the outlet. The effects of temperature, time on stream and ozone inlet concentration on carbon removal efficiency were studied. Moreover, elemental analysis showed that a maximum of 74.3% of carbon could be removed from the coked catalyst after 6.5 h. Moreover, the total specific surface area, the pore size distribution and the total pore volume (mainly mesopores) have been evaluated on coked and regenerated samples.

KEYWORDS

Ozone; Coke; Heterogeneous Catalyst; Oxidation; Regeneration; Zeolite

Introduction

Approximately 80% of industrial processes currently use heterogeneous catalysts because of their various advantages, the most significant being the possible reuse of these solid catalysts, either immobilized in the reactor or easily separated from the reaction medium by filtration. Zeolites are largely used as heterogeneous catalysts in many industrial processes because of their unique properties of molecular sieving, acidity, high thermal stability and shape selectivity (Weitkamp and Puppe 1999). Heterogeneous catalysts are used in various applications, such as petrochemicals and fine chemicals or air/wastewater treatment. However, one major drawback is their unavoidable deactivation, which can occur over variable time scales (from seconds to several years).

This phenomenon results from several mechanisms (Bartholomew 2003): poisoning (chemisorption of impurities or by-products on active sites), fouling (carbon or coke deposition) and/or degradation (chemical, physical or mechanical). Coke deposition can involve (i) the blocking of pores from reacting molecules, (ii) the poisoning of active acid catalytic sites (Ivanov, Sobolev, and Panov 2003; Magnoux and Guisnet 1988; Moljord, Magnoux, and Guisnet 1994), (iii) the reduction of heat transfer in reactors, and (iv) an increase of pressure drop and possibly even reactor plugging. Therefore, catalysts must be changed or regenerated. This study focuses on the

regeneration of a zeolite catalyst that has been deactivated by fouling with coke (Guisnet 2002).

The most common process to remove coke is thermal treatment or combustion, generally carried out with air, oxygen or nitrous-oxide-containing mixtures (López et al. 2011; Magnoux and Guisnet 1988). Oxidative treatments using oxygen usually operate under severe conditions (between 400 °C and 600 °C), which may result in irreversible chemical modification of the zeolites through hydrothermal processes with generated water vapor (Copperthwaite et al. 1986; Hughes and Parvinian 1989). To a lesser extent, other regeneration processes have been developed. Among them, a way to regenerate coked catalysts consisted of burning their carbonaceous content in the presence of air or molecular oxygen-containing gas with the addition of an alcohol such as methanol or ethanol (Shimizu et al. 1991).

Depending on catalysts and/or reactions, temperatures varied from 350 °C to 600 °C. The nature and amount of carbonaceous species deposited onto the catalysts also influenced the regeneration time (several hours). Moreover, the regeneration of coked catalysts via reduction with H₂ was investigated (Chen 2003): the process was also performed at high temperatures (427 °C and then 482 °C for several hours), and results similar to the oxidative treatment were obtained. Other works (Shiriyazdanov 2011; Zhang, Zong, and Qiao 2009) carried out experiments with supercritical

fluids due to their unique properties, such as a high dissolving power with respect to heavy organic substances (including coke precursors) and a low viscosity. They showed that high pressures allowed the regeneration of two different catalysts and a quite good restoration of their activity.

The aim of our work was to study the possibility of replacing all these high energy consuming processes by an oxidation under milder conditions. Previous studies showed that a high oxidizing molecule such as ozone (Boyle 1993; Marley et al. 1996) could be used to attack adsorbed compounds on zeolites in gaseous phase (Alejandro et al. 2012; Brodu et al. 2013; Masuda, Fukuyama, and Fujii 2001; Monneyron et al. 2003; Zaitan, Manero, and Héctor 2016), and particularly at room temperature for zeolite-supported metal oxide nanoparticles (Huang et al. 2015).

