Influence of synthesis parameters on physicochemical properties of CuO/ZrO₂ catalysts

Michał Śliwa¹ · Katarzyna Samson¹

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Abstract

CuO/ZrO₂ (Cu/Zr) catalysts were synthesized via the co-precipitation method using Na₂CO₃ as the precipitating agent. The influence of CuO/ZrO₂ ratio, aging time and calcination temperature of catalyst precursors on the physicochemical properties of Cu/Zr catalysts was studied. The catalysts were characterized by means of N₂ adsorption, temperature-programmed reduction, N₂O dissociative chemisorption, X-ray diffraction, inductively coupled plasma optical emission spectrometer and CO₂ temperature-programmed desorption. It was found that only for samples calcined at 550 °C the ZrO₂ was present as the tetragonal phase (t-ZrO₂). In the case for samples which were aged for 1 h, metallic copper dispersion (D_{Cu}) does not depend on calcination. On the other hand, for non-aged catalysts a decrease in D_{Cu} is observed with higher temperature of calcination. The temperature corresponding to maximum reduction rate (T_{max}) decreases for samples with higher D_{Cu} . The contribution of weak basic site is the highest for catalysts which were aged, whereas for non-aged catalysts mainly medium basic sites dominate on the surface.

Keywords CuO/ZrO₂ catalysts · Tetragonal ZrO₂ · Metallic copper dispersion

Introduction

Cu/ZrO₂ catalysts are commonly used in various catalytic reactions, e.g., methanol synthesis (Denise and Sneed 1986; Samson et al. 2014), steam reforming of methanol (Oguchi et al. 2005; Ritzkopf et al. 2006), water gas shift reaction (Águila et al. 2008), selective catalytic reduction of NO_x (Okamoto et al. 1998) and hydrogenation of levulinic acid to γ -valerolactone (GVL) (Ishikawa et al. 2017). The influence of zirconia polymorphism in Cu/ZrO₂ catalysts plays an important role both in the physicochemical catalyst properties and catalyst activity. It has been shown that monoclinic (m-ZrO₂) and tetragonal (t-ZrO₂) ZrO₂ exhibit different acid–base properties (Morterra et al. 1994; Bolis et al. 1998; Zhao et al. 2002) and surface hydroxyl

group concentration (Pokrovski et al. 2001; Ardizzone and Bianchi 1999). The phase of ZrO₂ being present in catalysts has influence on catalyst reducibility (Zhao et al. 2004) and CO₂ adsorption capacity (Pokrovski et al. 2001). Additionally, ZrO₂ prevents Cu particles from sintering during catalytic activity which enhances copper dispersion (Agrell et al. 2003; Shimokawabe et al. 1990).

Cu/ZrO₂ catalysts containing monoclinic ZrO₂ (m-ZrO₂) exhibit higher selectivity to methanol than Cu catalysts deposited on tetragonal ZrO₂ (t-ZrO₂) (Jung and Bell 2002). The effect of ZrO₂ phase on product selectivity is also visible in the ethanol dehydrogenation over Cu/ZrO₂ catalysts. In this case, the highest rate of ethyl acetate formation is observed for Cu/m-ZrO₂ catalyst and results from high oxygen mobility from the bulk m-ZrO₂ phase to copper species. On the other hand, Cu deposition on t-ZrO₂ leads to by-product formation (Sato et al. 2013). Maruya et al. (2000) came to the same conclusion that increased fraction of m-ZrO₂ in the catalyst results in higher rate of isobutene formation from the H₂/CO mixture. In methanol steam reforming, it has been stated that interaction of copper oxide with amorphous ZrO₂ (am-ZrO₂) is one of the factors responsible for high stability and activity of Cu/ZrO₂ catalysts (Koeppel et al. 1992).

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✉ Michał Śliwa
ncsliwa@cyf-kr.edu.pl

¹ Jerzy Haber Institute of Catalysis and Surface Chemistry,
Polish Academy of Sciences, Niezapominajek 8,
30-239 Kraków, Poland

The objective of the conducted work was to evaluate the influence of synthesis conditions on the physicochemical properties of CuO/ZrO₂ catalysts. Particularly, the influence of the composition of the catalyst, aging time and calcination temperature on catalyst basicity, reducibility and copper dispersion was determined.

