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Methanol Synthesis from CO_2 and H_2 on Cu/ZnO/Al_2O_3 – ZrO_2 Catalysts. Catalytic Activity and Adsorption of Reactants

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Effect of preparation method and substitution of Al_2O_3 by ZrO_2 on the adsorption of CO, CO_2, H_2O and methanol on the Cu/ZnO/Al_2O_3 – ZrO_2 catalysts as well as their activity in the synthesis of methanol from CO_2 and H_2 were investigated. The catalytic activity increases in the series: Cu/ZnO/Al_2O_3 obtained by co-precipitation < Cu/ZnO/Al_2O_3 < Cu/ZnO/Al_2O_3 – ZrO_2 obtained by the amorphous precursor (citric acid) method < Cu/ZnO/ZrO_2 obtained by the amorphous precursor (citric acid) method. It has been found that catalysts obtained by using citric acid as complexing agent show higher adsorption of methanol compared to water than the catalysts obtained by the co-precipitation. A partial substitution of Al_2O_3 by ZrO_2 evidently decreases the reversible adsorption of water and CO. A correlation between adsorptive and catalytic properties has been established. With increasing ratio of reversible CO_2/CO or CH_3OH/H_2O adsorption, an increase of the catalysts activity in the synthesis of methanol from CO_2 and H_2 is observed.

Key words: methanol synthesis, CO_2 hydrogenation, Cu based catalysts

Methanol is a key material for the C1 chemistry [1] and till today is obtained on a large scale by synthesis with the use of heterogeneous catalysts [2]. The Cu/ZnO/Al_2O_3 catalyst developed by ICI and employed since 1960-ies has proved particularly active in the low pressure synthesis of methanol from CO and H_2 [3]. A similar catalyst was patented in 1947 by Błasiak [4] and has been used for many years in the Polish chemical industry.

Błasiak and Kotowski [5] have also established a promoting effect of CO_2, consisting in an increase of the methanol formation rate by small admixtures of CO_2 into the synthesis gas. Further investigations have led to the conclusion that CO_2 participates directly in the methanol synthesis and that the rate of this process exceeds considerably that of the methanol formation from CO and H_2 [2]. A considerable interest

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in the process of the methanol synthesis from carbon dioxide and hydrogen has been observed recently. On one hand CO_2 constitutes a cheap and easily available source of carbon for the synthesis of methanol. On the other hand any method utilizing CO_2 is of interest, since it counteracts a growing global emission of this gas. It has been found recently that the rate of the methanol synthesis from CO_2 increases when Al_2O_3 is replaced by ZrO_2 in the classical $Cu/ZnO/Al_2O_3$ catalysts [6–13]. The promoting mechanism of ZrO_2 has not been, however, elucidated satisfactorily in spite of numerous investigations.

In the present study we have investigated the effect of preparation of the classical methanol synthesis catalysts of the $Cu/ZnO/Al_2O_3$ type on their catalytic activity in the synthesis of methanol from CO_2 and H_2 and on their adsorptive properties with regard to the reactants as well as the effect of a partial replacement of Al_2O_3 by ZrO_2 on the above properties of the catalysts. The main aim of the study was to look for a correlation between the adsorptive properties of the investigated catalysts and their catalytic activity.

EXPERIMENTAL

Preparation of the catalysts: The oxide precursors of the catalysts, containing CuO, ZnO and Al_2O_3 or ZrO_2, were obtained by decomposing the citrate complexes of the metals according to Courty [14]. The required amounts of nitrates of Cu, Zn, Al or Zr were added in small portions under intense stirring to 2M solution of citric acid (CA). The amount of citric acid used was calculated as 1/3 mole CA per gram-equivalent of each metal plus extra 2%. Reagent grade chemicals were used. The solution obtained was evaporated in a revolving flask *in vacuo* overnight at 363 K, then dried at 403 K for 8 h, then calcined on air for 1 h at subsequently 373, 473, 523 and 573 K. We have also investigated the industrial catalyst obtained by the co-precipitation of hydroxides of Cu, Zn and Al from the solution of their nitrates using solution of NaOH according to [4]. Prior to the adsorption measurements the oxide precursors were reduced *in situ* at 473 K in flowing mixture of 5 vol% H_2 in He (prior to measurements of the active surface of copper and XRD) or statically in hydrogen under the pressure of *ca*. 5.3 kPa (prior to the gravimetric and BET measurements). High purity gases from BOC Gases (UK) were used in which the impurities did not exceed 10 ppm. The specific surface area of the oxide precursors and of the reduced catalysts was determined with the BET method, using argon at 77.5 K. The phase composition of the oxide precursors were determined with XRD using DRON-2 diffractometer, CuK_α radiation and Ni filter. The reduction of the precursors was carried out in a high temperature chamber with a gas flow and the diffraction patterns were recorded after cooling down the catalyst to room temperature in He atmosphere.

