

## SYNTHESIS OF COPPER CONTAINING ZEOLITES: NEW, SIMPLE AND EFFICIENT METHOD FOR QUANTITATIVE EXCHANGE\*

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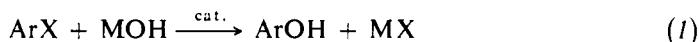
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A new technique is described which allows the quantitative exchange of copper(II) into ZSM-5 zeolites. The sequence consists of two steps: (i) impregnation of the zeolite with copper(II) in amounts higher than the exchange capacity; (ii) leaching of the copper in excess with respect to the exchange capacity with a chlorobenzene-water mixture at high temperature. The performances of the new materials in the hydrolysis of chlorobenzene, as well as preliminary informations on the nature of the catalyst and the type of mechanism are presented.

Phenols and anilines are essential starting materials for the production of basic organic intermediates<sup>1-4</sup>. Among the cheapest and most reactive molecules used to functionalize an aromatic ring, chlorine and bromine are frequently chosen<sup>1,2</sup>. The subsequent hydrolysis step then leads to the phenol derivative (Eq. (1)).



As indicated in Eq. (1), the use of a catalyst is required to perform the hydrolysis in the best conditions. Both liquid and vapour phase techniques have been described and used in the industry<sup>1,2</sup>. Most catalytic systems contain copper as the active component<sup>5</sup>. For liquid phase processes, copper is frequently employed in conjunction with a cocatalyst and concentrated sodium hydroxide, at temperatures between 200 and 250°C and under pressure<sup>6</sup>. Hydrolysis in the vapour phase is performed with water at temperatures above 400°C and deactivation frequently occurs either by coking or loss of copper. Thus, it is highly desirable to develop new copper containing heterogeneous systems to prevent corrosion, salty effluents and loss of copper.

Very recently, copper exchanged zeolites have appeared and shown excellent performances in the catalytic decomposition of nitrogen oxides from the emissions

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of diesel engines<sup>7</sup> and from industrial effluents<sup>8,9</sup>. Some Japanese patents mention the use of these materials in the hydrolysis of haloaromatics<sup>10</sup>. In this paper we report on a new technique for quantitative exchange of copper in ZSM-5 type zeolites. The catalytic behaviour of the CuHZSM-5 materials has been studied with the hydrolysis of chlorobenzene as a test reaction. The performances on stream as well as the structure of the catalyst and the mechanism are discussed.

## EXPERIMENTAL

### Compounds Used

Chlorobenzene and  $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  were used as provided without further purifications. ZSM-5 zeolites were synthesized following a literature procedure<sup>11</sup>. The zeolites were characterized by elementary analysis and X-ray diffraction patterns (Cu-K $\alpha$ ; 45 kV and 30 mA). Acidity and porosity were checked by *m*-xylene isomerization at 623 K using 50 mg of the zeolite<sup>12</sup>. Specific surface and porous volume were obtained by continuous flow  $\text{N}_2$  adsorption-desorption isotherms at 77 K.

Three different methods were used to introduce copper into the zeolite structure:

A) Exchange of HZSM-5 or NaZSM-5 with diluted  $\approx 0.03\text{M}$  aqueous solutions of  $\text{Cu}(\text{NO}_3)_2$  for 24 h followed by washing with distilled water, drying at 373 K and calcination at 773 K under dry air ( $4\text{ dm}^3\text{ h}^{-1}\text{ g}^{-1}$ ).

B) Impregnation of the zeolites with an aqueous  $0.3\text{M}$  solution of  $\text{Cu}(\text{NO}_3)_2$ , evaporation of the water at 353 K for two hours, followed by drying and calcination as under A).

C) Impregnation as under B), followed by leaching of the copper in excess with respect to the exchange capacity (E.C.) under the conditions of the catalytic test.

Copper and chlorine contents were obtained by atomic absorption and potentiometry, respectively.

### Catalytic Activity

Hydrolysis of haloaromatic was performed at 673 K using a fixed bed flow glass reactor, containing 0.5 g of the catalyst. The molar composition of the feed was (%):  $\text{PhCl}/\text{H}_2\text{O}/\text{N}_2 = 7/38/55$ , with a WHSV of  $2\text{ h}^{-1}$ .

