

## Determination of the active phase structure in CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts by TPR kinetic model discrimination\*

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The results of temperature-programmed reduction with hydrogen of alumina supported copper oxide catalysts were used to find the best model describing the kinetics of Cu ions' reduction. On the basis of the rate determining step of this reaction the structure of copper oxide was revealed. This kinetic approach was compared with BET and UV-vis-DRS results. The catalytic activity of various copper oxide forms was tested in toluene combustion.

### 1. INTRODUCTION

Complex heterogeneous reactions can be effectively described by the kinetic models based on the following assumptions:

- 1) a process consists of subsequent steps (consecutive reactions),
- 2) one step is significantly slower than others and determines the rate of the overall process.

These models can be simplified if only one effect related to reagents' transfer or reaction initiation/propagation is taken into consideration. However, the simplified equations still involve many parameters connected with the structure of reactants such as the shape and size of particles. It has been found that the transformation of many models with similar main assumptions into a function of conversion vs. time  $f(\alpha)$  results in the same algebraic forms described widely in

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\*This article is dedicated to Professor Tadeusz Borowiecki on the occasion of his 65<sup>th</sup> birthday

literature. All of them include characteristic steps (factors) clearly limiting the reaction rate. Table 1 (column A) presents main isothermal model functions where the process kinetics is expressed with the equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where:  $\alpha$  – conversion vs. time (t), k – reaction rate constant involving specific model parameters.

The isothermal model functions can be used for description of polythermal processes with a linear temperature growth after the transformation into the following equation:

$$\frac{d\alpha}{dT} = \frac{k(T)}{\beta} f(\alpha) \quad (2)$$

where:  $\alpha$  – conversion vs. temperature (T),  $\beta$  – heating rate ( $\beta = dT/dt$ ),  $k(T)$  – reaction rate constant dependent on temperature, according to the Arrhenius equation.

The equation (2) is a theoretical basis for dynamic thermal analytical methods like thermogravimetry (DTA and DSC) as well as temperature-programmed methods (for instance TPR, TPOx, TPD).

In this paper we have used the TPR study for the description of the structural properties of copper oxide supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which is recognized as an active catalyst for the total oxidation of volatile organic compounds (VOCs) [1-3]. A new approach was the interpretation of TPR measurements by fitting their results to a wide range of known kinetic models. Assumptions of the best fitted models indicated the structure of the investigated catalysts.

## 2. MATERIAL AND METHODS

The oxide-type catalysts containing 2, 4, 6, 8 and 10 wt.% of copper were prepared by the incipient wetness method. 1 g of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Merck) support was impregnated with the proper amount of a Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O aqueous solution. The obtained precursors were dried at room temperature for 12 hours and then calcined at 550 °C (achieved at a heating rate of about 5 °C) for 8 hours in air.

Reducibility of the calcined samples was determined by means of the temperature-programmed reduction with hydrogen (TPR). Measurements were carried out in a quartz plug-flow differential microreactor using 2 vol.% H<sub>2</sub> in Ar as a reducing mixture at a flow rate 20 ml/min. A sample (20 mg) was placed on

quartz wool and reduced in the temperature range 100–1000 °C at a heating rate of 15 °C/min. The amount of consumed hydrogen was determined using a thermal conductivity detector (TCD) connected on-line to the reactor outlet after condensation of water at -40 °C.

For all the obtained samples, fitting TPR experimental points to model kinetic equations was performed by means of MATHCAD 14 software (Parametric Technology Corporation). The reactor mass balance was transformed into a linear function according to the following equation [4,5]:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} \quad (3)$$

(Table 1, column B). As a fitting quality criterion the analysis of statistical errors' parameters was conducted:  $R^2$  (the determination coefficient) and *StdErr* (standard error). A tested kinetic model was considered as most likely describing the mechanism of the catalysts' reduction, when its fitting was characterised by the largest  $R^2$  and simultaneously by the smallest standard error (*StdErr*). The fitting procedure was performed for 19 kinetic models, contained in Table 1, over two different conversion ranges:  $\alpha=0.05-0.95$  and  $0.005-0.995$ . The latter one allowed observing phenomena occurring at low conversions.

