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Deactivation of supported copper catalysts for methanol synthesis

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Binary Cu/ZnO and Cu/Al_2O_3 as well as ternary Cu/ZnO/Al_2O_3 catalysts were investigated with respect to their catalytic activity and stability in methanol synthesis. In a rapid aging test, activity measurements were carried out in combination with the determination of the specific Cu surface area. A close correlation between the loss of catalytic activity and the decrease in specific Cu surface area was found due to sintering of the Cu particles. Differences in the deactivation behavior and the area–activity relationship of each catalyst system imply that the catalysts should be grouped in different classes.

KEY WORDS: deactivation; Cu/ZnO catalyst; Cu/ZnO/Al_2O_3 catalyst; Cu/Al_2O_3 catalyst; methanol synthesis; N_2O reactive frontal chromatography (N_2O RFC).

1. Introduction

Today, Cu-based supported catalysts are primarily employed in large-scale commercial processes such as methanol synthesis and the water–gas shift reaction. The improvement of purification methods for synthesis gas had made the low-pressure methanol synthesis over Cu/ZnO/Al_2O_3 catalysts available for practical application in the 1950s. Consequently, the lifetime of these Cu catalysts and their deactivation behavior are of great commercial importance to meet the requirements for optimal process conditions. Despite this fact, data with respect to the deactivation of Cu catalysts are sparsely published in the literature.

Industrial plant data [1,2] show a strong initial decrease in methanol formation, suggesting that the Cu-based catalysts undergo a relatively fast deactivation within the first hundreds of hours of operation. Laboratory tests confirm the fast initial deactivation in the first few hours [3]. Deactivation processes of Cu catalysts are supposed to occur mainly either due to thermal sintering of the metallic Cu particles or because of poisoning of the active Cu centers by sulfur or chlorine. An accelerated deactivation of the catalyst was particularly found in detailed kinetic studies when a CO-rich feed was used [4,5]. This evidence can be interpreted by over-reduction of Cu which causes an enhanced sintering of the metallic Cu particles.

In this contribution, we present long-term deactivation experiments, the results of a rapid aging test and the results of catalytic measurements, which have been obtained from dozens of catalysts in a standardized manner [6,7]. This procedure allows us to compare the deactivation behavior of Cu/ZnO, Cu/Al_2O_3, and Cu/ZnO/Al_2O_3, which is presented, to the best of our knowledge, for the first time. Based on these results a grouping of the catalysts into classes is suggested.

2. Experimental

The Cu catalysts were prepared by coprecipitation using aqueous solutions of $Cu(NO_3)_2$, $Zn(NO_3)_2$, and $Al(NO_3)_3$. Na_2CO_3 was employed as a precipitation agent. High-purity chemicals were used in order to avoid impurities of chlorine and sulfur. Good reproducibility and comparability of the catalysts was achieved by controlling the preparation conditions (i.e. the pH value, stirring velocity, duration of precipitation, aging, etc.) carefully. The calcination treatment was conducted in flowing air at 600 K for 3 h. Nitrogen physisorption was used to determine the BET surface area. The characterization results for the catalysts are summarized in table 1.

An amount of 100 mg catalyst of the 250–355 μm sieve fraction was reduced in a packed-bed microreactor in a mixture of 2.1% H_2 in He by raising the temperature from 300 to 513 K. The CuO contents of the catalysts were calculated from the H_2 uptakes during the reduction. The specific Cu surface areas were determined by the N_2O reactive frontal chromatography method [8] under moderate reaction conditions [9]. Kinetic data for a long-term test were collected over nearly 60 days during a detailed kinetic study. In general, the methanol synthesis activity was measured in synthesis gas under steady-state conditions (i.e. holding the temperature for 1.5 h) at ambient pressure and at temperatures of 473 and 493 K. A modified space velocity of $500\,\mathrm{Nml}\,(\mathrm{min}\,g_{\mathrm{cat}})^{-1}$ was chosen. The synthesis gas was composed of 14% He, 72% H_2, 4% CO_2, and 10% CO.

