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THE CATALYTIC ACTIVITY OF COPPER-EXCHANGED ZEOLITES AS COMPARED TO COPPER-OXIDES

COMPARAÇÃO DA ACTIVIDADE CATALÍTICA DE ZEOLITAS PERMUTADAS COM COBRE E ÓXIDOS DE COBRE

Rate coefficients for the oxidation of CO and C_3H_8 on various oxides of copper and copper-exchanged synthetic faujasite were determined under strictly isothermal conditions, eliminating all mass transfer resistences. These rate coefficients were normalized by the number of accessible copper-ions in the surface or lattice of the solids. The rate coefficient per acessible copper-ion in the zeolithe is negligible as compared to the corresponding quantity for the surface reaction on various oxides. It is concluded that the catalytic activity of these copper-compounds in oxidation reactions is due to the reactivity of oxygenions at the surface of the lattice.

1. INTRODUCTION

Synthetic zeolites appear to be particularly suitable as catalyst carriers due to their capacity for ion-exchange. This conjecture is based on the assumption that a particular cation exchanged into the zeolite can be considered as an active component. The validity of this assumption has been examined experimentally for the case of copper (II)–ions in a zeolite and in other compounds as catalysts for the oxidation of CO and of C_3H_8. In order to make a meaningful comparison between the catalytic activity of copper-ions in different solids any effect from transport phenomena had to be avoided or eliminated and reaction rates per accessible copper-ion were evaluated.

2. EXPERIMENTAL

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 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 2.10^{-3} $cm^2\,sec^{-1}$ as its lower limit;
2. by locating the temperature-range where the effectiveness factor η is essentially unity ($0.9 < \eta < 1$) from an observation of the rate over a wide range of temperatures as described previously (1).

Reaction mixtures were 0.013 mol % of C_3H_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 chromotograph 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 (2). The reactions were found to be first order in CO or C_3H_8, oxygen being in large excess in either case. A rate coefficient k^m per unit mass of catalyst can thus be defined by the differential equations

$$-\frac{dn_{CO}}{dt} = k^m_{CO} \cdot m_K \cdot c_{CO} \qquad (1a)$$

$$-\frac{dn_{C_3H_8}}{dt} = k^m_{C_3} \cdot m_K \cdot c_{C_3H_8} \qquad (1b)$$

where m_K is the mass of the catalyst, c_i the volume-concentration of in the gas-phase. k^m has the dimension of $cm^3\,g^{-1}\,sec^{-1}$ and was evaluated from the integral conversion in the reactor.

Surface areas S per unit of mass were determined from the adsorption of N_2 at 77 K on the basis of the BET-isotherm (except for the zeolite where this method is not applicable). From the surface area S and the rate coefficient k^m a rate coefficient k^F per unit of surface area can be obtained:

$$k^F = \frac{k^m}{S} \qquad (2)$$

it has the dimension $cm\,sec^{-1}$.

According to Scholten and Konvalinka (3) the amount of CO-chemisorption (at saturation) is a measure of the number of accessible copper-ions in a surface. CO chemisorption-isotherms were determined volumetrically at $P_{CO} \leq 0.6$ bar and $T = 357$ K as $\frac{n_{CO}}{m_K}$ (amount chemisorbed at saturation per gram of catalyst).

2.1. MATERIALS

Zeolite Y was synthesized from sodium aluminate, NaOH, H_2O and silica sol containing 26 percent SiO_2 following the procedure described by Breck (4). The resulting material was 100 % zeolite Y characterized by X-ray diffraction, crystal sizes ranging from 2 μm to 10 μm. Chemical analysis indicated a product composition of

$$1.0\,Na_2O : 1.0\,Al_2O_3 : 4{,}16\,SiO_2\,.\,xH_2O$$

22 % of the sodium was exchanged by Cu^{2+} from an aqueous solution of $Cu(NO_3)_2$ resulting in a material corresponding to the dry composition

$$Na_{1,56}\,Cu_{0,22}\,O \cdot Al_2O_3 \cdot (SiO_2)_{4,16}$$

Copper oxide, CuO, was prepared by heating $CuCO_3 \cdot Cu(OH)_2$, extra pure (Merck) to 550°C.
Copper (II)-aluminate, $CuAl_2O_4$, was synthesized by heating a mixture of 54,1 g $Al(NO_3)_3 \cdot 9H_2O$ and 8 g $CuCO_3 \cdot Cu(OH)_2$ at increasing temperatures up to 900 °C for different periods of time (total time 10 days). The resulting material consisted entirely of the spinel-structure.
Copper (II)-titanate, Cu_3TiO_5, which has a tetragonal structure was prepared by heating a mixture of CuO, pure (Merck) and TiO_2 at 1000°C for two hours.
The resulting solid contained 20 % Cu_2TiO_3 with monovalent copper besides 80 % of Cu_3TiO_5.
The phase-composition of all materials used as catalysts was established by X-ray diffraction and chemical analysis.

