Catalysts based on zeolite beta for the oxidation of chlorinated VOCs

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Background

Chlorinated volatile organic compounds (CVOCs) like trichloroethylene (TCE) are widely used in industry. Their emission results in problems related to destruction of the ozone layer, groundwater pollution and photochemical smog. Catalytic oxidation is an effective option for the control of different CVOCs emissions. Metal oxides and noble metals are active catalysts for TCE oxidation, but they are easily poisoned by chlorine [1] or generate polluting by-products at high temperatures [2]. Recently, catalysts based on acidic zeolites were also proposed as active catalysts for this reaction [3]. However, their catalytic behaviour needs to be improved.

Objective

Study the catalytic behaviour for the TCE oxidation of Cu-catalysts based on zeolite beta.

Experimental

Chemical reaction

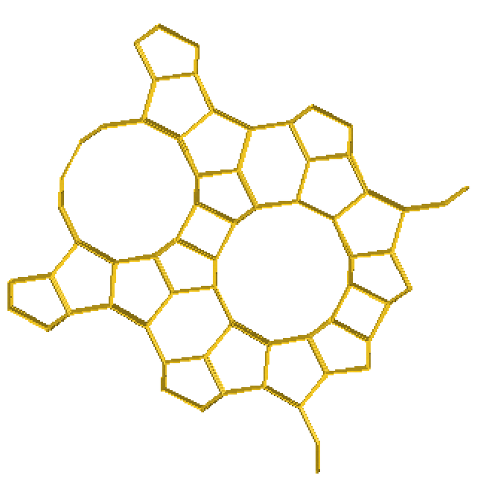
$$C_2HCl_3 + 2O_2 \xrightarrow[\text{catalyst}]{} 2CO_2 + HCl + Cl_2$$

Reaction conditions

- quartz fixed bed reactor
- catalyst bed = 0.68 g
- gas flow rate = 400 ml min^{-1}
- GHSV = 15000 h^{-1}
- [TCE] = 1000 ppm in air

Catalysts preparation

Table 1. Preparation methods and catalysts studied.



	Catalyst
Reference catalyst Zeolite beta CP811	H-beta
Method IE (Ion exchange)	beta-Cu (IE) 0.6% beta-Cu (IE) 3.2% beta-Cu (IE) 5.2%
Method HS (Hydrothermal synthesis)	beta-Cu (HS) 2.4%

Commercial acidic zeolite beta (CP811, Zeolyst Int.) was used as reference catalyst. In order to improve the performance of this catalyst, Cu was added to zeolite beta by two different ways: ion exchange and hydrothermal synthesis [4].

Results

Characterization

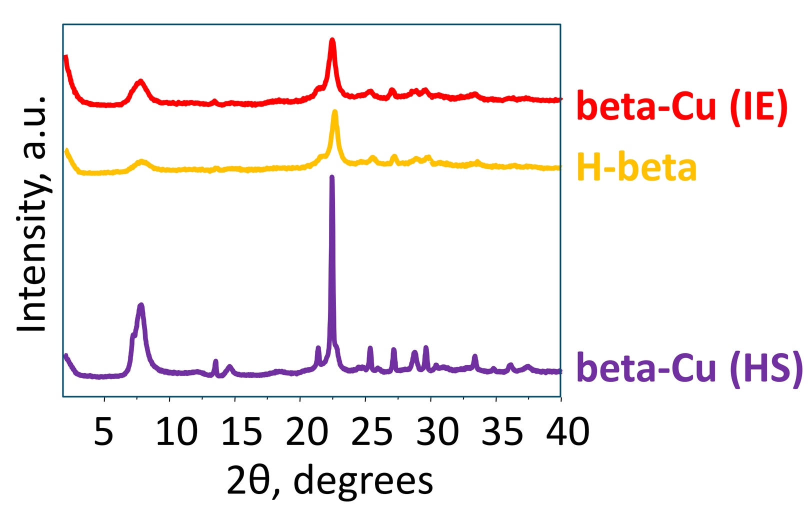
Table 2. Physic-chemical properties of the zeolites.