However, very few publications can be found on the regeneration of coked catalysts by ozone (Copperthwaite et al. 1986; Khangkham et al. 2013). Such a process could be used for thermosensitive catalysts such as Cu/ZnO/Al₂O₃ catalysts involved in methanol synthesis, for which treatment temperature must be below 300 °C (Twigg and Spencer 2003). This work focused on the regeneration of an industrial coked zeolite with ozone. The objective of the study was to investigate the feasibility of the process in a fixed bed reactor and to study the influence of operating parameters in order to propose paths to a future optimization of the process.

Materials and methods

Materials

Coked zeolite catalyst was provided by a chemical company (confidential information) in the form of 1 mm × 4 mm extrudates. This catalyst was used in a petrochemical process. No data was given concerning the chemical structure of this zeolite. Dry air or pure gaseous oxygen (99.99% purity from Air Liquide) was used to carry out these experiments. Moreover, potassium iodide (KI) was purchased from Sigma Aldrich, and was used as a trap to destroy ozone.

Characterization of the coked and regenerated zeolites

Several techniques were used to determine the physicochemical properties of the coked and regenerated catalysts. To characterize the modifications of the catalyst surface and catalyst pores, N₂ adsorption/desorption isotherms were performed at a temperature of -196 °C (on Micromeritics ASAP 2010). For these

analyses, the samples were crushed using a mortar and pestle, prior to N₂ sorption, and resulting solid samples were degassed at 200 °C. The mean pore diameter (D_p) and the specific surface area were calculated from Brunauer-Emmett-Teller (BET) plot at relative pressures between 0.01 and 0.2 (Brunauer, Emmett, and Teller 1938). The mesoporous volume (V_p) was estimated from gas porosimetry measurements according to the Barrett-Joyner-Halenda method (Barrett, Joyner, and Halenda 1951).

Moreover, the amounts of carbon, hydrogen and nitrogen present in the catalyst were determined by CHN elemental analysis (on Perkin Elmer 2400 series II analyzer). Complete and instantaneous oxidation of the sample was carried out by “flash combustion” at a temperature of about 1300 °C in pure oxygen. Prior to analysis, the samples were also crushed using a mortar and pestle.

Experimental setup and procedures

Coked zeolite was cut into two equal pieces: one kept as reference and the other loaded into the reactor for the experiment. The reference halves were crushed and mixed, to give the initial content of carbon in the coked zeolite, which was 10.6 ± 0.1 wt %. Moreover, the initial BET surface of coked samples was about 122 m²/g.

The regeneration tests were carried out in a tubular glass reactor (4 mm internal diameter, 6 mm external diameter, 20 cm length), which was loaded as a fixed bed reactor with the other halves of zeolite. Oxidation treatment was applied using ozone at low temperatures, between 50 °C and 200 °C. The effects on carbon removal efficiency of temperature, time on stream and ozone inlet concentration were studied. Moreover, experiments were led using air or pure dioxygen to produce ozone (see Figure 1).

A lab-scale ozone generator (HTU-500 ozone generator, Azcozon) was used to produce ozone in the range of 4–25.4 g/m³. Air was used to produce ozone at low concentrations (4–10 g/m³), whereas oxygen was used for higher ones (10–25.4 g/m³). After passing through the ozone generator, a three-way valve allowed the gas to flow (i) directly to the ozone analyzer (Ozone Analyzer BMT 964) to determine the inlet ozone concentration or (ii) in the reactor to analyze ozone concentration in the outlet stream. The reactor was placed in a controlled temperature oven (Heratherm oven OGS60), and temperature at the reactor inlet and outlet was measured by thermocouples. After the regeneration process, ozone was destroyed before being vented to the

