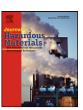
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Kinetic study of trichloroethylene combustion on exchanged zeolites catalysts

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ARTICLE INFO

Article history: Received 9 December 2010 Received in revised form 1 April 2011 Accepted 4 April 2011 Available online 8 April 2011

Keywords: Oxidation Trichloroethylene Exchanged zeolites Kinetic data

ABSTRACT

In this paper is presented a kinetic study of the catalytic combustion of trichloroethylene (TCE) over Yzeolites exchanged with several cations. The catalysts, based on zeolite, were prepared by ion exchange and characterized by means of physico-chemical techniques and then tested under kinetic conditions. The kinetic results obtained were interpreted using kinetic models of power-law type and Eley–Rideal. The results obtained indicate that catalyst Y-Cr is more active than Y-Co catalyst. The greater activity of catalyst exchanged with Cr can be attributed to the higher acidity that presented these catalysts.

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1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs) such as carbon tetrachloride (CTC) and trichloroethylene (TCE) are extensively applied to dissolve organic compounds. However, they are considered to be quite harmful since they contribute to the atmospheric contamination and tend to accumulate in biological systems. The abatement of these contaminants by means of catalytic oxidation is an interesting technology due to the energy saving and to the fact that the formation of by-products such as dioxins and nitrogen oxides (NOx) can be minimized [1]. The use of catalysts allows for the conversion of these contaminants into less harmful or innocuous compounds, working at high spatial velocities and low temperatures, being the desired reaction the total oxidation to CO₂, H₂O and HCl without formation of by-products. The lower temperature required for the catalytic combustion results in lower energy consumption and therefore it is more effective than thermal oxidation. The catalysts used in the oxidation of chloride compounds usually contain noble metals [2-4] or transition metal oxides such as chromium oxide [5]. In addition, it has been reported [6–8] that zeolites with different Si/Al ratios are highly active for the destruction of chlorinated compounds. However, the structure of the zeolites could be dramatically affected by the deactivation produced by HCl and/or Cl₂ produced during the reaction. The aim of this work is to study the catalytic behaviour of a series of zeolites exchanged with metals such as Cr, Co, Mn and Fe in the TCE combustion. In addition, a kinetic study of the most active catalyst is also reported. Based on these results a reaction mechanism is proposed, providing more insight into the catalytic behaviour of the catalysts.

2. Experimental

2.1. Materials and catalyst characterization

A commercial Y-Zeolite (Si/Al=2.5) in its sodic form was exchanged in rotary evaporator system with metals such as Cr, Co, Mn and Fe. The exchange solutions were obtained from the respective nitrates. The exchange conditions were: temperature = 80 °C, time = 2 h [9]. The solutions concentration were suitable in order to achieve a pH 3.5. Accordingly, the Cr solution was more diluted than Co solution in order to avoid the destruction of zeolitic matrix. The zeolite exchanged with Co was subjected to three successive exchanges, while the zeolite exchanged with Cr was subjected to two exchanges only one exchange was carried out for the zeolites exchanged with Fe or Mn. After each step, and prior to next successive exchange, samples were washed with distilled water and dried for 12 h at 100 °C and then calcined at 500 °C in air for 2 h. In this manner, different numbers of exchanges were possible carried out, and obtained zeolites with different metal content. Therefore, metal loadings were measured by atomic absorption spectrometry.

The BET specific surface was determined by adsorption of N_2 at $-196\,^{\circ}\text{C}$ in a Quanthacrome instrument. The samples were previously evacuated at 300 $\,^{\circ}\text{C}$, under high-vacuum conditions.

The X-ray diffractograms were registered in a Shimadzu SD-1 instrument with $CuK\alpha$ radiation. The crystallinity of the exchanged

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zeolites was determined considering that the crystallinity of the Y-zeolite in its sodic form is 100%.

The TPD of NH $_3$ was performed in flow equipment connected to a Balzers gas analyzer equipped with mass spectrometer. Prior to the experiments, the samples were treated in air at 500 °C and cooled down to 100 °C, the NH $_3$ adsorption was performed at this temperature. Afterwards, NH $_3$ was desorbed in a He flow by increasing the temperature to 600 °C at 10 °C min $^{-1}$.