Low-temperature sorption of nitrogen was applied to determine total pore volume and specific surface area. Measurements were carried out at -196 °C by means of a ASAP 2010 sorptometer (Micromeritics). Before a test, a sample was outgassed at 350 °C under vacuum for 12 h. Copper species dispersion was investigated by UV-vis-DRS in the wavelength range of 190–900 nm using a Nicolet Evolution 600 spectrometer with resolution of 2 nm.

The prepared samples were tested as catalysts in the total oxidation of toluene. In a quartz flow microreactor 0.05 g of a catalyst was placed on quartz wool. A temperature in the catalyst bed was controlled by a thermocouple. Before catalytic tests, samples were outgassed in flowing air at 500 °C for 30 minutes and then cooled to the temperature of 200 °C, at which measurements started. Toluene was injected at a rate of 100  $\mu\text{l/h}$  by a syringe pump into a flowing air (50 ml/min). Three 15 minute analyses were carried out at 200, 250, 300, 350, 400, 450, 500 and 550 °C. Products were analysed using a gas chromatograph Varian Chrompack CP 3800 equipped with a column DB-1 (J&W Scientific, internal diameter – 0.32 mm, length – 30 m, thickness of stationary phase – 5  $\mu\text{m}$ ) and a TCD.

Tab. 1. Tested kinetic models of heterogeneous reactions [4,6].

Model number	Rate determining step	Model name	Model function f( $\alpha$ )	Model function g( $\alpha$ )
			A	B
1 (N=1) 2 (N=2) 3 (N=3) 4 (N=4)	Nucleation and growth	Avrami	$N \cdot (1-\alpha) \cdot \sqrt[N]{-\ln(1-\alpha)}$  N = 1, 2, 3 and 4 – dependent on the way of growth	$\sqrt[N]{-\ln(1-\alpha)}$ N = 1, 2, 3 and 4
5	Nucleation and growth	Prout-Tompkins	$\alpha \cdot (1-\alpha)$	$\ln\left(\frac{\alpha}{1-\alpha}\right)$
6 (N=1) 7 (N=2) 8 (N=3) 9 (N=4)		t <sup>n</sup>	$\frac{N}{k} \cdot \sqrt[N]{k \cdot (1-\alpha)^{N-1}}$ N = 1, 2, 3 and 4	$\sqrt[N]{\alpha}$ N = 1, 2, 3 and 4
10		Exponential	$\alpha$	$\ln(\alpha)$
11	Diffusion in particles	Parabolic	$\frac{1}{2\alpha}$	$\alpha^2$
12	Diffusion in particles	2D	$\frac{1}{-\ln(1-\alpha)}$	$(1-\alpha) \cdot \ln(1-\alpha) + \alpha$
13	Diffusion in particles	Jander	$\frac{3\sqrt[3]{(1-\alpha)^2}}{2 \cdot (1-\sqrt[3]{1-\alpha})}$	$\left(1-\sqrt[3]{1-\alpha}\right)^2$
14	Diffusion in particles	Ginstling-Brounshtein	$\frac{3/2}{\sqrt[3]{1-\alpha}-1}$	$1-\frac{2}{3} \cdot \alpha - \sqrt[3]{(1-\alpha)^2}$
15 (N=2) 16 (N=3)	No diffusion inside particles	Reaction on N-dimensional phase boundary	$\frac{N}{N-1} \sqrt[N]{1-\alpha}$ N=2 – surface contraction, N=3 – volume contraction	$1-\sqrt[N]{(1-\alpha)^{N-1}}$ N = 2, 3
17	Reaction	0 order	$(1-\alpha)^0$	$\alpha$
18	Reaction	1 <sup>st</sup> order	$(1-\alpha)$	$-\ln(1-\alpha)$
19	Reaction	2 <sup>nd</sup> order	$(1-\alpha)^2$	$(1-\alpha)^{-1} - 1$

### 3. RESULTS AND DISCUSSION

Profiles of temperature-programmed reduction with hydrogen for the alumina support and the copper oxide/alumina catalysts are shown in Figure 1.