	Molar ratio	BET surface area	Mesopore volume	Micropore volume
Catalyst	**Si/Al**	**m²/g**	**cm³/g**	**cm³/g**
H-beta	12.5	587	0.36	0.18
beta-Cu (IE) 0.6%	10.9	572	0.36	0.18
beta-Cu (IE) 3.2%	10.8	541	0.27	0.16
beta-Cu (IE) 5.2%	9.5	506	0.24	0.16
beta-Cu (HS) 2.4%	without Al	444	0.06	0.19

* % next to the catalyst name indicates the %wt Cu of the sample.

After the Cu ion exchange of zeolite beta, the samples have a similar pore volume and surface area indicating that the structure was not modified. The sample prepared by hydrothermal synthesis have a lower surface area than the other zeolites due to its higher crystallite size.

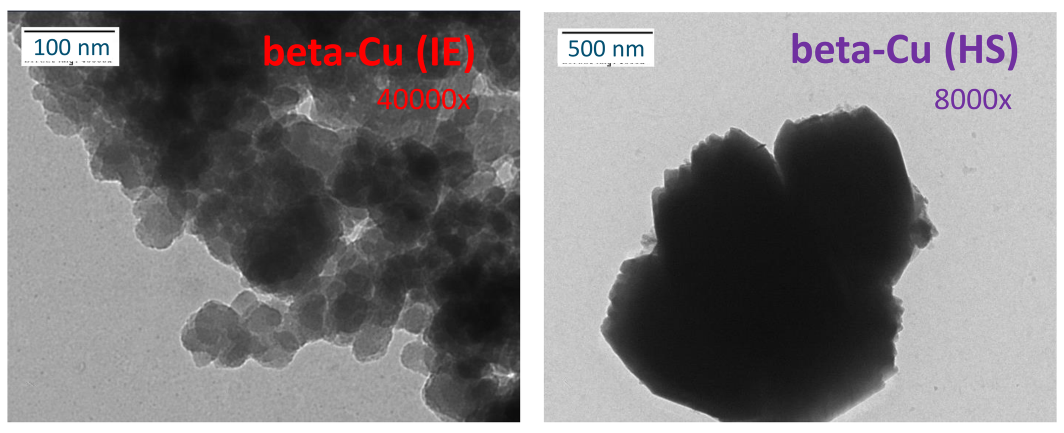
Figure 1. XRD analysis.



No peaks associated to Cu oxides were observed in the XRD patterns of zeolites before reaction. Metals are well dispersed on the catalyst surface.

No changes are observed after reaction: the catalyst structure remains constant during the catalytic test.

Figure 2. TEM analysis.



The catalyst prepared by hydrothermal synthesis presents a higher crystallite size than the catalyst prepared by ion exchange.