## RESULTS AND DISCUSSION

### *Method for Introducing Copper into the Zeolite*

The three different methods described above were compared using ZSM-5 zeolites with Si/Al ratios of 35 and 40 (Table I). As can be seen from the results neither normal exchange conditions nor exchange in impregnation conditions, enable to reach exchange levels higher than 50% as observed in the literature<sup>13-15</sup> whereas the impregnation-leaching sequence leads to a quantitative incorporation of copper.

Simple experiments have been carried out to understand better this new finding and to identify the active component responsible for the leaching (Table II). From

the data in Table II it appears that chlorobenzene (PhCl) alone is responsible for the leaching and that the presence of water in the feed only enhances the process. These observations are summarized in Eqs (2) and (3).

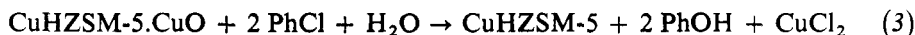
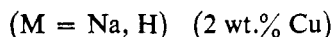


TABLE I

Efficiency of different methods for introducing copper into HZSM-5 zeolites

Atomic ratio Si/Al	Method for introduction of $\text{Cu}^{2+}$	$[\text{Cu}(\text{NO}_3)_2]$ $\text{mol l}^{-1}$	$T$ $^\circ\text{C}$	Duration h	Mole ratio <sup>a</sup> ( $\text{Cu}^{2+}/\text{E.C.}$ ) $\times 2$	Copper content <sup>b</sup> wt. %	Exchange level <sup>c</sup> %
35	A	0.03	20	24	1.5	0.25	17
35	A	0.03	80	24	1.5	0.25	17
35	A	0.3	20	24	1.5	0.4	27
35	A	0.3	80	24	1.5	0.6	41
40	B	0.3	80	2	1.5	2	154
40	C impregnation step-leaching step	0.3	80 400	2 4	1.5 —	2 1.3	154 100 <sup>d</sup>

<sup>a</sup> E.C. theoretical exchange capacity (for Si/Al = 35, E.C. = 0.46 meq.  $\text{M}^+$ /g; for Si/Al = 40, E.C. = 0.41 meq.  $\text{M}^+$ /g. <sup>b</sup> Total amount of copper in the material as synthesized. <sup>c</sup>  $2 \times$  (mole of introduced copper/E.C.). <sup>d</sup> Copper balance  $\approx 90\%$  ( $= \{\text{mole of Cu in the zeolite after leaching} + \text{mole of Cu leached}\} / \text{mole of Cu in the zeolite before leaching}$ ).

TABLE II

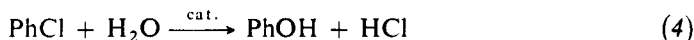
Stability of the copper content of the CuHZSM-5 (Si/Al = 40) zeolite (2 wt. % Cu by impregnation) as a function of the composition of the feed (temperature 400°C; time on stream 6 h)

Composition of the feed	Final copper content (wt. %)
$\text{N}_2$	1.9
$\text{H}_2\text{O}/\text{N}_2$	1.9
$\text{HCl}/\text{H}_2\text{O}/\text{N}_2$	1.9
$\text{PhCl}/\text{N}_2$	1.6
$\text{PhCl}/\text{H}_2\text{O}/\text{N}_2$	1.3 <sup>a</sup>

<sup>a</sup> Calculated content for 100% exchange level of Cu is 1.3 wt. %.

### Catalytic Activity

The activity of all the materials was evaluated using the hydrolysis of chlorobenzene as a test reaction (Eq. (4)).



First of all, the influence of the copper content of the zeolite was studied (Fig. 1). It appears that the optimum copper content of the CuHZSM-5 (Si/Al 35) catalyst lies in the range of 70–100% exchange level. These are precisely the levels which can be attained by the impregnation-leaching sequence.