Experimental

CuO/ZrO₂ (Cu/Zr) catalysts were synthesized via the coprecipitation method at pH 7, using Na₂CO₃ as the precipitating agent with nominal composition (wt%) Cu/Zr = 70/30 (70Cu/Zr) and Cu/Zr = 50/50 (50Cu/Zr). Cations in the form of nitrates and Na₂CO₃ were simultaneously added dropwise into the beaker containing 100 mL of deionized water at 60 °C. During the precipitation, the mixture was vigorously stirred. For non-aged samples, the precipitates were subsequently washed by five times centrifugation and dried at 100 °C. For aged catalysts, prior to washing, the precipitates were kept in mother liquor for 1 h. After drying, samples were calcined at 300 °C, 350 °C and 550 °C. Catalysts which were aged for 1 h are denoted as 70Cu/Zr/X_1 h, while non-aged catalysts are denoted as 70Cu/Zr/X and 50Cu/Zr/X where X is the temperature of calcination.

X-ray diffraction patterns (XRD) were recorded on Bruker AXS D505 with CuK α radiation. The analysis was performed between 0.6° and 90° 2 θ range with accumulation time 5 s. The mean crystallite sizes of CuO and ZrO₂ were calculated based on Rietveld refinement.

CO₂ temperature-programmed desorption (CO₂-TPD) measurements were carried out in quartz-fixed bed flow reactor connected online to a mass spectrometer (QMG 220 PRISMA PLUS). Signals: $m/z = 2$ (H₂), $m/z = 44$ (CO₂), $m/z = 40$ (Ar) were monitored during TPD. Prior to TPD run, the sample (100 mg) was reduced in 5% H₂/Ar flow (30 mL/min) at 250 °C for 2.5 h. Next, the reactor was cooled down to room temperature (RT) and pulses (250 μ L) of 5% CO₂/Ar were introduced until saturation. Then, the sample was flashed with He flow (40 mL/min) for 0.5 h until obtaining stable CO₂ line. TPD was done from RT to 400 °C with $\Delta T = 10^\circ/\text{min}$ under He flow (40 mL/min).

N₂O dissociative chemisorption (Shuyten et al. 2008) was performed using the same setup line as for CO₂-TPD. The sample (100 mg) was reduced in the same manner as for CO₂-TPD. The pulses (100 μ L) of N₂O were introduced at 90 °C under He flow (30 mL/min) until reoxidation was completed. Signals: $m/z = 44$ (N₂O) and $m/z = 28$ (N₂, N₂O) were monitored. The metallic copper surface area (S_{Cu}) was calculated assuming atomic copper surface density of 1.47×10^{19} Cu atoms/m², corresponding to 6.1×10^{-6} O₂ mol/m² for the stoichiometry Cu/O = 2. The Cu metal dispersion (D_{Cu}) was measured as percentage ratio of surface

Cu moles from N₂O chemisorption to the total moles of Cu present in the catalysts. Additionally, Cu⁰ particle size (P_{Cu}) was determined using the following equation:

$$P_{\text{Cu}} \text{ (in nm)} = (\text{wt\% Cu loading} \times 6000) / (100 \times d \times S_{\text{Cu}}),$$

where d is the density of Cu metal (8.92 g/cm³) and wt% Cu loading is based on ICP. N₂O chemisorption experiments were repeated few times for each sample resulting in relative standard deviation (RSD) below 1%.

Temperature-programmed reduction with hydrogen (H₂-TPR) was carried out on Chembet-3000 (Quantachrome). The hydrogen consumption was monitored with TCD detector. For typical H₂-TPR run, the sample (25 mg) was placed in quartz U-shaped tube reactor and conditioned at 100 °C under He flow (30 mL/min) for 1.5 h. Next, the sample was cooled down to RT under He flow and the H₂-TPR experiment was performed in 5% H₂/Ar (30 mL/min) in the temperature range RT – 850 °C ($\Delta T = 10^\circ/\text{min}$). For quantitative H₂-TPR studies, a four point calibration curve was prepared using appropriate amounts of CuO standard (Aldrich) mixed with Al₂O₃ in wt% ratio = 1:2, 1:4, 1:16, 1:12 (mechanical mixture). The calibration covered the hydrogen consumption range corresponding to TPR analysis. The H₂-TPR and CO₂-TPD profiles were deconvoluted into Gaussian peaks. Deconvolution was performed in Origin 2018 Pro software.