Gravimetric measurements of the reactant adsorption: Adsorption of the methanol synthesis reactants on the reduced catalysts was investigated in a static equipment using S3DV Sartorius vacuum microbalance of the 0.1 μg sensitivity, connected to a standard vacuum system (dynamic vacuum of 10^{-4} kPa). A membrane manometer – 122A Baratron from MKS Instruments of the 10^{-3} kPa sensitivity was used to measure the pressure of the adsorbates. The samples of the catalysts (0.5 g) after catalytic tests were evacuated at 523 K prior to the measurements, then were cooled down to 473 K and reduced in hydrogen under 30–40 Tr until a constant mass (about 1 hour). Water formed was removed from the system by a cold trap, cooled with liquid nitrogen. After reduction the samples were evacuated at 473 K for 24 h in order to desorb the water from the catalyst surface.

Determination of the active surface of copper: The active surface of copper in the reduced catalyst was determined by reactive adsorption of N_2O at 363 K, according to the method described in [2 and references contained therein]. The measurements were carried out in a flow micro-reactor of stainless steel-length 18 cm, inner diameter 1.3 cm. Approximately 0.5 g of a catalyst, after catalytic test, was reduced at

473 K during 3 h and cooled to 363 K. Then 100 μl of N_2O pulses were injected until the reaction was completed. Amount of reacted N_2O was determined by mass spectrometer (VG/Fisions Quartz 200D). In calculations it has been assumed that the reoxidation of the surface copper follows the equation:

$$Cu_{(s)} + N_2O_{(g)} = Cu_2O_{(s)} + N_2(g) \quad (1)$$

and 1 m^2 of elemental copper corresponds to 6.1 μmol O_2.

Measurement of the catalyst activity: A tubular, flow, high-pressure, fixed-bed reactor of an inner diameter of 2.5 cm and operating pressures of up to 10 Mpa, made of stainless steel, was used. The bed consisted of 216 g of the catalyst mixed with the same amount of an inert material (porcelain). The catalyst was reduced in a stream of diluted hydrogen (10% H_2 in N_2 at 473 K under atmospheric pressure for 15 h and then activated in the mixture of the reactants by raising the temperature by steps of 30° between 473 and 623 every 2 h. The preliminary experiments have shown that during the heating of the catalyst between 473 and 623 K the specific activity (calculated per kg of the catalyst) first increases then decreases. The increase in the activity reflects the desorption of water from the catalysts surface and unblocking of the active centres, whereas the decrease of the activity observed at a higher temperature results from the sintering of the catalyst and the agglomeration of the dispersed metal copper, which was formed during the reduction of the catalyst at 473 K. The observed changes of the activity have a continuous character, which points to a participation of the same copper centres in the reaction within the temperature range investigated. A similar tendency was observed by Nitta *et al.* for the Cu-ZnO-ZrO_2 catalyst [12]. The catalysts, which were subjected to the thermal treatment described above, show a constant activity at 493 K, at which the catalytic measurements were performed. The catalytic activity determination was carried out under the following conditions: pressure 8 Mpa, temperature 493 K, space velocity of the reactants flow GHVS 1000–10000 h^{-1}, composition of the reactant mixture $H_2/CO_2 = 3$. After leaving the reactor, the gases were decompressed to the atmospheric pressure and cooled to separate the liquid fraction composed exclusively from water and methanol. The condensate, as well as the remaining gaseous products, were analysed chromatographically by the FID detector and the Megaborg DB-5 30 m column together with the TCD 4 m column filled with silica gel.

RESULTS AND DISCUSSION

Characterization of the catalysts investigated: Phase composition of the catalysts investigated prior to the reduction and after the reduction in hydrogen, as well as their specific surface areas determined with the BET method, are given in Table 1. The specific surface areas of all catalysts are similar. A slight increase of the surface area after reduction is observed and is due to formation of dispersed copper. The determined active surfaces of copper after the reduction in hydrogen, as well as after the reduction in hydrogen and subsequently in carbon monoxide are given in the last column of Table 1. The TPD measurements, which will be subject of a separate publication [15], have indicated that the catalysts after reduction contain considerable amounts of adsorbed water, which may be removed by the reaction with CO. The action of carbon monoxide after the reduction in hydrogen aimed indeed the removal of water, which could block the surface of copper and reduce the values determined. As one can see, the effect of the reduction in carbon monoxide is insignificant, which indicates that water only marginally blocks the surface of copper and hence is bound mainly to oxides surface (ZnO, Al_2O_3). Replacing a part of Al_2O_3 with ZrO_2 diminishes the active surface of copper, in contrast change in the preparation method does not affect the value determined.