2.2. Catalytic activity measurements

The oxidation of trycholoroethylene (TCE) was carried out in a fixed-bed tubular reactor operating at atmospheric pressure. The TCE, in liquid form, was fed by means of a syringe pump, which allowed for the use of variable flows of reactant, and different concentration of TCE consequently. The air to perform the oxidation (O_2/N_2) was fed and controlled with a mass gas flow controller. Samples were crushed and sieved to retain particles with 0.35-0.42 mm diameter and loaded to the reactor. Standard catalytic tests were performed using catalyst loadings (W) of 0.1 g, contact times (W/F_{TCE}^{0}) of $88 \,\mathrm{g} \,\mathrm{h} \,\mathrm{mol}^{-1}$ and total gas flow rate of 500 mL min⁻¹. The existence of internal and external diffusional limitations was studied varying particle size between 0.15 and 0.5 mm, and contact times between 50 and 700 g h mol⁻¹, respectively. In order to avoid internal diffusional effects in the kinetic experiments, the fraction with particle diameter ranged from 0.35 to 0.42 mm, and varying contact times between 50 and 600 g h mol⁻¹ were employed. The results indicated that catalytic tests were performed in kinetic regime under our experimental conditions. The reactor effluent was analyzed on-line using a GC with FID detector. The reaction was followed through the conversion of TCE. Two types of experiments were performed: (i) measurement of TCE conversion as a function of temperature and (ii) measurement of the TCE conversion as a function of time, under isothermal differential conditions.

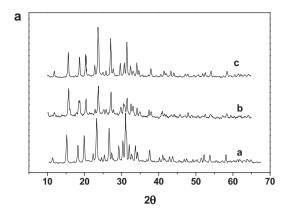
3. Results and discussion

3.1. Catalyst characterization

The main characteristics of the samples are presented in Table 1. In the case of Y-Co catalyst, it can be observed that, as the number of exchanges increases, the amount of Na in the solid decreases and, consequently, the amount of exchanged Co also increases. After successive exchanges, an exchange degree between 65 and 82% is achieved. At the same time, as the exchange degree increases, the specific surface decreases, indicating a slight missing of the zeolitic matrix structure, probably caused by the acidity of the exchange solutions.

In the case of the Cr-exchanged catalyst, it can be observed that there is an increase in the amount of exchanged Cr as the number of exchanges increases but at the same time, the specific surface is marginally affected as compared to the base zeolite. In the Y-Fe and Y-Mn catalysts, it is observed that both retain the specific surface after the respective ionic exchanges. The difference observed in metal loading in Y-Cr and Y-Co samples is due to both the concentration of the exchange solutions and number of ionic exchanges. The Cr solution was more diluted than Co solution in order to avoid the destruction of zeolitic matrix. Besides, Cr ion has three positive charges and Co has only two, in consequence, to add one Cr³+ three Na¹+ ion must be replaced. Instead, to add Co²+ two Na¹+ ion must be replaced. Due to this, a lower concentration of Cr than Co in the final exchanged zeolite is achieved.

The X-ray diffractograms were performed to verify if the crystalline samples retained their structure after the successive



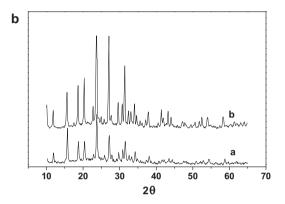


Fig. 1. (A) XRD exchanged zeolites before reaction (a) Y-Na; (b) Y-Co(3); (c) Y-Cr(2); (B) XRD of exchanged zeolites after combustion reaction (a) Y-Co(3), (b)Y-Cr(2).

exchanges. Fig. 1A shows the XRD patterns of the base zeolite and Co or Cr-exchanged zeolites. In both cases, it is observed that the crystallinity decreases at values between 80 and 85%. This diminution in the crystallinity is consistent with the slight decrease of specific surface area. In the samples exchanged with Fe and Mn, it was also found that crystalline was not significantly affected by the exchange. These results are in agreement with results reported in the literature for zeolites with a high degree of dealuminization which retain their high crystallinity [10].