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Table 1
Composition and specific BET area of the coprecipitated Cu catalysts

Catalyst	Composition (mol%)	CuO content (wt%)	BET area of the fresh catalyst ($m^2\,g_{cat}^{-1}$)
Cu/ZnO	70/30	69.3	63.6
Cu/Al_2O_3	70/30	84.2	78.8
Cu/ZnO/Al_2O_3	65/28/07	67.8	53.7

The so-called rapid aging test consisted of a well-defined recurring sequence, which comprised the determination of the catalytic synthesis activity at 473 K and a special sintering procedure of the catalyst induced under severe reaction conditions. For the sintering procedure the synthesis gas flow was decreased to $10\,\mathrm{Nml\,min^{-1}}$ at a constant temperature. At the beginning of the experiment, the temperature was kept initially at 473 K. Then, the sintering temperature was successively increased by increments of 50 K. At each temperature step, the temperature was held for 8 h followed by the assessment of catalytic activity at 473 K. A temperature of 723 K was chosen as a maximum in order to effect more severe sintering conditions.

3. Results and discussion

Figure 1 displays the catalytic results measured under methanol synthesis conditions with a conventional Cu/ZnO/Al_2O_3 catalyst at 473 K during a period of nearly 60 days. The striking observation is the exponential decrease in activity over the first few days which is typical for Cu/ZnO/Al_2O_3 catalysts. A similar deactivation behavior was also found by other research groups in laboratory tests [1,5,10,11]. In our case, it should be mentioned that a detailed H_2 TPD study [12] was performed while the catalyst was on stream. Although the treatment for this experiment is known to be non-destructive [13], this long-term run should be regarded nevertheless as an experiment that rather qualitatively supports the literature results. We include the line in order to guide the eyes. Relatively large deviations of the data points from the line become obvious after a time on stream (TOS) of 15 days, indicating that the treatment prior to each data point of the actual activity measurement had a major impact on the methanol synthesis activity. Upon changing the gas atmosphere, a slow approach to steady state is known to occur for Cu catalysts in methanol synthesis [14–16]. A poisoning of the active centers can be excluded because of the high purity of the synthesis gas used. Since a rapid decline in the specific Cu surface area was recorded in the first few days, the thermal sintering of the metallic Cu particles completely accounts for the deactivation, as will be shown in the following (figure 4).

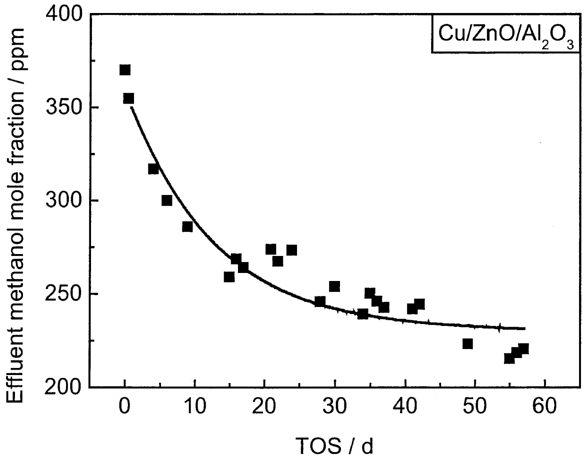

Figure 1. Deactivation behavior of a conventional Cu/ZnO/Al_2O_3 catalyst. Experimental conditions: $Q = 50\,\mathrm{Nml\,min^{-1}}$, $T = 473\,\mathrm{K}$, $p = 0.1\,\mathrm{MPa}$, $w_{cat} = 0.2\,\mathrm{g}$.

Figure 2 shows a direct comparison between the coprecipitated catalysts Cu/ZnO, Cu/Al_2O_3, and Cu/ZnO/Al_2O_3 in the rapid aging test which was performed subsequent to the reduction. Cu/ZnO/Al_2O_3 displayed the highest initial catalytic activity followed by Cu/ZnO. The ZnO-free binary Cu/Al_2O_3 catalyst had a rather low activity, but was quite stable for the first 75 h. In the first 10 h Cu/ZnO/Al_2O_3 and Cu/ZnO deactivated to a greater extent than Cu/Al_2O_3. Then, the activity leveled off during the subsequent 65 h. A strong decline in the catalytic activity was observed when the sintering temperature was increased. This behavior is in agreement with literature results and it is well known that under industrial operation temperatures should not exceed 573 K [17]. However, the striking result is that the differences in the deactivation behavior of the three catalysts are so strong. Since the decrease in the catalytic activity is particularly pronounced for the Al_2O_3-free Cu/ZnO catalyst, Al_2O_3 can be regarded as a stabilizer for the Cu crystallites preventing the Cu particles from sintering.