3. RESULTS

Results of rate measurements, surface-area determination and CO-chemisorption are summarized in the table 1.

Table 1

	Catalyst Composition	Surface area S CO – chemisorption	Reactant	ϑ/°C	Rate coefficients in the temperature range not influenced by intrapellet diffusion	
					k^m in $\frac{cm^3}{g\,sec}$	k^F in $\frac{cm}{sec}$
1	CuO	$S = 2.0\,m^2g^{-1}$	CO	135 152	0.11 0.46	$5.2 \cdot 10^{-6}$ $2.4 \cdot 10^{-5}$
		$\frac{n_{CO}}{m_K} = 1.7 \cdot 10^{-5}\,\frac{mol}{g}$	C_3H_8	253 315	0.11 2.2	$5.7 \cdot 10^{-6}$ $9.6 \cdot 10^{-5}$
2	$CuAl_2O_4$	$S = 5.4\,m^2g^{-1}$ $\frac{n_{CO}}{m_K} = 1.4 \cdot 10^{-5}\,\frac{mol}{g}$	CO	135 182	$7 \cdot 10^{-3}$ 0.14	$1.3 \cdot 10^{-7}$ $2.5 \cdot 10^{-6}$
3	$Cu_3TiO_5 + Cu_2TiO_3$ (8 : 2)	$S = 1.0\,m^2g^{-1}$ $\frac{n_{CO}}{m_K} = 7.6 \cdot 10^{-7}\,\frac{mol}{g}$	CO	144 171	$2.5 \cdot 10^{-3}$ $2.6 \cdot 10^{-2}$	$2.4 \cdot 10^{-7}$ $2.5 \cdot 10^{-6}$
4	Zeolite Cu Na Y $Na_{1.56}Cu_{0.22}O.Al_2O_3.(SiO_2)_{4.16}$		CO	215 253	$3.7 \cdot 10^{-2}$ 0.13	
			C_3H_8	298 372	$1.2 \cdot 10^{-2}$ 0.22	
5	Zeolite Na Y		C_3H_8	394 441	$6.7 \cdot 10^{-3}$ $6 \cdot 10^{-2}$	

Rate coefficients k^m as a function of temperature are shown in figure 1 and 2 for CO-oxidation and C_3H_8-oxidation, respectively.

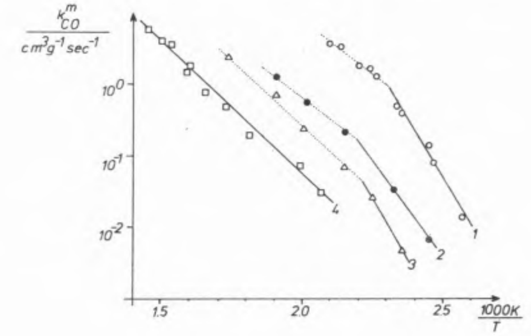

Fig. 1

Rate coeficient k^m_{CO} per unit of mass of catalyst for CO,oxidation. Numbers refer to catalysts as given in table 1

A change of the slope of log k^m vs. 1/T due to the influence of mass-transfer resistance in the porous agglomerates is clearly visible in many cases (dotted lines).

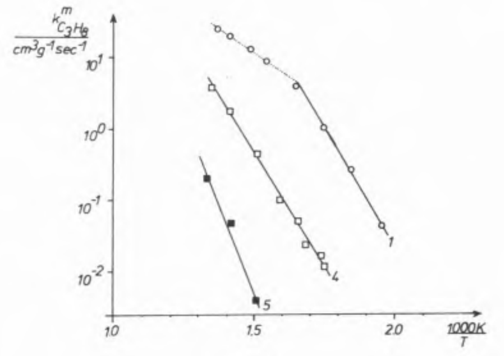

Fig. 2

Rate coefficients $k_{C_3H_8}$ per unit of mass of catalyst for C_3H_8 oxidation numbers of catalysts as in table 1.