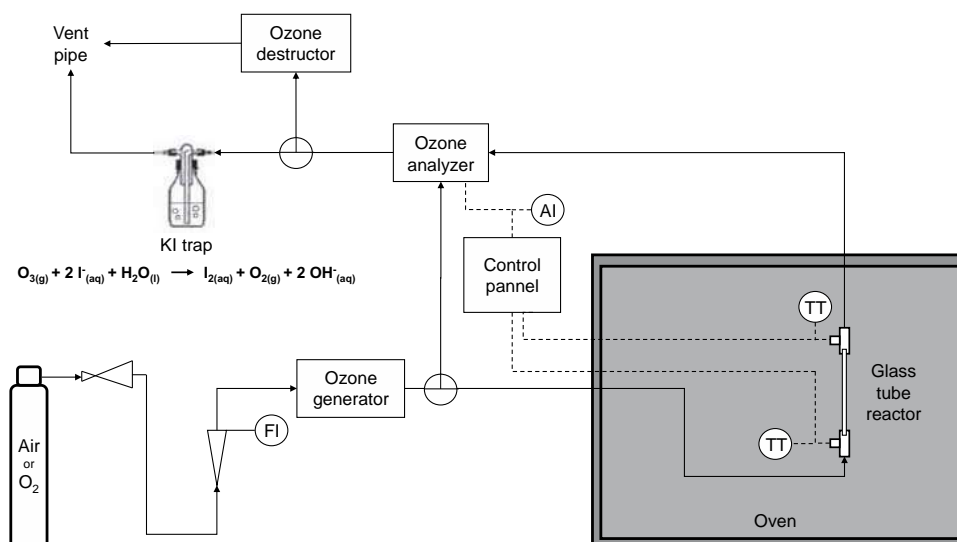


Figure 1. Scheme of the lab-scale regeneration of coked catalyst using ozone.

atmosphere, by a high temperature destructor or by reaction with KI (Van de Wiel et al. 1979).

At the beginning of the experiment, the sample was heated under air or oxygen flow (up-flow mode) until the desired temperature (within 50–200 °C range) was reached. Flowrate was varied from 10 to 46 L/h (corresponding to superficial velocity from 0.221 to 1.017 m/s and residence time from 0.9 to 0.2 s). Thereafter, the ozone generator was turned on and the gas flow was switched to O₃ containing mixture, keeping same flowrate. Regeneration time was between 2 and 8.5 h.

To determine the process efficiency, instantaneous ozone consumption was measured with the ozone analyzer and remaining carbon on zeolite was determined a posteriori by elemental analysis (after crushing). The experimental data were displayed in terms of carbon removal (%) given by the following equation:

$$\%C \text{ removal} = \frac{C_{ref} - C_s}{C_{ref}}$$

Where C_{ref} is reference carbon content and C_s is the final carbon content after the regeneration experiment.

Results and discussion

Several experiments were performed in order to approach the optimal parameters for the regeneration process, using ozone produced either from air or oxygen. The following table (Table 1) reports the operating parameters that were varied for the tests: temperature (T), time on stream (tos), nature of the feed gas, flowrate (F) and mass of catalyst loaded inside the reactor before starting the regeneration process (m_{cat}).

Reference conditions were: total flowrate of 15.3 L/h, temperature of 150 °C and time on stream of 6.5 h.

First of all, a blank experiment (E0) was carried out with pure oxygen. It can be checked that absolutely no coke was removed from the zeolite, meaning that coke removal in further experiments will be exclusively due to ozone. This confirmed that low temperature O₂ is not efficient to remove coke.

Influence of regeneration time

Regeneration kinetics was first examined for both gas feeds by varying time on stream (tos). The temperature was set at 100 °C, whereas the total gas flowrate was set at 30.7 L/h. On one hand, for experiments with O₃ made from air (E1, E5–E8), the mean inlet concentration of O₃ was 5.3 g/m³, which gave a mean mass flowrate of O₃ (Q_{m,O_3}) of 0.16 g/h. On the other hand, for experiments with O₃ made from O₂ (F1, F5–F8), the mean inlet concentration of O₃ was 13.8 g/m³, which gave an ozone flowrate of 0.42 g/h. Figure 2 depicts the corresponding evolution of regeneration efficiency as a function of tos, calculated from these experiments.

