

# THE CATALYTIC ACTIVITY OF COPPER(II)-IONS IN ZEOLITES AS COMPARED TO COPPER(II)-OXIDE AND COPPER-ALUMINIUM-SPINEL

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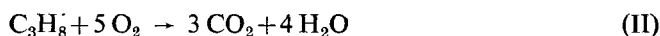
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## 1. Introduction and Scope

The object of the present investigation was to compare the catalytic activity of various copper compounds in oxidation reactions, including Cu<sup>2+</sup>-exchanged zeolites. Zeolites are generally supposed to be particularly active as catalysts, due to the high degree of dispersion of the catalytically active species within the porous structure of the crystals.

It appears doubtful, however, whether this expectation must be true in general. If the reactivity of lattice oxygen is responsible for the catalytic properties of a bulk oxide (*e.g.* CuO) then a zeolite containing the same cation (*e.g.* Cu<sup>2+</sup>) may not exhibit a corresponding catalytic activity, the reactivity of its oxygen in the silica-alumina framework being not affected by the cation-composition. On the other hand, if the cations in the surface of an oxide are the catalytically active species, then a zeolite containing the same cation should exhibit catalytic activity, corresponding to the high degree of accessibility of the cations in the zeolite-lattice for the reactants. A well defined quantitative measure of catalytic activity is necessary in order to resolve this question by experiment. Such a measure is the rate constant of the reaction at a fixed temperature, provided it is not affected by mass- or heat transfer in the reactor and the reaction-order (rate low) is the same for the various catalysts to be compared. The rate constant has to be defined per unit amount of catalyst, which could be unit of mass, volume, surface area or amount of catalytically active species; the choice of this basis being essential to a meaningful comparison of different solids.

The kinetics of oxidation of CO and of propane



were studied on copper oxide (CuO), copper-aluminum spinel (CuAl<sub>2</sub>O<sub>4</sub>) and on Cu<sup>2+</sup>-exchanged zeolites Y and mordenite in order to compare the catalytic activity of these solids in oxidation reactions.

## 2. Experimental

### a) Catalysts

CuO was obtained in the form of porous cylinders (4 mm diameter) by pressing  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (Merck, No 2722) into tablets and heating to 550 °C for two hours.

$\text{CuAl}_2\text{O}_4$  (copper-aluminum spinel):

8 g  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  was dissolved together with 51 g  $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$  in 100 ml  $\text{H}_2\text{O}$  and the water evaporated. The remaining solid was heated to 900 °C for 10 days.

The resulting red-brown powder analyzed 35 wt% Cu and 30 wt% Al; its X-ray diffraction pattern corresponding to that of the spinel-structure, no other phase being detectable.

Zeolite Y was synthesized following the procedure described by BRECK [1] from sodium aluminate, NaOH and silica sol (27 wt%  $\text{SiO}_2$ ). Crystallization at 75 °C for six days yielded crystals from 2 to 10  $\mu\text{m}$  in diameter analyzing  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot (\text{SiO}_2)_{4.16}$ .

Zeolite mordenite was obtained from the Norton company (type 100, analyzing  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3(\text{SiO}_2)_{10}$  as a crystalline powder with particle sizes between 2 and 12  $\mu\text{m}$ ).

$\text{Cu}^{2+}$ -ions were incorporated into these zeolites by partial ion-exchange with a solution of 0.1 mol/l  $\text{Cu}(\text{NO}_3)_2$  in a citrate buffer at pH 6.0 (in order to avoid hydrolysis of  $\text{Cu}^{2+}$ -eq.). No phases other than the zeolite structures were detectable by X-ray diffraction in the ion-exchanged materials:

Structure Designation	Faujasite (Y)		Mordenite		
	Y0	Y22	M0	M5	M12
% of $\text{Na}^+$ exchanged by $\text{Cu}^{2+}$	0	22	0	5	12

The spinel as well as the zeolites were pressed into tablets of 4 mm diameter before being used as catalysts.

### b) Characterization of solids

The surface area of CuO and  $\text{CuAl}_2\text{O}_4$  was determined by adsorption of  $\text{N}_2$  at 77 K using the two-parameter BET-equation and assuming a monolayer capacity of  $1 \cdot 10^{-5}$  mol  $\text{N}_2$  per  $\text{m}^2$ .

According to SCHOLTEN and KONVALINKA [2] the amount of CO-chemisorption is a measure of the number of accessible copper-ions in a surface. CO-adsorption isotherms were determined volumetrically at 357 K and  $p \leq 0.6$  bar after degassing the solids at 625 K and  $p < 0.3$  Pa.