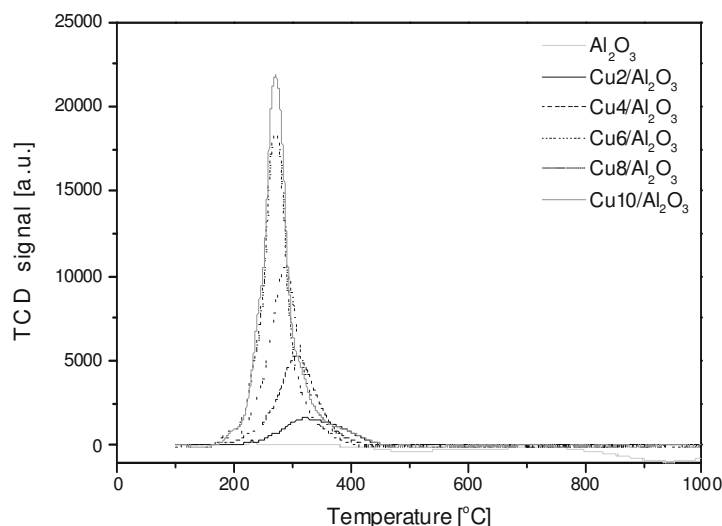


Fig. 1. TPR profiles of the alumina support and copper oxide/alumina catalysts.

The  $\text{Al}_2\text{O}_3$  support did not undergo reduction. Slight changes observed in the TPR profile of this material can be attributed to dehydroxylation of  $\text{Al}_2\text{O}_3$  surface. For all Cu-containing catalysts reduction with  $\text{H}_2$  was a one-step process. For the sample with the lowest copper loading 2 wt.%, reduction started above  $200^\circ\text{C}$  and achieved the rate maximum at ca  $320^\circ\text{C}$ . With increasing Cu loading the temperature of process beginning as well as of its maximum lowered and was equal 170 and  $270^\circ\text{C}$ , respectively, for the sample  $\text{Cu10}/\text{Al}_2\text{O}_3$ . One can claim that highly dispersed copper species interact strongly with the support and require higher temperatures to undergo reduction. The amount of consumed  $\text{H}_2$  suggests the entire reduction of  $\text{CuO}$  to metallic Cu for the tested samples.

The experimental results of temperature-programmed reduction with hydrogen obtained for the copper containing samples were fitted to model kinetic equations. Table 2 comprises the results of the fit procedure. For the narrower range of conversion (0.05–0.95) the model was regarded as describing the process properly if the determination coefficient was higher than 0.94 and the standard error lower than 0.23, whereas for the wider range of conversion (0.005–0.995) these values were equal 0.98 and 0.11, respectively.

The Avrami and n order reaction models are based on the assumption of the free access of gas reactants to a reacting solid. In the case of the Avrami model

nucleation occurs statistically in the whole volume of solid. For the  $n$  order reaction model a process takes place in all points of a reacting volume with the same probability. The unsatisfactory results of fitting to the other tested models, assuming limitations in gas migration into solid particles, confirm that the reacting gas has free access to the whole solid volume. Such free access of gas to the reacting solid can be obtained for very small particles or for the particles characterized by high porosity. The assumptions of the  $n$  order reaction model are fulfilled when particles are sufficiently small. In this case the pseudo-homogenous system can be considered. The Avrami model describes suitably solids consisted of large particles which ensure nucleation.

One can observe that a fitting quality decreases with the copper content for the 1<sup>st</sup> order reaction model. The opposite effect is visible in the fitting to the Avrami model ( $N=4$ ), where the best results were obtained for the Cu10/Al<sub>2</sub>O<sub>3</sub> sample. Basing on the structural assumptions of these models it can be concluded that at low Cu loadings copper oxide forms a highly dispersed monolayer on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. An increase in the copper content results in an appearance of highly porous CuO agglomerates.