Table 1. Characterization of studied catalysts.

catalysts	chemical composition of the catalysts [weight %]								specific surface area of the catalysts $m^2 (g\ cat)^{-1}$		copper surface area after reduction $m^2 (g\ cat)^{-1}$	
	before reduction				after reduction				before reduction	after reduction	H_2	H_2/CO
	CuO	ZnO	Al_2O_3	ZrO_2	Cu	ZnO	Al_2O_3	ZrO_2				
I. $CuO/ZnO/Al_2O_3$	65.6	26.5	7.9	–	60.4	30.5	9.1	–	20.3	20.5	12.8	13.2
II. $CuO/ZnO/Al_2O_3$	65.6	26.5	7.9	–	60.4	30.5	9.1	–	18.8	22.4	13.7	14.9
III. $CuO/ZnO/Al_2O_3/ZrO_2$	65.8	26.3	3.95	3.95	60.6	30.3	4.6	4.5	19.6	24.8	8.8	10.4
IV. $CuO/ZnO/ZrO_2$	65.8	26.3	–	7.9	60.6	30.3	–	9.1	19.5	23.4	6.1	–

I. Błasiak's type catalysts obtained by co-precipitation.
II–IV. Obtained by complexes of citric acid.

Adsorption of the reactants: Two types of adsorption were observed for all adsorbates investigated: a strong adsorption irreversible at a given temperature and a weak reversible one. The weakly adsorbed fraction can be removed from the surface by reducing pressure at a given temperature. The magnitude of the strong adsorption does not in general depend on the pressure of the adsorbate, thus, it constitutes a constant component adding up to the weak adsorption which increases with increasing pressure. Therefore, the following measurement procedure was employed: The adsorbate was introduced under maximum pressure for a given measurement. Then, after the equilibrium had been reached, the pressure was reduced stepwise producing the desorption of weakly adsorbed gases. The amount remaining at the surface after evacuation of the sample under high vacuum was assumed to be a measure of the strong adsorption. Isotherms of the reversible adsorption of CO, CO_2, H_2O and methanol on the catalysts investigated at 473 K are shown in Fig. 1. The isotherms of the reversible adsorption can be described with a good accuracy by the Langmuir equation:

$$n = n_\infty \frac{bp}{1 + bp} \tag{2}$$

where n is the amount adsorbed under pressure p, n_∞ – maximum amount adsorbed (extrapolated for $p \to \infty$), b – an adsorption coefficient, which is a measure of the binding energy between an adsorbate molecule and the catalysts surface. The correlation coefficients for the adsorption isotherms of H_2O, CH_3OH and CO exceed 0.99, the correlation is slightly worse for the CO_2 adsorption (the correlation coefficients are about 0.97). The values of the maximum reversible adsorption (n_∞) as well as the adsorption coefficients b for the reactants of the methanol synthesis, as determined from (2), are given in Table 2. The presented data agree with the results of our previous investigations of the adsorption on the $Cu/ZnO/Al_2O_3$ catalysts [16], as well as with other authors [17–22]. The results contained in Table 2 indicate that the reactant adsorption proceeds similarly on catalysts I and II, which have the same composition and differ only in the method of preparation. For both groups a small and similar adsorption of CO and CO_2 is observed as well as by far larger adsorption of water and methanol. Differences, however, appear for the last two adsorbates: the Błasiak type catalyst I adsorbs more water than methanol, in contrast to catalyst II of the same composition, obtained by citric precursor method, which adsorbs more methanol than water. Catalyst II is characterized also by higher adsorption coefficients, compared to catalyst I. One can conclude that a similar number of weak adsorption centres of CO and CO_2 are present at the Błasiak type catalyst surface, whereas the number of strong adsorption centres of water and methanol is considerably higher. This points that adsorption of water and methanol proceeds competitively on the same surface centres of the catalyst, which agrees well with our earlier results [23]. Roberts and Griffin observed the analogous effect of blocking the adsorption centres of methanol by pre-adsorbed water on the surface of ZnO [20]. Change in the catalyst composition, consisting in replacing Al_2O_3 with ZrO_2 (catalysts III and IV), leads to a decrease in adsorption of all the reactants, but brings about a parallel systematic increase of the ratios of adsorption CO_2/CO and CH_3OH/H_2O.