The chemisorbed amount was obtained by extrapolating these isotherms to  $p_{\text{CO}}=0$ ; in the case of the zeolites this amount was equal to the increment of CO adsorption observed at a given pressure on the  $\text{Cu}^{2+}$ -exchanged zeolite as compared to the parent material.

### c) Reaction rate measurements

The rates of total oxidation of propane or of carbon monoxide, *resp.*, were obtained from the conversion in an integral reactor at atmospheric pressure, containing 1.5  $\text{cm}^3$  of catalyst. Catalyst materials were compacted into tablets of 0.4 cm diameter.

The absence of appreciable concentration gradients of reactants in the porous pellet was established in two ways

- (1) by estimating the Thiele modulus and effectiveness factor of the pellet on the basis of an effective diffusivity of  $2 \cdot 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$  as its lower limit;
- (2) by locating the temperature-range where the effectiveness factor  $\eta$  is essentially unity ( $0.9 \leq \eta \leq 1$ ) from an observation of the rate over a wide range of temperatures as described previously [3].

Reaction mixtures were less than 0.013 mol% of  $\text{C}_3\text{H}_8$  in air or 0.05 mol% CO in oxygen, corresponding to adiabatic temperature rises of 10 K or 5 K, *resp.*, at total conversion so that the temperature rise in the reactor was limited to 1 K under the conditions of the experiments. A gas chromatograph with flame-ionization-detector was used to analyze the gas mixtures before and after the reactor; analysis for the very low content of CO was possible by hydrogenating CO on a nickel catalyst prior to detection in the FID.

Since the concentration of excess oxygen is constant, the rate coefficients  $k_i$  per unit of mass of catalyst can be defined by the equation

$$-\frac{1}{m} \cdot \frac{dn_i}{dt} = k_i \cdot c_i^\alpha \quad (1)$$

( $i = \text{CO}, \text{C}_3\text{H}_8$ ) where  $m$  is the mass of catalyst,  $c_i$  the concentration of reactant  $i$  and  $\alpha$  the order of reaction with respect to  $i$ . In the case of first order ( $\alpha = 1$ ) integral conversion  $X_i$  and volumetric flow rate  $\dot{v}_0$  are related to the mass  $m$  of catalyst in the reactor and to the rate constant  $k$  by equation (2):

$$\dot{v}_0 \ln \frac{1}{1 - X_i} = k_i \cdot m \quad (2)$$

$k_i$  is obtained in  $\text{cm}^3 \text{ g}^{-1} \text{ sec}^{-1}$ .

### 3. Results

#### a) Surface area and CO-chemisorption

BET surface areas and corresponding numbers of  $\text{N}_2$ -adsorption sites in a monolayer, CO-chemisorption at 357 K and Cu-content are shown in the following Table I:

Table I

Catalyst	CuO	CuAl <sub>2</sub> O <sub>4</sub>	Y22	M5	M12
BET surface in m <sup>2</sup> /g	2.0	5.4	—	—	—
N <sub>2</sub> -sites in mol/g	$2.0 \cdot 10^{-5}$	$5.5 \cdot 10^{-5}$	—	—	—
CO-chemisorption $n_{\text{CO}}/m$ in mol/g	$1.8 \cdot 10^{-5}$	$1.45 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$4.2 \cdot 10^{-4}$
Cu-content $n_{\text{Cu}}/m$ in mol/g	$1.26 \cdot 10^{-2}$	$5.51 \cdot 10^{-3}$	$5.3 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$	$2.5 \cdot 10^{-4}$
Density of pellets in g/cm <sup>3</sup>	1.6	2.5	1.3	1.1	1.1

The CO-chemisorption capacity of the bulk oxides corresponds to the amount of  $\text{Cu}^{2+}$  expected at the surface, as far as the order of magnitude is concerned. In the Cu-containing mordenites roughly 2 molecules are chemisorbed per  $\text{Cu}^{2+}$ -ion, whereas only 0.25 molecules of CO are chemisorbed per  $\text{Cu}^{2+}$ -ion in zeolite Y, indicating that  $\text{Cu}^{2+}$  in zeolite Y is only partially accessible for CO-chemisorption as has already been reported in the literature [4, 5].