Acid site density measured by TPD of NH_3 adsorbed at $100\,^{\circ}$ C, as previously described. It should be mentioned that this acidity characterization technique is not able to distinguish between Brönsted and Lewis acid sites and only allows for the quantification total acidity. According the results, presented in Table 1, the more acidic samples are the exchanged Y-Co and Y-Cr samples. These values indicate that the exchange with Cr or Co promotes the increase of the acidity to a greater extent than the other cations (Mn and Fe).

3.2. Catalytic tests: effect of the exchanged cation

In order to evaluate the stability of the exchanged zeolite during the TCE combustion, a series of experiments were carried out measuring the TCE conversions at several reaction temperatures ranging from 200 to 500 °C, as show in Fig. 2. In the case of non-exchanged Y-Na, it can be seen that the conversion is very low in the whole temperature range, indicating that the presence of a transition metal is necessary to promote this reaction. For the rest of the exchanged zeolites, the increase of conversion with temperature follows the order: Cr > Co > Mn > Fe.

Thus, while with the Y-Cr sample, conversions around 80% at 500 °C are reached, the Y-Co and Y-Mn catalysts give at the same temperature, 500 °C, 50% and 20% respectively. In sample Y-Fe (not

 Table 1

 Physico-chemical characterization of the catalysts.

| Catalyst | % Naª | % Cation ^a | Sg (m ² g ⁻¹) ^a | % Cation ^b | Sg (m ² g ⁻¹) ^b | μmol NH ₃ desorbed⋅m ⁻² 10 ⁶ |
|----------------------|-------|-----------------------|---|-----------------------|---|---|
| Y-Na | 7.60 | - | 720 | - | = | 2.5 |
| Y-Co(1) ^c | 2.78 | 5.70 | 708 | 5.61 | 695 | 4.8 |
| Y-Co(2) | 2.05 | 6.90 | 680 | 6.54 | 615 | 4.7 |
| Y-Co(3) | 1.36 | 7.80 | 587 | 6.73 | 522 | 4.9 |
| Y-Cr(1) | 6.96 | 0.46 | 690 | 0.40 | 680 | 5.7 |
| Y-Cr(2) | 6.21 | 1.10 | 700 | 0.90 | 675 | 6.2 |
| Y-Fe | 5.96 | 1.54 | 710 | 1.43 | 702 | 3.0 |
| Y-Mn | 4.79 | 4.79 | 712 | 4.41 | 709 | 3.2 |

- ^a Values prior to the combustion reaction.
- ^b Values after the combustion reaction at 500 °C.
- ^c Numbers in brackets indicate exchange number.

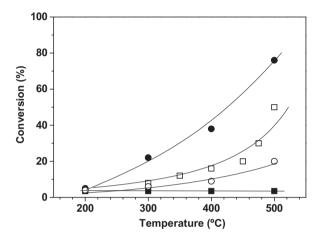


Fig. 2. Conversion-temperature curves for TCE oxidation. ■ Y-Na, \bigcirc Y-Mn, \square Y-Co(3), ● Y-Cr(2). $W/F_{\text{TCE}}^0 = 88 (\text{ghmol}^{-1})$, $p_{\text{TCE}} = 0.06$ atm, $p_{0_2} = 0.10$ atm.

shown), the conversion values obtained at the different temperatures were similar to those of sample Y-Mn; at 500 °C conversion was around 18%. The most active catalysts are those exchanged with Cr and Co, which are those with a greater density of active sites. Similar results were obtained by Lopez-Fonseca et al. [6] with zeolites of different acidity. In their study, the zeolites of higher acidity were the most active ones for the elimination of TCE.

3.3. Effect of the exchange degree

In order to analyze the effect of number of ionic exchanges on the catalytic behaviour, a series of experiments were carried out, in which conversion was evaluated as a function of temperature for the catalysts exchanged with Cr and Co. Table 2 shows the results obtained from the conversion experiments, as a function of temperature, for the series of zeolites exchanged with Co and Cr. For the Y-Co series, the conversion values at different temperatures are practically not affected by the exchange degree, i.e. the amount of Co incorporated to the catalyst.

However, for the Y-Cr series, it can be seen that as the content of Cr increases there is a noticeable increase in the catalyst activity.