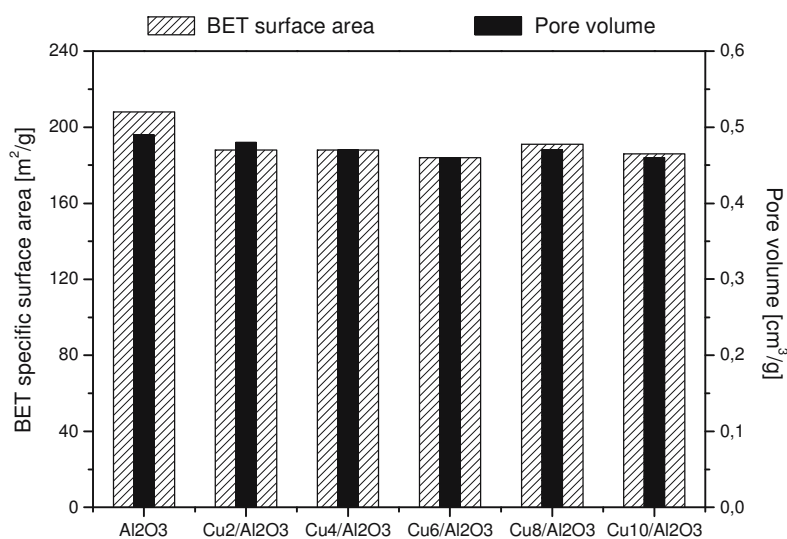


Fig. 2. BET specific surface area and pore volume for copper oxide/Al<sub>2</sub>O<sub>3</sub> catalysts.

Tab. 2. Fitting results.

Model number	Cu <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>			Cu <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>			Cu <sub>6</sub> /Al <sub>2</sub> O <sub>3</sub>			Cu <sub>8</sub> /Al <sub>2</sub> O <sub>3</sub>			Cu <sub>10</sub> /Al <sub>2</sub> O <sub>3</sub>		
	$\alpha=0.05-0.95$ R <sup>2</sup>	$\alpha=0.005-0.995$ StdErr	$\alpha=0.05-0.995$ R <sup>2</sup>	$\alpha=0.05-0.95$ R <sup>2</sup>	$\alpha=0.005-0.995$ StdErr	$\alpha=0.05-0.995$ R <sup>2</sup>	$\alpha=0.05-0.95$ R <sup>2</sup>	$\alpha=0.005-0.995$ StdErr	$\alpha=0.05-0.995$ R <sup>2</sup>	$\alpha=0.05-0.95$ R <sup>2</sup>	$\alpha=0.005-0.995$ StdErr	$\alpha=0.05-0.995$ R <sup>2</sup>	$\alpha=0.05-0.95$ R <sup>2</sup>	$\alpha=0.005-0.995$ StdErr	$\alpha=0.05-0.995$ R <sup>2</sup>
1	0.9104	0.5844	0.9659	0.238	0.948	0.3103	0.9345	0.572	0.9759	0.2152	0.5003	0.9822	0.2971	0.9941	0.109
2	0.9248	0.2974	0.9716	0.1218	0.9053	0.3701	0.9435	0.2915	0.9791	0.1095	0.9585	0.2548	0.9849	0.1535	0.054
3	0.9357	0.2018	0.9758	0.083	0.9185	0.251	0.9505	0.198	0.9817	0.0742	0.9633	0.1729	0.9861	0.0646	0.0358
4	0.9441	0.154	0.9791	0.0636	0.9289	0.1915	0.9561	0.1512	0.9838	0.0566	0.9671	0.132	0.9876	0.049	0.0267
5	0.7919	0.446	0.765	0.4595	0.6971	0.5233	0.6694	0.4926	0.6608	0.5244	0.5299	0.6057	0.512	0.7029	0.4739
6	0.8984	0.8066	0.929	0.4082	0.9494	0.6538	0.9623	0.3322	0.8984	0.9148	0.9207	0.4713	0.875	1.0443	0.713
7	err	err	err	err	err	err	err	err	err	err	err	err	err	err	err
8	0.8762	0.4088	0.9102	0.2069	0.9381	0.333	0.8794	0.4628	0.906	0.2375	0.8548	0.5268	0.8856	0.271	0.3585
9	0.8091	0.21	0.8473	0.1063	0.9034	0.1726	0.9285	0.0863	0.825	0.2368	0.8631	0.1207	0.7997	0.2681	0.1813
10	0.6889	0.1437	0.711	0.0727	0.8388	0.1192	0.8789	0.059	0.735	0.1614	0.7894	0.0817	0.7152	0.1818	0.1222
11	0.4721	0.1105	0.4028	0.0559	0.7075	0.0925	0.7075	0.0622	0.5828	0.1238	0.6552	0.0622	0.5841	0.1387	0.0927
12	err	err	err	err	err	err	err	err	err	err	err	err	err	err	err
13	0.9582	0.6082	0.9748	0.3002	0.9843	0.4264	0.9843	0.2158	0.9531	0.7354	0.9658	0.3843	0.9329	0.9083	0.7075
14	0.9376	0.6987	0.9607	0.3475	0.9725	0.5315	0.9815	0.2653	0.9329	0.824	0.9512	0.4245	0.9107	0.9798	0.7171
15	0.9324	0.342	0.9569	0.1698	0.9713	0.2563	0.981	0.1274	0.9286	0.4045	0.9485	0.2082	0.9053	0.4839	0.3588
16	0.914	0.369	0.9429	0.1844	0.9606	0.2873	0.9732	0.1431	0.9119	0.4292	0.9354	0.2201	0.8877	0.5029	0.3602
17	0.8762	0.4088	0.9102	0.2069	0.9381	0.333	0.9541	0.1683	0.8794	0.4628	0.906	0.2375	0.8548	0.5268	0.3585
18	0.9777	0.2296	0.987	0.1118	0.9949	0.1255	0.9957	0.0724	0.9742	0.286	0.9795	0.1583	0.9566	0.3863	0.344
19	0.6728	0.6559	0.8244	0.2864	0.646	0.762	0.7965	0.3397	0.7665	0.6582	0.8844	0.2735	0.8245	0.6	0.1396