### b) Kinetics of oxidation reactions

The kinetics of reactions (I) and (II) were found to be first order in the concentration of CO or  $\text{C}_3\text{H}_8$ , *resp.*, the coefficients  $k$  in eq. (2) being independent of space velocity and initial concentrations at least up to 0.05 or 0.013 mol %, *resp.* Rate coefficients  $k$  per unit of mass of catalyst as a function of reciprocal temperature are shown in Figs. 1 and 2 on a logarithmic scale; all results were reproducible when the temperature was increased or decreased. The region where the observed rates of reaction are affected by mass transfer limitations can be detected in the  $\log k$  vs.

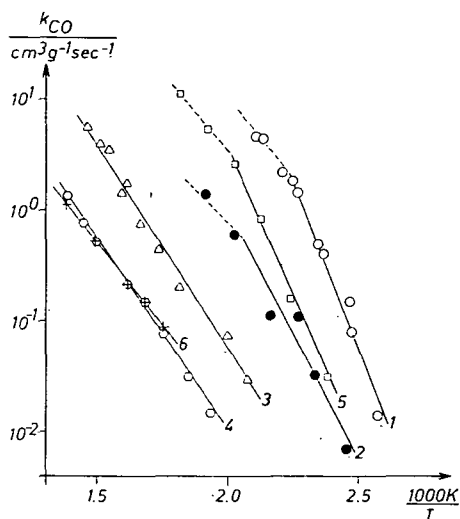


Fig. 1. Arrhenius plot of rate constants (CO-oxidation) 1=CuO, 2=CuAl<sub>2</sub>O<sub>4</sub>, 3=Y22, 4=Y0, 5=M5, 6=M

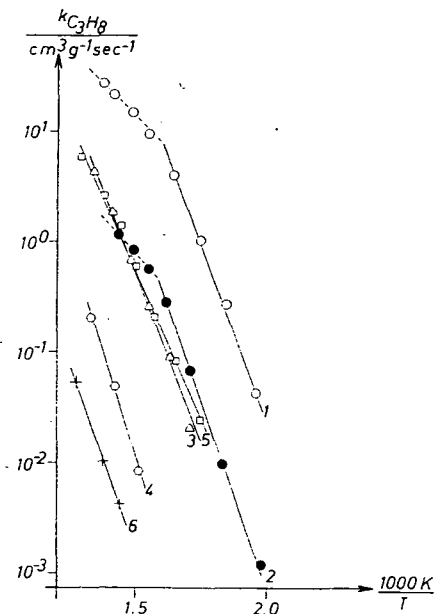


Fig. 2. Arrhenius plot of rate constants ( $\text{C}_3\text{H}_8$ -oxidation) 1=CuO, 2=CuAl<sub>2</sub>O<sub>4</sub>, 3=Y22, 4=Y0, 5=M5, 6=M

$1/T$ -plot, since the slope will change by a factor 0.5 as soon as concentration gradients in the porous pellets are significant. Mass transfer limitations exert an influence on the observed rates only if  $k$  is greater than  $1 \text{ cm}^3 \text{ g}^{-1} \text{ sec}^{-1}$ , as can be seen from Figs. 1 and 2 (dotted lines). Time constants of diffusion of small molecules in zeolite crystals are very small compared to the time constants  $R^2/D_{\text{eff}}$  of diffusion in the macropores of pellets made from these crystals [6]. It can be concluded, therefore,

that the observed rates of reaction are also not affected by mass-transfer limitations in the zeolite crystals if  $k$  is smaller than  $1 \text{ cm}^3 \text{ g}^{-1} \text{ sec}^{-1}$ .

The rate per unit of mass of catalyst on the pure Na-forms of the zeolites is less than 10% of the value observed on the same zeolites after partial ion-exchange with  $\text{Cu}^{2+}$ .

#### 4. Discussion

In the following Table II rate data which are not influenced by mass effects are compared for different catalysts at two arbitrarily chosen temperatures (440 K for CO-oxidation, 570 K for  $\text{C}_3\text{H}_8$ -oxidation). In a few cases the values given have been obtained by extrapolating the Arrhenius plot at low-temperatures ( $\eta=1$ ) to the reference temperature, any influence of mass transfer resistance being eliminated in