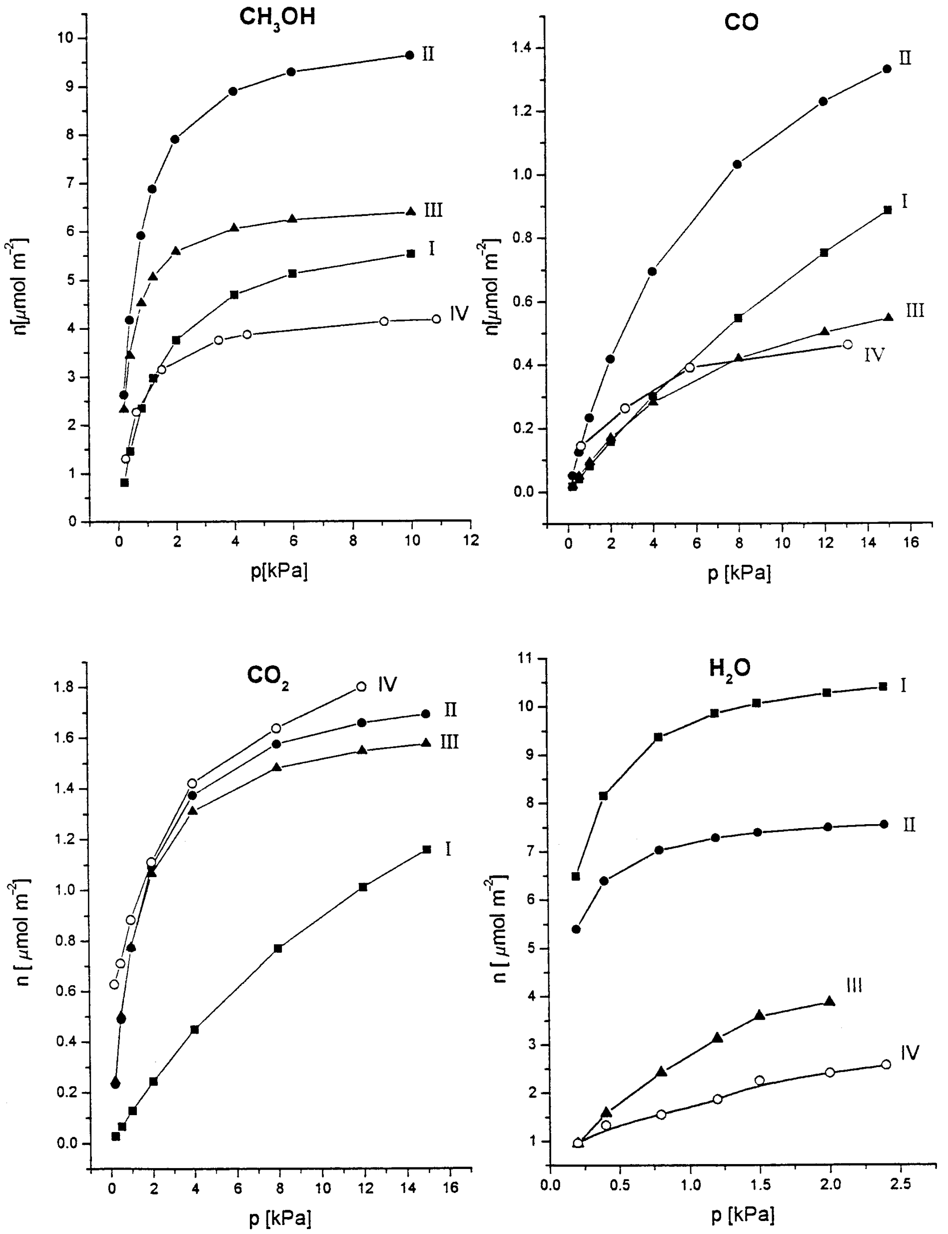

Figure 1. Reversible adsorption of methanol synthesis reactants on $Cu/ZnO/Al_2O_3$-ZrO_2 catalysts at 473 K. Symbols of the catalysts (I, II, III and IV) as in Table 1.