The  $\gamma$ -alumina support is a mesoporous solid. An introduction of CuO on Al<sub>2</sub>O<sub>3</sub> did not change significantly porosity of the support. The total pore volume calculated by the one point method was equal 0.49 cm<sup>3</sup>/g for Al<sub>2</sub>O<sub>3</sub> and varied between 0.46-0.48 cm<sup>3</sup>/g for the supported samples as a result of the deposition of copper oxide in pores. Modification of alumina with copper oxide caused decreasing BET specific surface area from 208 m<sup>2</sup>/g for the pure support to 184–191 m<sup>2</sup>/g for Cu/Al<sub>2</sub>O<sub>3</sub> catalysts without any dependence on metal loading. The textural parameters of the studied samples are compared in Figure 2.

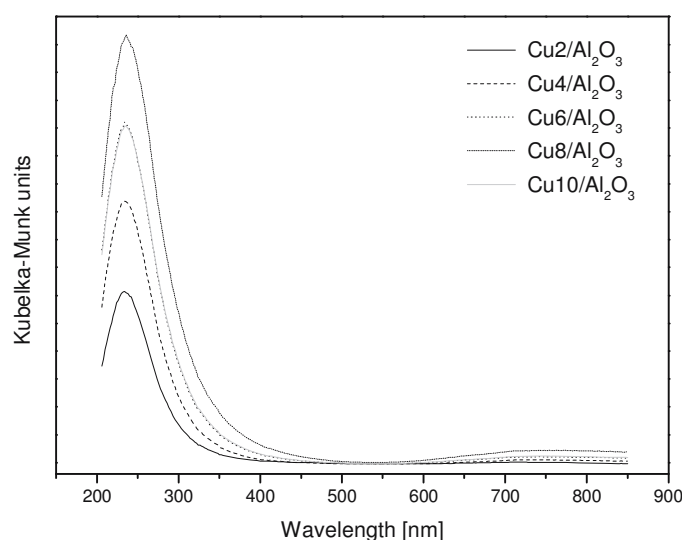


Fig. 3. UV-vis-DR spectra of alumina supported copper oxide catalysts.