Table II

	CuO	$\text{CuAl}_2\text{O}_4$	Y22	M5	M12
Reaction: normalized rate data CO-oxidation (440 K):					
(1) $k$ in $\text{cm}^3/\text{g}\cdot\text{sec}$	1.4	$6.3 \cdot 10^{-2}$	$5.2 \cdot 10^{-3}$	0.115	
(2) $k \cdot m/n_{\text{CO}}$ in $\text{cm}^3/\text{mol}\cdot\text{sec}$	$8.2 \cdot 10^4$	$4.3 \cdot 10^3$	$4.0 \cdot 10^1$	$5.0 \cdot 10^2$	
(3) $k \cdot m/n_{\text{CO}}$ relative to CuO	(1.00)	$5.3 \cdot 10^{-2}$	$4.9 \cdot 10^{-4}$	$6.1 \cdot 10^{-3}$	
$\text{C}_3\text{H}_8$ -oxidation (570 K):					
(4) $k$ in $\text{cm}^3/\text{g}\cdot\text{sec}$	0.94	$3.8 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$2.4 \cdot 10^{-2}$	$5.3 \cdot 10^{-2}$
(5) $k \cdot m/n_{\text{CO}}$ in $\text{cm}^3/\text{mol}\cdot\text{sec}$	$5.5 \cdot 10^4$	$2.6 \cdot 10^3$	$1.1 \cdot 10^2$	$1.0 \cdot 10^2$	$1.3 \cdot 10^2$
(6) $k \cdot m/n_{\text{CO}}$ relative to CuO	(1.00)	$4.7 \cdot 10^{-2}$	$1.95 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$

this way. The highest rate per unit of mass of catalyst (lines (1) and (4)) is observed with CuO for both reactions, however, mordenite M5 reaches 8% of the value observed with CuO. A comparison on the basis of unit of mass of catalyst does not appear very meaningful, however, if one wants to characterize the catalytic activity of a given species in different environments, since in the bulk oxides only the surface can be involved in the catalytic reaction. The rate constants  $k$  per unit of mass have therefore been normalized by the amount of CO-chemisorption per unit of mass (lines (2) and (5)). The resulting quantities  $k \cdot \frac{m}{n_{\text{CO}}}$  can be considered as rate coefficients per unit amount of active species or sites and will thus be proportional to turnover-numbers, provided CO-chemisorption measures the amount of active species or active sites. Again these numbers are highest for CuO; ratios of  $k \cdot \frac{m}{n_{\text{CO}}}$

relative to the values observed on CuO are given in line (3) and (6). Whereas the rate per CO-adsorption-site on  $\text{CuAl}_2\text{O}_4$  is roughly 5% of the value observed on CuO, it does not reach 1% of this value in the zeolites. Since CO-chemisorption measures the amount of  $\text{Cu}^{2+}$  which is accessible to the reactants, one can conclude that  $\text{Cu}^{2+}$  is not the active species in these oxidation-reactions. There is strong evidence that lattice oxygen is an intermediate in catalytic oxidation on oxides as has been shown by several authors [7—9] particularly by BORESKOV and his school [10—12]. This view is in agreement with the above conclusion, since the properties of oxygen in the lattice of CuO or  $\text{CuAl}_2\text{O}_4$  can be expected to be very different from those of oxygen in a zeolite-framework.

#### References

- [1] *Breck, D. W.*: U. S. Pat., 3, 170, 007 (1964).
- [2] *Scholten, J. J. F., J. A. Konvalinka*: Trans. Faraday Soc. **65**, 2465 (1969).
- [3] *Kotter, M., P. Lovera, L. Riekert*: Ber. Bunsenges. phys. Chem., **80**, 61 (1976).
- [4] *Egerton, T. A., F. S. Stone*: Trans. Faraday Soc. **69**, 1, 22 (1973).
- [5] *Benn, F. R., J. Dwyer, A. Esfahani, N. P. Evmerides, A. K. Szczepura*: J. Catalysis **48**, 60 (1977).
- [6] *Doelle, H.-J., L. Riekert*: ACS Symposium Ser. **40**, 401 (1977).
- [7] *Winter, E. R. S.*: Advances in Catalysis **15**, 196 (1958).
- [8] *Sachtler, W. M. H., G. J. H. Dorgelo, J. Fahrenfort, R. J. H. Voorhoeve*: Rec. Trav. Chim. Pays Bas **89**, 460 (1970).
- [9] *Hertl, W.*: J. Catalysis **31**, 231 (1973).
- [10] *Boreskov, G. K.*: Advances in Catalysis **15**, 285 (1964).
- [11] *Boreskov, G. K.*: Kinetika i Kataliz **11**, 374 (1970).
- [12] *Popovskii, V. V.*: Kinetics and Catalysis **13**, 1065 (1972).