For both the gas feeds, oxidation kinetics almost reached a plateau after 3 h, resulting only in partial catalyst regeneration after the maximum fixed duration of 8.5 h (to achieve experiment within a single day). Despite large differences in ozone content ($Q_{m,O_3} = 0.16$ vs. 0.42 g/h), it is noticeable that both sets of experiments resulted in rather similar carbon removal at given tos of 8.5 h: 48.2% for air stream vs. 58.4% for oxygen stream. Concerning ozone consumption during regeneration process, trends were

Table 1. Set of regeneration experiments.

Exp	F (L/h)	T (°C)	m _{cat} (g)	[O ₃] _{in} (g/m ³)	tos (h)	Air/O ₂	% ozone consumed	% C removal	S _{BET} (m ² /g)	V _p (cm ³ /g)	D _p (nm)
E0	15.3	150	1.471	0.0	6.5	O ₂	NA	0.0	NA	NA	NA
E1	30.7	100	1.395	5.1	4.5	Air	19.2	39.5	147.1	0.413	11.24
E2	15.3	100	1.498	9.1	6.5	Air	23.9	50.0	150.6	0.413	10.96
E3	23.0	100	1.552	6.5	6.5	Air	23.9	43.9	148.6	0.406	10.92
E4	46.0	100	1.544	4.0	6.5	Air	10.7	39.0	137.0	0.459	13.39
E5	30.7	100	1.546	5.4	6.5	Air	16.0	45.9	143.5	0.461	12.84
E6	30.7	100	1.568	5.6	2.0	Air	32.5	30.2	132.9	0.379	11.40
E7	30.7	100	1.533	5.3	3.0	Air	26.7	36.0	147.2	0.383	10.40
E8	30.7	100	1.571	5.3	8.5	Air	13.7	48.2	148.5	0.472	12.72
E9	15.3	150	1.519	8.9	6.5	Air	67.7	74.3	229.6	0.516	8.99
E10	15.3	200	1.595	8.6	6.5	Air	100.0	32.0	156.6	0.458	11.71
E11	15.3	50	1.500	9.1	6.5	Air	14.3	27.0	125.9	0.386	12.27
E12	15.3	125	1.573	8.9	6.5	Air	46.3	67.7	194.0	0.482	9.94
E13	15.3	175	1.489	9.1	6.5	Air	95.1	47.0	174.4	0.453	10.39
F1	30.7	100	1.478	12.9	4.5	O ₂	22.7	47.9	124.0	0.430	13.88
F2	15.3	100	1.582	25.4	6.5	O ₂	57.5	64.2	139.7	0.449	12.85
F3	23.0	100	1.635	18.3	6.5	O ₂	44.9	56.2	152.0	0.429	11.28
F4	46.0	100	1.437	10.3	6.5	O ₂	27.2	51.8	147.6	0.420	11.39
F5	30.7	100	1.465	13.9	6.5	O ₂	41.3	51.2	148.2	0.459	12.38
F6	30.7	100	1.427	13.9	2.0	O ₂	34.3	35.5	135.6	0.428	12.62
F7	30.7	100	1.554	14.2	3.0	O ₂	36.8	43.8	136.4	0.356	10.45
F8	30.7	100	1.492	14.2	8.5	O ₂	47.9	58.4	142.9	0.378	10.59
F9	15.3	150	1.453	24.1	6.5	O ₂	97.7	42.6	NA	NA	NA
F10	15.3	200	1.529	23.8	6.5	O ₂	99.6	19.1	NA	NA	NA
F11	15.3	50	1.488	23.9	6.5	O ₂	14.2	28.8	NA	NA	NA
F12	15.3	125	1.445	24.5	6.5	O ₂	93.7	58.1	NA	NA	NA
F13	15.3	175	1.513	24.9	6.5	O ₂	98.8	30.6	NA	NA	NA