Only rate data not influenced by mass-transfer resistance shall be discussed in the following paragraph.

4. DISCUSSION

Comparing the rate coefficient k^m per unit of mass one can see from figures 1 and 2 or from table 1 that the rate coefficient for the zeolite is roughly 2 orders of magnitude smaller than the rate coefficient for the oxides. Such a comparison does not appear very meaningful, however, since it was our purpose to investigate whether Cu-ions in the zeolite are as active catalytically as Cu-ions at the surface of an oxide. In any event the matter in the bulk of the oxide crystals can not participate in the catalytic reaction, whereas all the copper-ions in the zeolite are accessible to the reactants. It is expedient, therefore, to normalize the rate coefficients by dividing k^m by the number $\frac{n_{Cu}}{m_K}$ of mols of accessible copper-ions per gram of catalyst to obtain

$$k^{Cu} = k^{m} \cdot \frac{m_K}{n_{Cu}} \qquad (3)$$

which has the dimension $cm^3\ mol^{-1}\ sec^{-1}$ (like the rate coefficient of a bimolecular reaction) and is thus a rate coefficient per mol of copper accessible to the reactants.

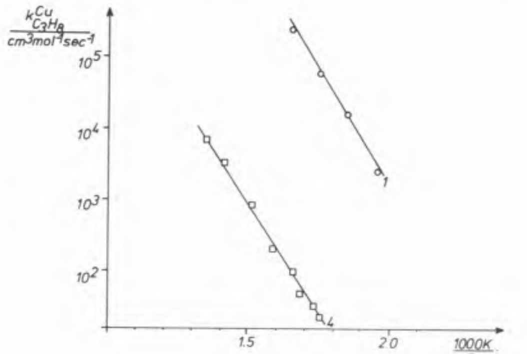

Fig. 3

Rate coefficient per unit amount of accessible copper for C_3H_8 –oxidation (catalysts numbered as in table 1)

For the zeolite the calculation of $\frac{n_{Cu}}{m_K}$ is straightforward; it has the value $5.27 \cdot 10^{-4}$ mol g^{-1}.

For the oxides one can compute $\frac{n_{Cu}}{m_K}$ from the surface area (Assuming a certain surface-area-equivalent per copper-ion) or one can obtain $\frac{n_{Cu}}{m_K}$ from the CO-chemisorption data, assuming that one molecule of CO is chemisorbed per copper-ion at the surface. Both methods yield approximately the same order of magnitude. E. g. for CuO one obtains $\frac{n_{Cu}}{m_K} = 6 \cdot 10^{-5}$ mol g^{-1} from the BET-surface area under the assumption that the copper-ions occupy 48 percent of the surface, whereas from CO-chemisorption one has $\frac{n_{Cu}}{m_K} = 1{,}7 \cdot 10^{-5}$ mol g^{-1}. Data of k^{Cu} in figure 3 and 4 are based on evaluation of $\frac{n_{Cu}}{m_K}$ for bulk oxides from CO-chemisorption. As can be seen from the figures the rate coefficient per accessible copper-ion is smaller in the zeolite by a factor of at least 1/300 for either reaction.

One may thus safely conclude that the catalytic activity of the copper-ion in the zeolite is practically negligible as compared to the oxides. This conclusion appears reasonable under the assumption that it is not the copper-ion alone which is responsible for the catalytic activity of these solids but that it is rather the reactivity of oxygen that matters. The exchange of oxygen between solid and gas and the participation of oxygen from the solid in the reaction have been shown to be essential in the mechanism of catalytic oxidation by Boreskov and his school (5, 6, 7); basically already Sabatier (8) had developed a similar concept about the nature of heterogeneous catalysis in general. Several authors (9, 10, 11) presented strong evidence that lattice oxygen is an intermediate in catalytic oxidation on oxides. Now the stability and reactivity of the oxygen linking silicon and/or aluminum in a zeolite should not depend strongly on the nature of the cation compensating the negative charge of the framework. Furthermore the oxygen can not be removed from the zeolite without destruction of the framework; there is no oxygen dissociation pressure over zeolites.