Table 2Effect of exchange degree on the conversion at several temperatures.

| T(°C) | Conversion (%) | | | | | | |
|-------|----------------------|---------|---------|---------|---------|--|--|
| | Y-Co(1) ^a | Y-Co(2) | Y-Co(3) | Y-Cr(1) | Y-Cr(2) | | |
| 200 | 4 | 5 | 5 | 6 | 8 | | |
| 300 | 8 | 10 | 10 | 20 | 25 | | |
| 400 | 22 | 20 | 20 | 30 | 40 | | |
| 500 | 50 | 49 | 50 | 43 | 80 | | |

^a numbers in brackets indicate exchange number.

Thus, the required temperature to reach 40% of TCE conversion is at least 100 °C lower in the case of Y-Cr(2) than in Y-Cr(1). On the other hand, the catalysts exchanged with Cr are more active than those exchanged with Co. Accordingly; at 500 °C the Cr catalysts reach conversions over 80%, whereas the Co catalysts reach conversions of just 45%. The highest exchange degree attained with Co zeolites was 83%, whereas for the Y-Cr zeolite; the maximum exchange was 20%. Therefore, the fact that the zeolites exchanged with Cr are more active cannot be ascribed to the cation exchange degree, because this is lower than in the zeolites exchanged with Co. Therefore, the greater activity in the TCE combustion of the Y-Cr zeolite would be related to the higher acidity of these catalysts. It is accepted in the literature that the acidity of the support plays an important role in the chlorinated compounds abatement [11-13]. Gutiérrez-Ortiz et al. [13] have found that the acid sites are responsible for the effective chemisorption of the chlorinated compounds.

3.4. Catalyst characterization after catalytic reaction

The results of the catalytic activity shown in Fig. 3 seem to indicate that there is no catalyst deactivation during the conversion-temperature experiments, even though the reaction atmosphere might be very aggressive for the catalyst structure. In order to confirm these results, several analyses were carried out with the following techniques: atomic absorption spectrometry as well as X-ray diffraction and specific surface. Table 1 show the atomic absorption and Sg results. According to those results and to those of the X-ray diffractograms shown in Fig. 1B, it could be observed that there are no appreciable differences in the catalysts properties before and after reaction. This evidence confirms

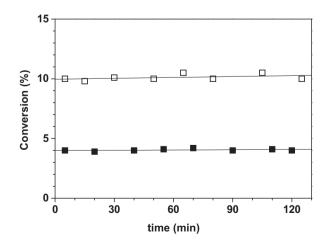
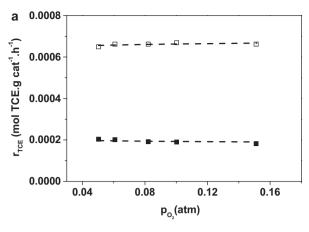


Fig. 3. Conversion vs time at T = 250 °C, ■ Y-Co, \Box Y-Cr. $W/F_{\text{TCE}}^0 = 88(\text{ghmol}^{-1})$, p_{TCE} = 0.06 atm, $p_{0_2} = 0.10$ atm.



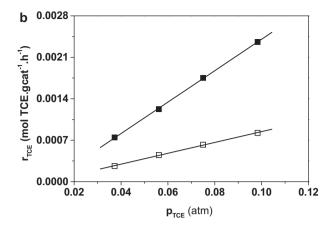


Fig. 4. A: Influence of oxygen concentration. Dotted lines: potential model and Eley–Rideal model data. \blacksquare Y-Co, \Box Y-Cr, $W/P_{\text{TCE}}^0 = 88(\text{ghmol}^{-1})$, $T = 250 \, ^{\circ}\text{C}$, $p_{\text{TCE}} = 0.030 \, \text{atm. B}$: Dependence of TCE oxidation upon TCE partial pressure. Solid lines: potential and Eley–Rideal model data. \blacksquare Y-Co, \Box Y-Cr, $W/P_{\text{TCE}}^0 = 88(\text{ghmol}^{-1})$, $T = 250 \, ^{\circ}\text{C}$, $p_{\text{O}_2} = 0.120 \, \text{atm.}$

the deactivation resistance shown by the Y-Co and Y-Cr catalysts during the TCE combustion.