Figure 3 presents UV-vis-DR spectra of the prepared alumina supported copper oxide catalysts. The main band observed at about 235 nm can be ascribed to charge transfer between isolated O<sup>2-</sup> and Cu<sup>2+</sup> ions in isolated copper oxide species [7]. An increase in the copper content caused a band shift to higher values typical of crystalline CuO, which suggests agglomerating copper oxide on the support surface. The formation of CuO crystallites at higher Cu loadings was also confirmed by appearance of a band at 750 nm typical of electron d-d transfer [8] and is in good agreement with conclusion based on the TPR kinetics study.



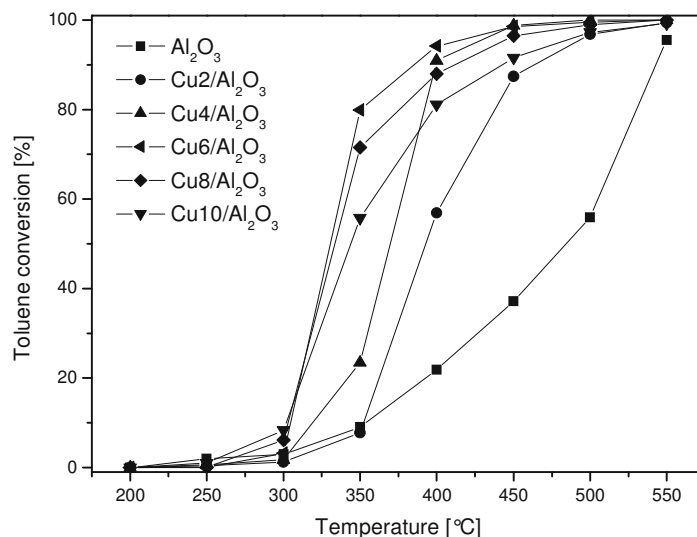
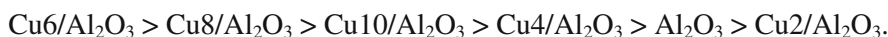


Fig. 4. Toluene conversion over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CuO/alumina catalysts.

The obtained samples were tested as catalysts in the total oxidation of toluene, their activity is shown in Figure 4. Toluene combustion, where the only detected product was carbon dioxide, started at 250°C and was completed at 500°C for the most active samples containing 4, 6 or 8 wt.% of copper. The Cu6/Al<sub>2</sub>O<sub>3</sub> sample exhibited the highest activity achieving ca 80% conversion at 350°C. To this temperature the descending activity sequence of the catalysts was following:



Above 350°C the activity of the Cu4/Al<sub>2</sub>O<sub>3</sub> sample increased and at 400°C was only slightly lower than the Cu6/Al<sub>2</sub>O<sub>3</sub> preparation. Additionally, at this temperature the Cu2/Al<sub>2</sub>O<sub>3</sub> catalyst began to catalyse toluene combustion much better than the support.

The Cu6/Al<sub>2</sub>O<sub>3</sub> sample underwent reduction by hydrogen with the maximum rate at 290°C, the temperature slightly higher than the most easily reducible samples Cu10/Al<sub>2</sub>O<sub>3</sub> and Cu8/Al<sub>2</sub>O<sub>3</sub> (Figure 1). The TPR of the Cu6/Al<sub>2</sub>O<sub>3</sub> sample occurred according to the Avrami model kinetics (N=4), where crystallite nucleation and growth is the rate determining step. These observations combined with the UV-vis-DRS results (Figure 3) prove the formation of highly dispersed CuO crystallites, which form active phase responsible for the high catalytic activity in the total oxidation of toluene.

#### 4. CONCLUSIONS

The interpretation of temperature-programmed reduction results based on the descriptions of recorded TPR curves by kinetic models allows to determine the structure of reducible catalysts' components. It was shown that such an approach is a useful method for studying CuO dispersion being a crucial parameter which influences the catalytic activity in the total oxidation of toluene. The obtained results were verified by UV-vis-DR spectroscopy which confirms the distribution of CuO on the alumina support proposed by TPR.

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#### CURRICULA VITAE



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