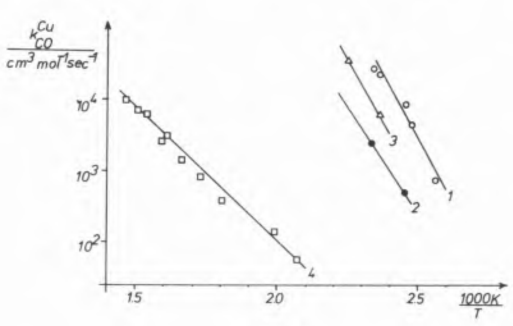

Fig. 4

Rate coefficient per unit amount of accessible copper for CO-oxidation (catalysts numbered as in table 1)

The situation is different for a simple binary or ternary oxide like CuO or $CuAl_2O_4$: here lattice-oxygen at the surface can be exchanged with O_2 in the gas-phase and it can be removed by reaction with an oxygen acceptor (e. g. CO) without destruction of the whole lattice. These compounds can therefore be characterized by a dissociation pressure and reactivity of oxygen. A simple closed sequence involving lattice oxygen, for example

$$O^{2-} + 2Cu^{2+} + CO \rightarrow CO_2 + 2Cu^{+}$$

$$2Cu^{+} + 1/2\,O_2 \rightarrow 2Cu^{2+} + O^{2-}$$

is thus possible on the surface of oxides like CuO or $CuAl_2O_4$ but not in the zeolite.

The experimental observation that the rate coefficient k^{Cu} per accessible copper-ion in the zeolite is less than 1 % of the value characteristic of the other oxides can be explained in this way.

The catalytic activity of the copper-exchanged zeolite per unit of mass is still higher by a factor of about 50 if compared to the parent material (Na Y without copper). One therefore must conclude that copper in the zeolite does have a catalytic activity which is not zero. Since the rate coefficient per accessible copper-ion is less than 1 % of that observed for CuO, we can, however, not exclude the possibility that the small residual activity of the copper exchanged zeolite is due to trace-amounts of CuO, which may have been formed by hydrolysis in the course of preparation and which can not be detected by X-ray diffraction.

The catalytic activities of the bulk oxides – as measured by the rate coefficient k^{F} per unit accessible surface area – are different by a factor of about 40. This spread is minor compared to the spread in k^{Cu} between bulk oxides and zeolite and it can be attributed to the differences in stability and reactivity of oxygen in different oxides (6, 12). Nevertheless we would like to point out the following observation.

If we consider k^{Cu} (the rate coefficient per accessible copper ion for the bulk oxides) and multiply it by number $Z(O^{2-}/Cu^{2+})$ of oxygen ions per copper-ion in the different solids, then we obtain figure 5.

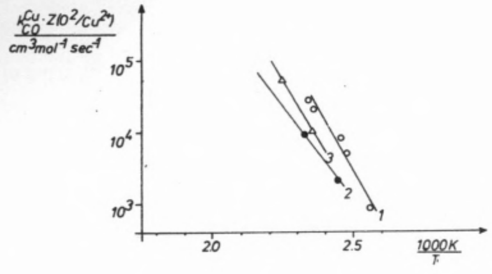

Fig. 5

Rate coefficient per unit amount of accessible copper multiplied by $Z(O^{2-}/Cu^{2+})$ for CO-oxidation Catalysts:

Catalysts : 1 CuO $Z(O^{2-}/Cu^{2+}) = 1$
2 $CuAl_2O_4$ » $= 4$
3 Cu_3TiO_5 » $= 1.67$

The product $k^{Cu} . Z(O^{2-}/Cu^{2+})$ does not spread by more than a factor of 2 for the different oxides. However, we would like to refrain from any further speculations about this result.

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RESUMO

Determinaram-se constantes de velocidade para a oxidação de CO e do C_3H_8 sobre vários óxidos de cobre e sobre a faujasite sintética permutada com cobre, em condições rigorosamente isotérmicas, eliminando todas as influências de transferência de massa.

Estas constantes de velocidade foram normalizadas em relação ao número de iões de cobre acessíveis, na superfície ou na rede cristalina dos sólidos. A constante de velocidade por ião de cobre acessível na zeolita é desprezável em face do valor correspondente determinado para a reacção superficial sobre os vários óxidos de cobre. Concluiu-se que a actividade catalítica destes compostos de cobre nas reacções de oxidação é devida à reactividade de iões oxigénio à superfície da rede cristalina.