3.5. Kinetic study

Since the conversion-temperature experiments previously shown were carried out in transient regime, conversion experiments as a function of time at constant temperature were also performed. These experiments were carried out at a TCE partial pressure of 0.030 atm, an oxygen partial pressure of 0.10 atm and at a temperature of 250 °C. Fig. 3 shows the evolution of conversion as a function of time for the Cr(2) and Co(3) exchanged zeolite, verifying that there is not deactivation during the time of reaction. The samples employed in the kinetic study correspond to catalysts Y-Co(3) and Y-Cr(2), after 3 and 2 exchanges, respectively. Since the Co and Cr catalysts were the most active ones, the kinetic analysis was performed only with these catalysts.

3.5.1. Influence of the oxygen partial pressure

In this study, the experiments were performed keeping the trichloroethylene partial pressure constant at 0.030 atm, while the O_2 partial pressure varied between 0.07 and 0.180 atm. In every case, the operating temperature was kept constant at 250 °C. Fig. 4A shows that the rate of reaction slightly decreases with the oxygen partial pressure, indicating a weak effect of oxygen during the TCE combustion.

On the other hand, the Y-Cr catalyst is approximately three times more active that the Y-Co catalyst, in terms of rate of reaction.

3.5.2. Influence of the TCE partial pressure

In order to determine the effect of the trichloroethylene partial pressure, the oxygen partial pressure was kept constant at 0.120 atm. The trichloroethylene partial pressure varied between 0.025 and 0.098 atm. Fig. 4B shows the results of the rate of reaction as a function of the TCE partial pressure for the Y-Cr and Y-Co catalysts. In both cases, it can be noticed that the rate of reaction increases almost linearly with the TCE partial pressure, which would be indicating a kinetic order with respect to TCE close to 1, in agreement with Everaert and Baeyens [14].

3.5.3. Influence of temperature

To analyze the effect of temperature on the rate of reaction, a series of experiments at different temperatures between 220 and 270 °C were performed. The reaction conditions were: oxygen partial pressure at 0.120 atm, and TCE partial pressure at 0.030 atm. The rate of reaction values was obtained from the conversion

experiments as a function of time, taking the values of the initial conversion for every temperature under study.

3.5.4. Kinetic modelling

3.5.4.1. Determination of the kinetic parameters. The results of the kinetic study presented in Fig. 4A and B were analyzed using two types of kinetic models, in order to obtain more information from the kinetic data respect the reaction mechanism: (i) a pseudohomogeneous power-law equation, and (ii) an Eley–Rideal model.

According to the power-law model, the reaction rate can be expressed as:

$$(-r_{\text{TCE}}) = k_{\text{P}} \cdot p_{\text{O}_2}^n \cdot p_{\text{TCE}}^m \tag{1}$$

where $(-r_{\text{TCE}})$ is the TCE oxidation rate, k_{P} the kinetic constant of oxidation according to the power-law model, and n and m the kinetic orders with respect to oxygen and TCE respectively.

In the case of the experiments carried out at constant oxygen concentration, the above expression is simplified to:

$$-r_{\text{TCE}} = k'_{\text{p}} \cdot p^{m}_{\text{TCE}}; \quad k'_{\text{p}} = k_{\text{P}} \cdot p^{n}_{\text{O}_{2}}$$

$$\tag{2}$$

Moreover, at the experiments carried out at constant TCE concentration, the Eq. (1) becomes:

$$-r_{\text{TCE}} = k_{\text{p}}^{"} \cdot p_{\text{O}_2}^n; \quad k_{\text{p}}^{"} = k_{\text{P}} \cdot p_{\text{TCE}}^m$$
(3)

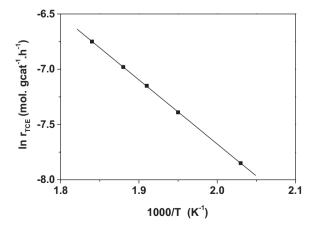


Fig. 5. Arrhenius plot for determining apparent energy activation. Catalyst Y-Cr, $W/P_{\text{TCF}}^0 = 88(\text{ghmol}^{-1})$, $p_{\text{TCE}} = 0.030$ atm, $p_{0_2} = 0.120$ atm.