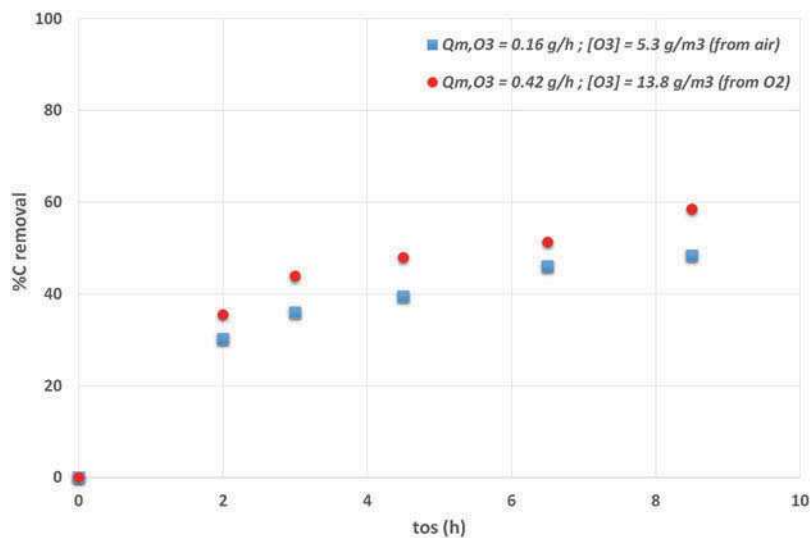


Figure 2. Influence of time on stream on carbon removal for two different gas feeds: $Q_{m,O_3} = 0.16$ g/h (ozone from air, blue points) and $Q_{m,O_3} = 0.42$ g/h (ozone from oxygen, red points) at 30.7 L/h and 100 °C.

different depending on inlet gas composition. According to Table 1, O₃ conversion increased with time on stream for concentrated gas mixture (ozone generated from oxygen), meaning that it was more readily converted on regenerated zeolite. Conversely, at low concentration (ozone generated from air), O₃ consumption was higher at the beginning of the process and decreased—following the evolution of

residual carbon content—up to a plateau. This suggests different dominant mechanisms in each case: low concentrated oxidant is mainly consumed by reaction with coke, while noncontributive decomposition pathway should prevail at higher O₃ concentration as described in the following results. Accounting for kinetics slowdown, the following experiments only lasted 6.5 h only.

Influence of inlet O₃ concentration

Besides, other sets of experiments (E2–E5 for O₃ made from air, and F2–F5 for experiments with O₃ made from O₂) were run, keeping the same temperature (100 °C) and the same time on stream (6.5 h), but varying total gas flowrates, thus O₃ concentration.

Corresponding results are gathered in Figure 3, where carbon removal is plotted as a function of resulting ozone concentration.

It is clear that the increase in O₃ concentration outweighed the decrease in total gas flow rate, resulting in a net benefit for the regeneration efficiency. The highest carbon conversion (64.2%) was achieved with a flowrate of 15.3 L/h using O₃ made from O₂ (lower flowrates could not be used due to technical limitations of our equipment). These results thus indicate that the oxidation process should not be limited by external mass transfer. Moreover, as concentration and total gas flowrates were varied, the amount of ozone consumed during this set of experiments did not show a clear tendency.

Influence of temperature

The last parameter investigated in this study was the temperature. It was varied from 50 °C to 200 °C (experiments E2, and E9–E13 with air resulting in ozone flowrate of 0.14 g/h, and experiments F2, and F9–F13 with oxygen and ozone flowrate of 0.37 g/h). Results are presented in Figure 4.

In both cases, carbon removal profiles exhibited a maximum with respect to temperature. However, its location

depended on the gas composition: 150 °C and 100 °C for ozone generated from air and oxygen, respectively. This kind of trend is very atypical and should be the results of different competing effects. First, ozone is degraded thermally into oxygen (Benson and Axworthy 1957; Michael 1971), resulting into an ozone loss between 10 and 35% on 100–180 °C range for oxygen stream at about 12.7 L/h and O₃ inlet concentration of 48 g/m³ (Khangkham et al. 2013). Moreover over regenerated catalytic sites, ozone could be decomposed into free radicals, which either recombine or attack the coke deposit. As these radicals exhibit a very short lifetime, they would only react with close vicinity species, which means that internal diffusional effects are critical for the catalyst regeneration. Indeed, it can be noticed that the percentage of O₃ consumed (Table 1) is close to 100% for experiments with temperatures over 150 °C, which means that a consequent part of O₃ was degraded because of thermal effect and/or radical recombination.