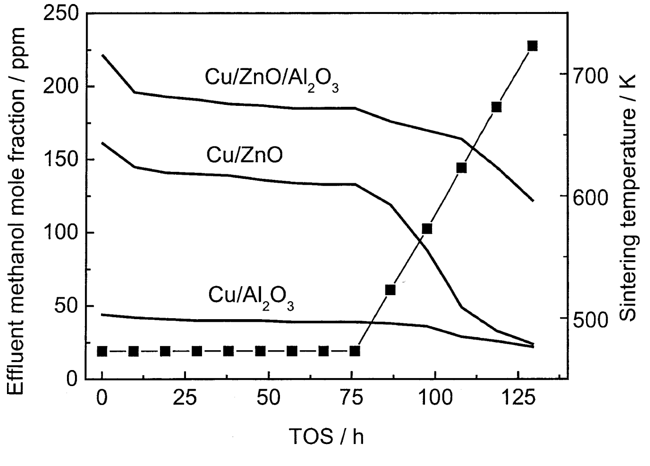

Figure 2. Deactivation behavior of the coprecipitated Cu/ZnO/Al_2O_3, Cu/ZnO, and Cu/Al_2O_3 catalysts. Experimental conditions: $Q = 50\,\mathrm{Nml\,min^{-1}}$, $T = 473\,\mathrm{K}$, $p = 0.1\,\mathrm{MPa}$, $w_{cat} = 0.1\,\mathrm{g}$.

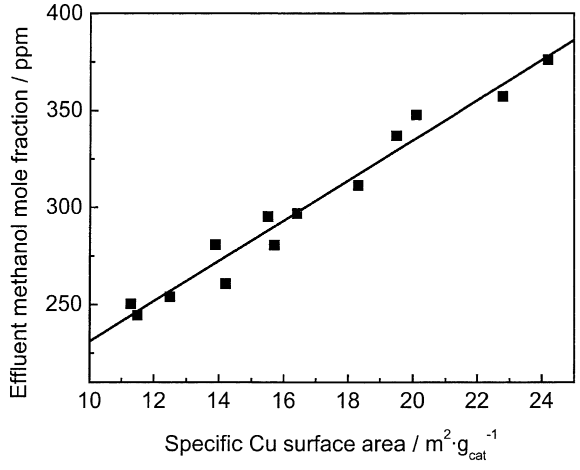

Figure 3. Methanol synthesis activity as a function of specific Cu surface area observed for various Cu/ZnO/Al_2O_3 catalysts. Experimental conditions: $Q = 100$ Nml min^{-1}, $T = 493$ K, $p = 0.1$ MPa, $w_{cat} = 0.2$ g.

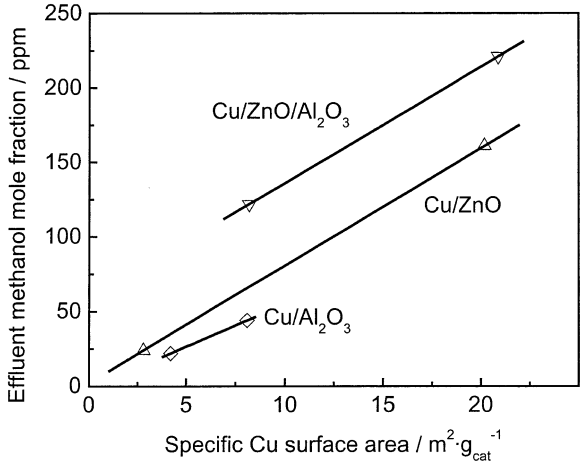

Figure 4. Initial and final methanol synthesis activities as a function of specific Cu surface area obtained with the coprecipitated Cu/ZnO/Al_2O_3 (▽), Cu/ZnO (△) and Cu/Al_2O_3 (◇) catalysts (figure 2). Experimental conditions: $Q = 50$ Nml min^{-1}, $T = 473$ K, $p = 0.1$ MPa, $w_{cat} = 0.1$ g.