Table 3 Kinetic parameters for Co and Cr catalysts.

| | Potential model | Parameter value | Standard error | Confidence interval (95%) |
|------------------|---------------------------|-----------------------|-----------------------|---------------------------|
| TCE influence | $k_p'(Co)$ | 1.14×10^{-2} | 1.36×10^{-3} | 3.98×10^{-3} |
| | m(Co) | 1.13 | 4.68×10^{-2} | 1.37×10^{-1} |
| | SSR(Co) | 0.4403 | _ | _ |
| | $k_p'(\operatorname{Cr})$ | 3.61×10^{-2} | 2.30×10^{-3} | 6.71×10^{-3} |
| | m(Cr) | 1.17 | 2.51×10^{-2} | 7.32×10^{-2} |
| | SSR(Cr) | 0.9757 | _ | _ |
| Oxygen influence | $k_p''(Co)$ | 1.80×10^{-4} | 1.99×10^{-5} | 5.81×10^{-5} |
| 30 | n(Co) | -0.03 | 4.37×10^{-2} | 1.28×10^{-1} |
| | SSR(Co) | 1.5845 | _ | _ |
| | $k_p''(Cr)$ | 6.87×10^{-4} | 1.96×10^{-5} | 5.73×10^{-5} |
| | n(Cr) | 0.016 | 1.13×10^{-2} | 3.31×10^{-2} |
| | SSR(Cr) | 1.2501 | - | _ |

SSR: Sum of squared residuals.

If the analysis of the kinetic results is made using the Eley-Rideal model, the reaction rate can be now expressed as:

$$(-r_{\text{TCE}}) = \frac{k_{\text{ER}} \cdot p_{\text{O}_2} \cdot p_{\text{TCE}}^m}{1 + K_{\text{O}_2} \cdot p_{\text{O}_2}} \tag{4}$$

In this expression, k_{ER} represents the kinetic constant of oxidation according to the Eley-Rideal model, m the kinetic order with respect to TCE and K_{0_2} the constant of adsorption of oxygen. According to the Eq. (4), it is assumed that the mechanism of the reaction involves the adsorption of the oxygen molecules and then the reaction with the TCE molecules in gas phase, being this stage the controlling step of the combustion process. Now, for the case of constant oxygen concentration, Eq. (4) is simplified to:

$$-r_{\text{TCE}} = k'_{\text{ER}} \cdot p_{\text{TCE}}^{m}; \quad k'_{\text{ER}} = \frac{k_{\text{ER}} \cdot p_{\text{O}_2}}{1 + K_{\text{O}_2} \cdot p_{\text{O}_2}}$$
 (5)

It can be observed that Eq. (5) is formally equal to Eq. (2), however the meaning of the lumped kinetic constants in both equations, k_{ER}' and k_{P}' , are very different. Now, in the case of the experiments carried out at constant *TCE* concentration, the Eq. (4) becomes:

$$(-r_{\text{TCE}}) = \frac{k_{\text{ER}}'' \cdot p_{\text{O}_2}}{1 + K_{\text{O}_2} \cdot p_{\text{O}_2}}; \quad k_{\text{ER}}'' = k_{\text{ER}} \cdot p_{\text{TCE}}^m$$
 (6)

The values of the kinetic parameters of both models were determined by non-linear regression. The results obtained for both catalysts are shown in Table 3 and in Fig. 4A and B. The values of the kinetic constants in both models indicate that the Cr catalyst is between 3.1 and 3.3 times more active than the Co catalyst, compared both at the same operating conditions. The observed increase of the TCE oxidation rate with Y-Cr catalyst is consistent with the work of Gutiérrez-Ortiz et al. [13] suggesting that the Y-Cr catalyst activity for TCE oxidation is promoted when the acidity is increased.

As regards the influence of TCE concentration, the kinetic order with respect to this reactant is approximately 1 for both catalysts, in accordance with other results presented in the literature [2,14]. We think that the result obtained for the kinetic order respect to TCE is not contradictory with the assumption of an E-R mechanism for this reaction. In fact, if it is taken into account the confidence interval 95% for the value of the kinetic order "m" that we obtained, the value of m=1 is within that interval. This result confirms the validity of the hypothesis of ER model, or at least indicates that the E-R mechanism cannot be ruled out. Of course, the fitting can be done setting m = 1. In this case, the rest of parameters take very similar values of that in Table 3. However, the kinetic order with respect to the oxygen concentration is near to zero, also for both catalysts [12-14]. This fact can be explained considering that the catalyst surface is covered mainly by oxygen atoms being this specie the most abundant at the surface. These results are in accordance to the high values of the oxygen adsorp-