The BET surface area was measured with nitrogen adsorption at – 196 °C on Quantachrome Autosorb-1. Prior to measurements, samples were degassed for 18 h at 150 °C to remove adsorbed water and other surface impurities. The pore size distribution (PSD) profiles were obtained by the BJH method from the desorption branch.

The elemental analysis was performed by inductively coupled plasma optical emission spectrometer (ICP-OES). For ICP-OES analysis, 100 mg of sample was dissolved in a mixture of HNO₃/H₂O.

Results and discussion

The XRD patterns of the CuO–ZrO₂ precursors (Fig. 1) show diffraction peaks which are assigned only to the malachite phase. As can be seen from XRD patterns for samples after calcination, the XRD signals for the malachite phase disappeared and the precursors were fully decomposed to oxides. In the case of calcined samples, the CuO XRD peaks (signals at $2\theta = 32.5^\circ, 35.5^\circ, 38.7^\circ, 48.9^\circ, 53.4^\circ, 58.3^\circ, 61.6^\circ, 66.4^\circ, 68.1^\circ, 72.5^\circ, 75.0^\circ, 82.9^\circ$) sharpened and their intensity increased with a calcination temperature for all samples, meaning that there was an increase in the samples' crystallinity. The Rietveld refinement (Table 1) confirmed that the crystallite sizes of CuO got bigger for samples which were calcined at higher

Fig. 1 XRD patterns of catalyst precursors: 70Cu/Zr_1 h (1), 70Cu/Zr (2) and 50Cu/Zr (3)

temperature. This is due to sintering which proceeds at higher temperatures. The estimated values of the CuO crystallite sizes for samples calcined at 550 °C are the biggest and are equal to 17.7 nm, 19.8 nm and 23.6 nm for 70Cu/Zr/550_1 h, 70Cu/Zr/550 and 50Cu/Zr/550, respectively. For samples calcined at 300 °C and 350 °C, only the CuO phase is visible. In this case, diffraction peaks for ZrO₂ phase are not observed suggesting that the ZrO₂ phase is present as the amorphous phase (Rhodes and Bell 2005) or its particles are too small to be detected by means of XRD (Figs. 2, 3, 4).

On the other hand, diffraction peaks ascribed to t-ZrO₂ appear for samples calcined at 550 °C ($2\theta = 30.5^\circ$, 50.9° and 60.7°). For non-aged catalysts, which were calcined at 300 °C and 350 °C, the increase in the ZrO₂ content had only minor influence on the CuO crystallite size. Nevertheless, the crystallite sizes of t-ZrO₂ phase increase with ZrO₂ content, reaching a value of 14.4 nm for 50Cu/

Fig. 2 XRD patterns of 70Cu/Zr/300_1 h (1), 70Cu/Zr/350_1 h (2) and 70Cu/Zr/550_1 h (3). Black diamond suit—CuO phase

Zr_550. Additionally, this catalyst possesses the biggest CuO crystallite size (23.6 nm) among all synthesized samples (Fig. 4).

The N₂ adsorption–desorption isotherms are presented in Figs. 5, 6 and 7 for aged 70/Cu/Zr samples, non-aged 70/Cu/Zr samples, and non-aged 50/Cu/Zr samples, respectively. All synthesized catalysts exhibit typical type V and type III isotherms with an H3-type hysteresis loop according to IUPAC classification (Thommes et al. 2015). The observed shape of the hysteresis loop is characteristic for samples possessing both mesoporous and macroporous (Basahel et al. 2016).