Then, the difference in optimal temperatures may be explained by the higher ozone concentrations obtained from pure oxygen (24.4 g/m³ compared to 8.9 g/m³): more radicals were present, which implied that their recombination was favored and thus, diffusion limitation effects started at earlier temperatures (100 °C instead of 150 °C for lower concentrations). This recombination of radicals, which is favored at higher concentrations, could also explain why the maximum carbon removal was lower (64.2%) at 24.4 g/m³ than at 8.9 g/m³ (74.3%). Therefore, in the regeneration process with ozone, a compromise between ozone concentration and temperature has to be found.

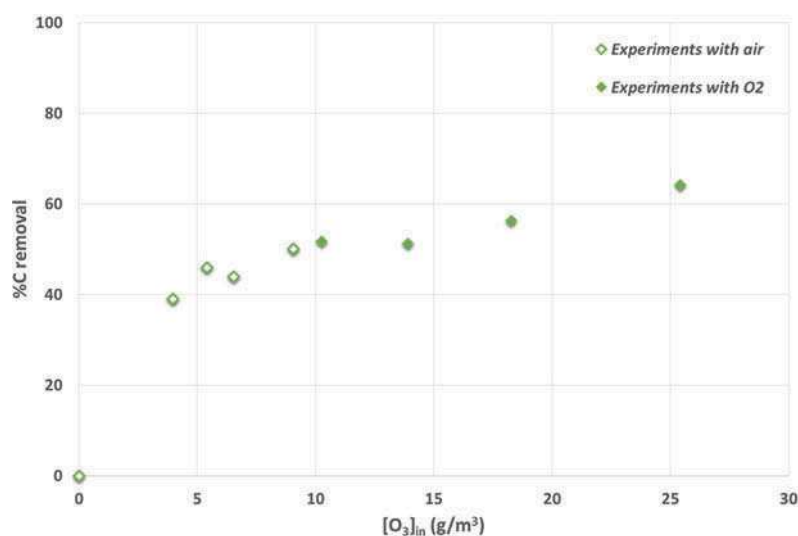


Figure 3. Influence of inlet concentration of O₃ (at varying total gas flowrates) on carbon removal for two different gas feeds: air (empty green points) and O₂ (filled green points), at 100 °C and tos of 6.5 h.

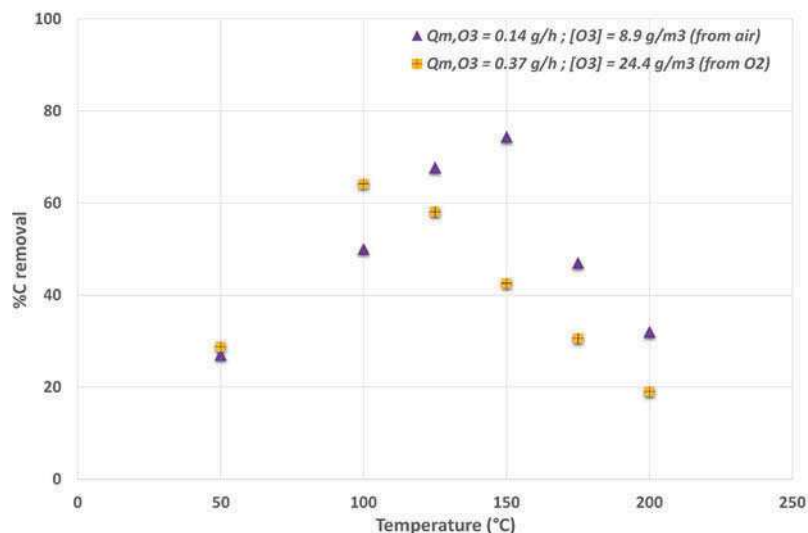


Figure 4. Influence of temperature on carbon removal for two different gas feeds: $Q_{m,O_3} = 0.14$ g/h (air, purple points) and $Q_{m,O_3} = 0.37$ g/h (oxygen, yellow points) at 15.3 L/h and t_{os} of 6.5 h.