Table 2. Parameters of reversible adsorption of methanol synthesis reagents for studied catalysts at 473 K.

catalysts	adsorbate	maximal reversible adsorption (for θ =1) μmol m^{-2}	adsorption coefficient kPa^{-1}	strong adsorption μmol m^{-2}
I. Cu/ZnO/Al_2O_3	CO	3.0	0.028	0.49
	CO_2	2.7	0.050	0.68
	H_2O	11.0	7.2	2.2
	CH_3OH	6.27	0.75	0.98
II. Cu/ZnO/Al_2O_3	CO	2.0	0.133	0.31
	CO_2	1.85	0.72	0.22
	H_2O	7.8	11.1	2.82
	CH_3OH	10.18	1.74	2.38
III. Cu/ZnO/Al_2O_3/ZrO_2	CO	0.83	0.129	1.36
	CO_2	1.70	0.84	0.46
	H_2O	2.4	2.80	3.94
	CH_3OH	6.62	2.71	1.68
IV. Cu/ZnO/ZrO_2	CO	0.54	0.46	0.10
	CO_2	1.85	1.46	0.20
	H_2O	2.83	3.82	0
	CH_3OH	4.40	1.69	0.95

Catalytic activity and adsorptive properties of the catalysts: Main reactions which occur during the hydrogenation of CO_2 are:
a) the direct synthesis of methanol

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O \tag{3}$$

b) the reaction reverse to the water vapour conversion (RWGS)

$$CO_2 + H_2 \Leftrightarrow CO + H_2O \tag{4}$$

CO, thus formed, may also react with hydrogen yielding methanol. Reaction (3) is exothermic and hence the methanol synthesis for thermodynamic reasons should be carried out at a lowest temperature possible. The relationship between the methanol yield and the space velocity of the reactants (GHSV) is shown for the catalysts investigated in Fig. 2. As one can see, the Błasiak type catalyst I obtained by the co-precipitation is the least active. Catalyst II of the same composition, but obtained by the citric acid complexing method, exhibits higher activity. Substitution of ZrO_2 for Al_2O_3 brings about an increase in the yield of methanol.

The hydrogenation of CO_2 along the reaction (4) is unfavourable for the methanol synthesis and its progress should be limited to a minimum. This can be attained by modifying the adsorption centres in such way that the ratio of CO_2 to CO concentrations on the catalyst surface (Θ_{CO2}/Θ_{CO}) is possibly high. A high value of this ratio points to a shift in the equilibrium of the surface reaction (4) to the substrates (CO_2, H_2). On the other hand, the rate of the methanol synthesis should be proportional to the concentration of the active centres on which methanol is formed. According to the current views on the reaction mechanism, these are the centres on which formate surface complexes, most probably anchored at Cu and Zr atoms or Cu and Zn, are formed [24–27]. Methanol adsorption can be taken as a measure of the concentration of these

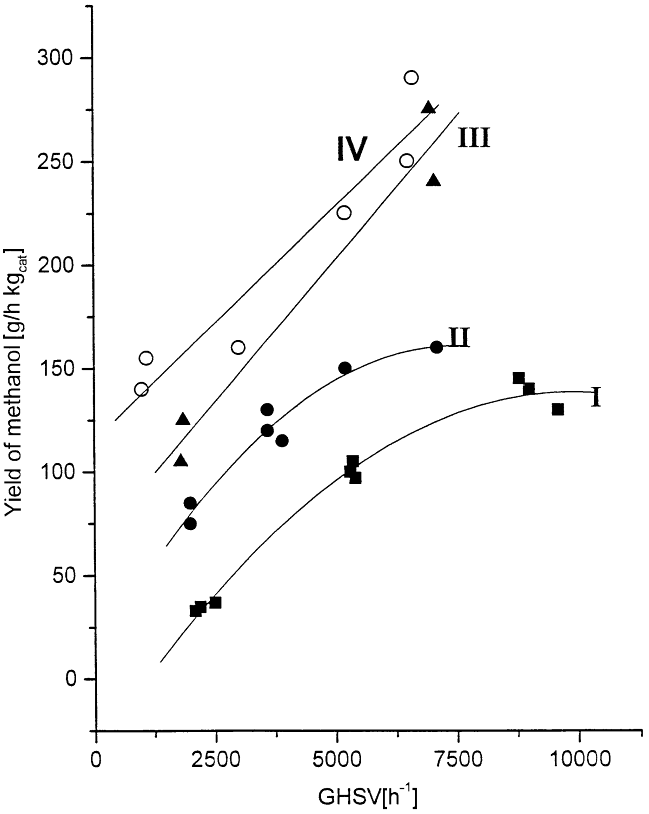

Figure 2. Yield of methanol as a function of GHSV for Cu/ZnO/Al_2O_3-ZrO_2 catalysts, p = 8 Mpa, T = 493 K, $H_2/CO_2 = 3$. Symbols of the catalysts (I, II, III and IV) as in Table 1.