After the excess of copper has been leached (6 h on stream), the catalyst has remarkable stable performances as can be seen in Fig. 2. The conversion of PhCl is

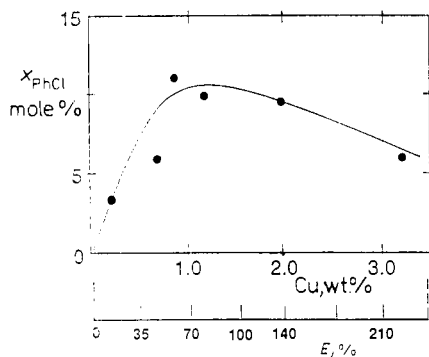


FIG. 1

Hydrolysis of chlorobenzene catalyzed by CuHZSM-5 zeolites. Effect of copper content (Si/Al = 35, copper introduced by impregnation) and exchange level (*E*, %)

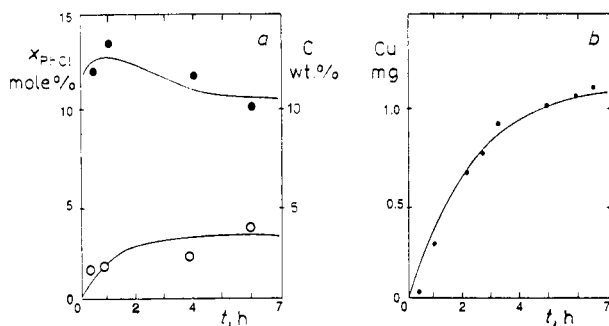


FIG. 2

Hydrolysis of chlorobenzene catalyzed by CuHZSM-6 (Si/Al = 35; initial copper content 2 wt. %; exchange level 140%). Performances on stream at 400°C. *a* ● Conversion of PhCl (mole %), ○ amount of coke (wt. %). *b* Amount of leached Cu (mg)

around 10 to 12% with a selectivity toward phenol higher than 98%. The amount of coke stays between 3 and 4 wt.%.

At exchange levels of 20 to 70% a synergic effect has been evidenced between the residual Brönsted acidity of the zeolite and the introduced copper (Fig. 3). This is surprising, when compared to the strong basicity needed in liquid phase processes<sup>3</sup>. It seems that in our case residual alkalinity can have an inhibitory effect (see point IV in Fig. 3). Furthermore, an acidic catalyst is much more favorable because it avoids the retention of phenol.

The catalyst before and after the hydrolysis reaction has been analyzed by elementary analysis and XPS (Table III). It appears that the calcination of the catalyst before hydrolysis induces at the surface an enrichment of aluminium and a decrease of

TABLE III

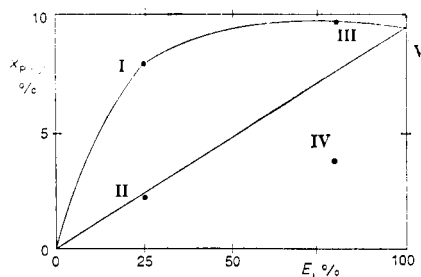
Analytical data on the CuHZSM-5 (Si/Al = 36) catalyst before and after the hydrolysis of chlorobenzene

Element	Catalyst before test reaction		Catalyst after test reaction	
	overall content, wt. % <sup>a</sup>	surface conc., wt. % <sup>b</sup>	overall content, wt. % <sup>a</sup>	surface conc., wt. % <sup>b</sup>
Cu	2.0	0.7	1.4	2.8
Si	46.0	48.5	43.3	49.4
Al	1.2	2.5	1.0	8.7
O	50.0	45.5	50.0	33.1
C	0	0	3.7	4.8
Cl	0	0	0.56	1.2

<sup>a</sup> Elemental analysis; <sup>b</sup> XPS.

FIG. 3

Synergic effect of H and Cu in the CuHZSM-5 (Si/Al = 35) catalyzed hydrolysis of PhCl. I HZSM-5 exchanged with Cu<sup>2+</sup> (method A); II H<sup>+</sup>-acidity of I neutralized by NaOH; III CuHZSM-5 obtained by impregnation of HZSM-5 (method B); IV H<sup>+</sup>-acidity of III neutralized by NaOH; V CuHZSM-5 prepared by impregnation-leaching sequence (method C)



copper. After hydrolysis of PhCl, the surface content of Al is much higher and Cu has been enriched as well. If one takes into account the HCl produced by the reaction at 400°C (Eq. (4)), it is not surprising to observe some dealumination of the zeolite. The increase of copper content at the surface can be explained by the continuous elimination during the initial leaching period. More precise measurements by XPS seem to indicate that the oxidation state of copper at the surface is +1. Further investigations are necessary to obtain a more precise picture of the nature of the catalyst.