Physical properties of regenerated samples

As indicated in Table 1, the mean pore diameter of all samples, determined by BET method, ranged between 9 and 14 nm, which indicates that the particles were essentially mesoporous (pore size between 2 nm and 50 nm). As a result, the total pore volume was approximately the mesoporous volume calculated by BJH method. V_P was 0.365 cm³/g for the coked samples, but it did not show any clear trends for the regenerated samples with respect to the different investigated conditions (cf. Table 1).

BET surface area was not significantly affected by the variations of t_{os} or inlet O_3 concentrations, but the effect of temperature was much more important.

Figure 5 shows the corresponding results for experiments with air (E2, and E9 to E13) which as expected exhibit the same trend as carbon removal, and in particular the same optimal value of 150 °C. It was possible to improve the BET surface area from 121.6 m²/g for the coked samples to 229.6 m²/g in best conditions, which represents an increase of about 89%.

Conclusions and outlooks

Regeneration of coked zeolite of 4 mm diameter was successfully achieved using an ozone-enriched air or oxygen stream. At 150 °C, up to 74.3% of coke was removed in the applied conditions ($Q_{v,tot} = 15.3$ L/h,

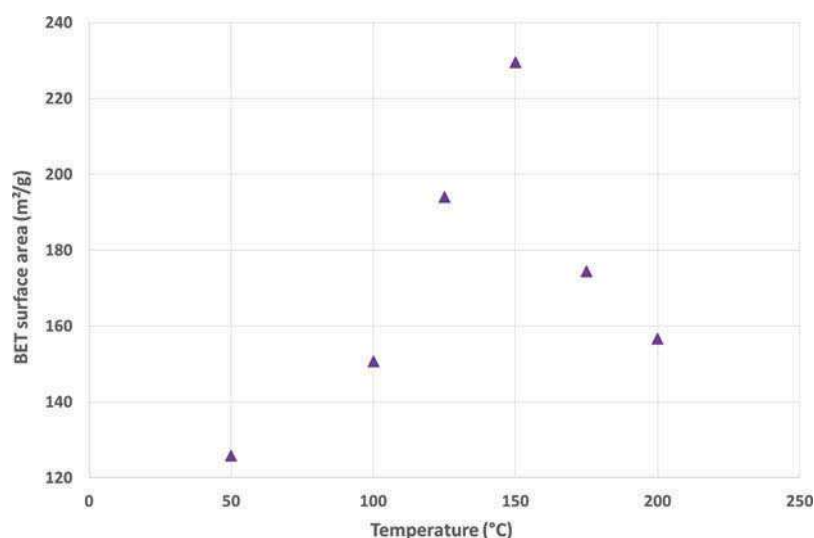


Figure 5. Influence of treatment temperature on the BET surface area of regenerated samples ($Q_{m,O_3} = 0.14$ g/h at 15.3 L/h and t_{os} of 6.5 h).

[O₃] = 8.9 g/m³, Q_{m,O₃} = 0.14 g/h and t_{os} = 6.5 h). The decoking rate was improved by an increase of O₃ concentration in the investigated range (4.0–25.4 g/m³). Temperatures higher than 150 °C were not beneficial due to the strong limitation of ozone diffusion inside the zeolite particles and its fast decomposition. Concerning physical properties, a maximum increase of 89% was obtained for the BET surface area at the optimal temperature. Future experiments will be carried out to better understand mechanisms of decoking.

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ORCID

Romain Richard  <http://orcid.org/0000-0002-6037-8254>

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