tion constant observed for these catalysts type. Aranzabal et al. [4] also proposed an Eley-Rideal mechanism to explain their results in this reaction. These authors obtained a reaction dependence of first order with respect to TCE and zero order dependence with respect to oxygen. These results are consistent with a mechanism that considers the reaction between TCE from the gas phase and chemisorbed oxygen covering most of the catalyst surface. In this case, the value of the oxygen adsorption term $K_{O_2} \cdot p_{O_2}$ is dominant in the denominator of the Eq. (4), and finally the reaction rate will be expressed as: $(-r_{TCE}) = k'_{ER} \cdot p_{TCE}$, where the apparent kinetic constant will be the ratio between the intrinsic kinetic constant and the oxygen adsorption constant: $k'_{ER} = k_{ER}/K_{O_2}$. In addition, under this situation both kinetic models considered are coincident, and the relationships between the kinetic constants are the following: $k'_P = k_P = k'_{ER} = k_{ER}/K_{O_2}$. Therefore, the values of the intrinsic kinetic constants for both catalysts are: $k_P(\text{Co}) = k'_{ER}(\text{Co}) = 0.0114 (\text{molg}_{\text{cat}}^{-1} \text{h}^{-1} \text{atm}^{-1.13})$ and $k_P(\text{Cr}) = k'_{ER}(\text{Cr}) = 0.0361 (\text{molg}_{\text{cat}}^{-1} \text{h}^{-1} \text{atm}^{-1.17})$.

$$k_{\rm P}({\rm Co}) = k_{\rm ER}'({\rm Co}) = 0.0114 \, ({\rm molg_{cat}^{-1}h^{-1}atm^{-1.13}}) \, \text{ and } \, k_{\rm P}({\rm Cr}) = k_{\rm CP}'({\rm Cr}) = 0.0361 \, ({\rm molg_{cat}^{-1}h^{-1}atm^{-1.17}}).$$

The effect of temperature was analyzed assuming Arrheniustype dependence for kinetic constant $k_{\rm P}$. This dependence may be expressed in terms of the re-parameterization temperature, $T_{\rm m}$ as:

$$k_{P} = k_{0} \cdot \exp\left(-\frac{E_{a}}{RT}\right) = k_{m} \cdot \exp\left(-\frac{E_{a}}{R}\left(\frac{1}{T} - \frac{1}{T_{m}}\right)\right)$$

$$k_{m} = k_{0} \cdot \exp(-E_{a}/RT_{m})$$
(7)

The apparent activation energy calculated for the Y-Cr catalyst (the most active one) was 45.2 kJ mol⁻¹ (Fig. 5). Similar results were reported by Everaert and Baeyens, [14], in the TCE catalytic oxidation, in which they obtained an activation energy of about 52 kJ mol⁻¹ on metal fibre fleece catalysts. Activation energies values of 54.5 kJ mol⁻¹ and 45 kJ mol⁻¹ were determined on metal noble catalysts [2,3].

4. Conclusions

Exchanged zeolites with Co and Cr are very active catalysts for trichloroethylene oxidation at atmospheric pressure and temperatures between 200 and 500 °C. Within this range of temperatures, it has been found that the most active catalyst, ca. three times, is Y-Cr zeolite. This result can be explained considering the higher acid sites density of Cr Zeolite determined by TPD of ammonia. In addition, XRD measurements after reaction of both catalysts indicate that the structure did not change and not deactivation was observed in the conditions employed.

A kinetic study of the reaction over a wide range of temperatures and partial pressures of reactants has been carried out, allowing us to obtain the values of the main kinetics parameters.

The reaction kinetic orders with respect to oxygen and trichloroethylene are 0 and 1, respectively. The kinetic data obtained were consistent with an Eley–Rideal model with the trichloroethylene molecule reacting from the gas phase. At the reaction conditions studied, oxygen coverage of the catalyst surface is high explaining the near zero order observed.

Acknowledgements

The authors thank to the Universidad Nacional del Litoral and CONICET for the financial support of this work.

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