centres. Our previous investigations on co-adsorption of the methanol synthesis reactants on the Cu/ZnO/Al_2O_3 catalyst have shown, however, that adsorption of methanol and water compete with each other [23]. The adsorbed water blocks a part of the surface centres responsible for the synthesis of methanol, which leads to a decrease of the reaction rate. This is confirmed also by the present results shown in Table 2. Change of the preparation method of the Cu/ZnO/Al_2O_3 catalyst from the co-precipitation to complexing with citric acid brings about a marked increase of the adsorption of methanol and an equivalent decrease in the adsorption of water. The substitution of ZrO_2 for Al_2O_3 diminishes the overall concentration of the above centres, but brings about a parallel increase of the ratio of methanol to water adsorption, which points to a decreased blocking of the active centres by water. The synthesis of methanol from CO_2 and H_2 is favoured by both factors discussed above, *i.e.* minimizing the hydrogenation of CO_2 along the reaction (4) and limiting the effect of blocking the centres active in the reaction by water. It should be thus expected that the yield of methanol in the synthesis from CO_2 and H_2 should correlate with the adsorptive properties of the catalysts expressed by a synthetic parameter "the reagent adsorption factor" (RAF)

$$\mathrm{RAF} = (\Theta_{CO_2}/\Theta_{CO})\,(\Theta_{CH_3OH}/\Theta_{H_2O}) \qquad (5)$$

where Θ are maximum coverages of the catalyst surface by the respective reactants when $p \to \infty$. RAF is a dimensionless quantity, which gives information on fractions of a given population of the active centers occupied by respective reactants.

The relationship between the yield of methanol and the adsorption factor RAF is shown in Fig. 3. As one can see, a marked correlation exists between adsorptive properties and catalytic activity in the series of the methanol synthesis catalysts investigated. Since the adsorptive properties of the catalysts investigated were varied both by modifying their preparation method and altering the catalyst composition, it can be assumed that the correlation established is of a general character and is not characteristic merely of the series of preparations studied. To verify this hypothesis further investigations of the broader population of the methanol synthesis catalysts are required. In particular investigations of the effect of the catalyst activation process on its catalytic activity and adsorption of the reactants are planned.

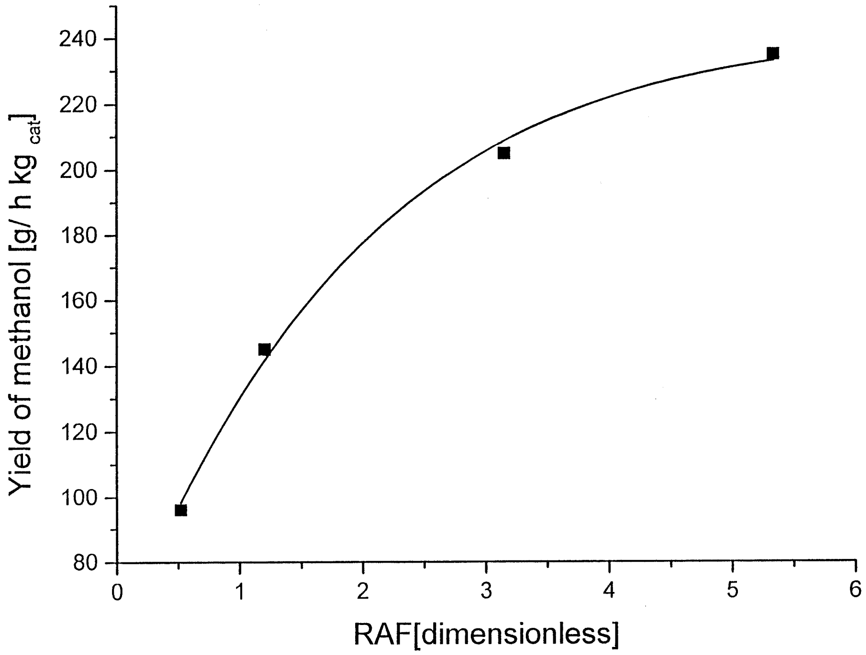

Figure 3. Correlation between catalytic activity and adsorptive properties factor (RAF) for $Cu/ZnO/Al_2O_3$-ZrO_2.

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