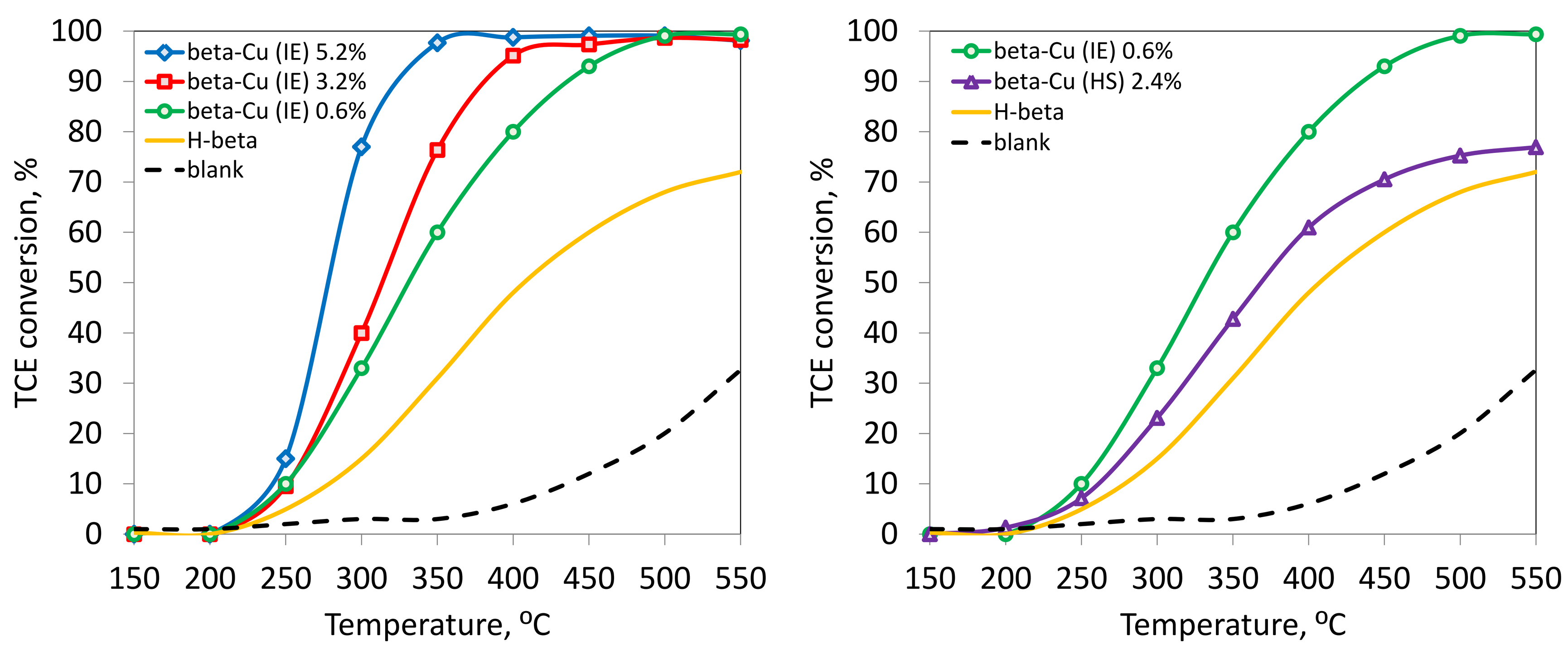
Table 3. H_2-TPR and NH_3-TPD analysis.

Catalyst	TPR mmol $_{H2}$ /g	H_2/Me^{2+} ratio	TPD µmol $_{NH3}$ /g
beta-Cu (IE) 3.2%	0,58	1,17	1606
beta-Cu (HS) 2.4%	0,13	0,33	78

The zeolite prepared by hydrothermal synthesis presents lower acid and redox properties than zeolites prepared by ion exchange.

Catalytic results

Figure 1. TCE oxidation light-off curves over Cu-catalysts based on zeolite beta.



The increasing addition of Cu (0.6, 3.2 and 5.2%wt) decreases the T_{50} (330, 310 and 275°C, respectively).

The catalyst prepared by hydrothermal synthesis was less active (T_{50}=370°C) than any of the catalysts prepared by ion exchange.

Conclusions

- Catalysts based on zeolite beta containing copper are active for the TCE oxidation reaction in the temperature range studied (350-550ºC).
- There is a correlation between the % of Cu-ion exchange and the catalyst activity.
- The preparation method influences the catalytic properties of the catalysts, being the most active those prepared by ion exchange.

  - Cu species are different depending on the synthesis method, being more active the Cu sites formed in the ion exchange process.

  - In the catalyst prepared by hydrothermal synthesis, Cu is located in the zeolite framework so it cannot interact with Cl-molecules because of its stability. Thus, the metal is not easily accessible by the feed molecule and as a result it can´t be oxidized.

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