A general rate law may be written for the hydrolysis reaction (Eq. (5)).

$$r = k p^x(\text{PhCl}) p^y(\text{H}_2\text{O}), \quad (5)$$

where  $p$  indicates a partial pressure and  $x$  and  $y$  stand for the partial orders in chlorobenzene and water, respectively. A simple study has been carried out and leads to values of 0 for PhCl and 0.3 for H<sub>2</sub>O (Fig. 4). These orders indicate a strong adsorption for PhCl and a weaker adsorption for water. The order obtained in case of water is quite surprising because of the hydrophobic nature of the HZSM-5 zeolite. Nevertheless, the presence of Cu<sup>2+</sup> may explain this result.

Finally, we would like to address the question of the mechanism. Basically two type of processes may be distinguished<sup>5</sup>: (i) an addition-elimination (S<sub>N</sub>Ar mechanism); (ii) an elimination-addition (arynic mechanism). Taking into account the synergic effect observed between H<sup>+</sup> and Cu<sup>2+</sup> (Fig. 3) and some preliminary results on the hydrolysis of dihaloaromatics<sup>16</sup>, the most reasonable mechanism in accordance with our experimental data is depicted in Scheme 1.

In conclusion, an efficient and simple method for introducing copper into ZSM-5 zeolites has been developed. The introduction of copper in amounts equivalent to

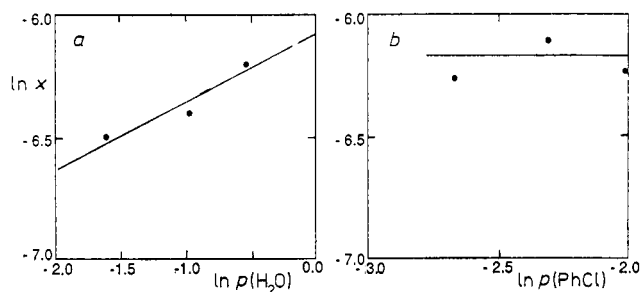
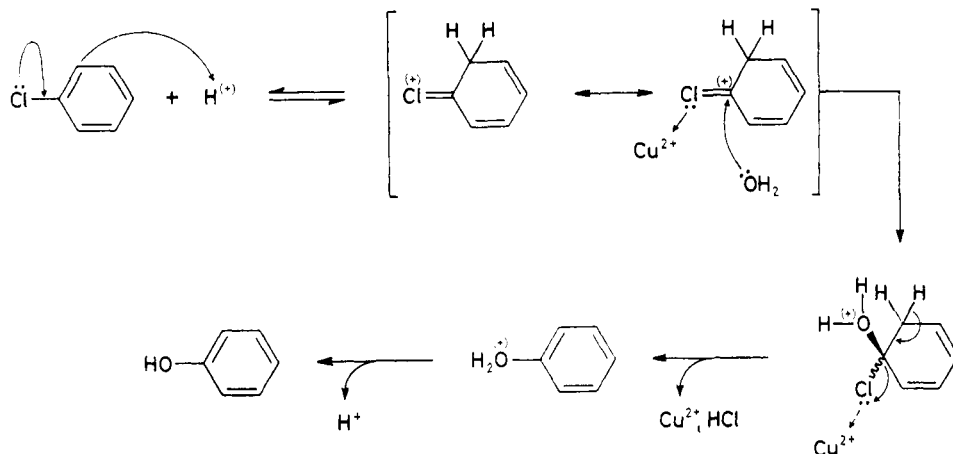


FIG. 4

Kinetic study of the CuHZSM-5 (Si/Al = 35) catalyzed hydrolysis of PhCl. Effects of partial pressures of water (a) and PhCl (b) on conversion  $x$

the E.C. has been achieved. After the excess of copper has been leached, the performances of the "CuZSM-5" materials are perfectly stable during the hydrolysis of PhCl. No loss of copper is observed. It seems that the hydrolysis reaction produces a new active material, which is quite different compared with a simply copper exchanged zeolite. To clarify this point, further analytical investigations are necessary.



SCHEME 1

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