Dozens of ternary catalysts were prepared by varying the Cu and ZnO content as well as the preparation conditions in order to observe a linear area–activity relationship which, in turn, would suggest a constant specific activity (activity/m^2_{Cu}). A linear correlation of the specific Cu surface area with the methanol synthesis activity within the class of Cu/ZnO/Al_2O_3 catalysts was found, indeed, as depicted in figure 3 for a couple of these catalysts. The findings agree well with literature results [18,19]. Nevertheless, the slight deviations from the depicted straight line, which is included to guide the eyes, suggest that additional effects, such as the strong synergy between Cu and ZnO, account for the difference in the catalytic activity. It has to be noted that the line extrapolated to 0 m^2 g$_{cat}^{-1}$ meets the ordinate at a value far above the origin.

Finally, a recurrent point in the literature is addressed, namely the discussion on grouping Cu-based methanol synthesis catalysts in classes with respect to the Cu area–activity relationship (cf. dispute published elsewhere [20–22]). An overall linear correlation between specific Cu metal area and methanol synthesis activity with minor deviations was reported in numerous studies [18,19,23,24]. The linear correlation included not only Cu/ZnO/Al_2O_3 catalysts but also Cu/MgO, Cu/Al_2O_3, Cu/MnO, and Cu/SiO_2. Nevertheless, it is still a much debated question as to whether the catalysts can be indeed grouped in a single class. Recently, Waugh [21] suggested re-examining their original data and reclassifying the catalysts in groups. In our study, the Cu surface areas after reduction and after the sintering experiment (figure 2) for each catalyst were determined. The straight lines depicted in figure 4 confirm the general assumption that a higher specific Cu surface area leads to a higher catalytic activity for each catalytic system. However, large differences between the three catalyst systems are obvious. These results also evidently demonstrate again that, in case of the ternary catalysts, the line extrapolated to 0 m^2 g$_{cat}^{-1}$ does not begin at the origin, whereas this is the case for Cu/ZnO and Cu/Al_2O_3. Furthermore, both ZnO-containing catalysts exhibited a large specific Cu surface area of about 20 m^2 g$_{cat}^{-1}$, but strongly differed in methanol synthesis activity. In general, Al_2O_3 is known to act as a structural promoter, inhibiting the thermal sintering of metal crystallites. Nevertheless, our experimental results also provided evidence of metal–support interactions, which, in turn, made possible the formation of more active Cu particles. The Cu/ZnO/Al_2O_3 catalyst had a specific Cu surface area of 8.2 m^2 g$_{cat}^{-1}$ determined after sintering, which is similar to the value for the Cu/Al_2O_3 catalyst (8.1 m^2 g$_{cat}^{-1}$) measured subsequent to reduction. Although both catalysts had nearly the same specific Cu surface area, the Cu/ZnO/Al_2O_3 catalyst exhibited a three to four times higher catalytic activity. Thus, our data clearly show that the Cu surface area is not the only factor controlling catalytic activity. In summary, it can be said that it is very reasonable to group Cu-based catalysts into different classes depending on their formulations, in which specific Cu area and catalytic activity are linearly correlated.

4. Conclusions

Cu catalysts were tested with respect to their catalytic activity and stability in methanol synthesis activity. The highly active ZnO-containing catalysts exhibited a pronounced deactivation behavior in the aging test, while the ZnO-free Cu/Al_2O_3 catalyst deactivated to a lesser extent. This deactivation behavior was attributed to the thermal sintering of the Cu crystallites. Al_2O_3 was found to be a structural promoter for Cu/ZnO catalysts inhibiting the thermal sintering of the Cu crystallites. Moreover, the Cu/ZnO/Al_2O_3 catalysts turned out to be far more active than the binary Cu/ZnO catalysts.

The catalysts had to be grouped in different classes to find systematic correlations between methanol synthesis activity and specific Cu surface area. A linear correlation between the catalytic activity and the specific Cu surface area was found within the class of ternary Cu/ZnO/Al_2O_3 catalysts. Deviations from this simple linear correlation can be attributed to additional factors which influence the microstructure of the Cu catalysts.

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