The BJH pore size distribution (PSD) profiles and BJH cumulative pore volume are presented in Figs. 8, 9 and 10 for aged 70Cu/Zr samples, non-aged 70Cu/Zr samples, and non-aged 50Cu/Zr samples, respectively. PSD profiles for all synthesized catalysts show maxima in the 5–20 nm mesoporous range, meaning no microporosity. For aged catalysts, the BJH cumulative pore volume (Fig. 8B) is

Table 1 Physicochemical properties of the synthesized catalysts

Catalyst	P_{Cu}^a /nm	D_{Cu}^a /%	S_{Cu}^a /m ² /g	BET/m ² /g	CuO ^b /nm	ZrO ₂ ^b /nm
70Cu/Zr/300_1 h	62	1.7	6.0	79	14.5	–
70Cu/Zr/350_1 h	62	1.7	6.0	57	16.7	–
70Cu/Zr/550_1 h	64	1.6	5.9	31	17.7	12.8
70Cu/Zr/300	68	1.5	5.5	59	14.2	–
70Cu/Zr/350	72	1.4	5.2	48	15.2	–
70Cu/Zr/550	97	1.1	3.9	18	19.8	13.2
50Cu/Zr/300	81	1.3	3.3	42	14.1	–
50Cu/Zr/350	71	1.5	3.8	32	15.5	–
50Cu/Zr/550	108	1.0	2.5	18	23.6	14.4

^aBased on dissociative N₂O chemisorption

^bBased on Rietveld refinement

Fig. 3 XRD patterns of 70Cu/Zr/300 (1), 70Cu/Zr/350 (2) and 70Cu/Zr/550 (3). Black diamond suit—CuO phase

Fig. 4 XRD patterns of 50Cu/Zr/300 (1), 50Cu/Zr/350 (2) and 50Cu/Zr/550 (3). Black diamond suit—CuO phase

0.18 cm³/g, 0.18 cm³/g, 0.17 cm³/g for 70Cu/Zr/300_1 h, 70Cu/Zr/350_1 h, and 70Cu/Zr/550_1 h, respectively, no matter the sample calcination temperature. On the other hand, the drop in BET specific surface area (Table 1) with increased temperature of calcination was observed for these samples. This is due to the changes in the PSD for aged samples which were calcined at different temperatures (Fig. 8A). As the temperature of calcination increases, the number of pores decreases but the diameter of pores become larger. For 70Cu/Zr/550_1 h the increase in the numbers of pores with diameter higher than 18 nm is visible which results in the value of the BJH cumulative pore volume being close to values for 70Cu/Zr/300_1 h and 70Cu/Zr/350_1 h. For

Fig. 5 N₂ adsorption–desorption isotherms for: A—70Cu/Zr/300_1 h, B—70Cu/Zr/350_1 h, C—70Cu/Zr/550_1 h

Fig. 6 N₂ adsorption–desorption isotherms for: A—70Cu/Zr/300, B—70Cu/Zr/350, C—70Cu/Zr/550

Fig. 7 N₂ adsorption–desorption isotherms for: A—50Cu/Zr/300, B—50Cu/Zr/350, C—50Cu/Zr/550

Fig. 8 The BJH pore size distribution (A) and BJH cumulative pore volume (B) for 70Cu/Zr/300_1 h (black square lines), 70Cu/Zr/350_1 h (red circle lines), and 70Cu/Zr/550_1 h (blue up-pointing triangle lines)

Fig. 9 The BJH pore size distribution (A) and BJH cumulative pore volume (B) for 70Cu/Zr/300 (black square lines), 70Cu/Zr/350 (red circle lines), and 70Cu/Zr/550 (blue up-pointing triangle lines)

Fig. 10 The BJH pore size distribution (A) and BJH cumulative pore volume (B) for 50Cu/Zr/300 (black square lines), 50Cu/Zr/350 (red circle lines), and 50Cu/Zr/550 (blue up-pointing triangle lines)

Fig. 11 CO₂-TPD profiles for blank TPD (1), 70Cu/Zr/300_1 h (2), 70Cu/Zr/350_1 h (3) and 70/30-C/Z-550-1(4). Signal—black line, cumulative curve—red line, deconvoluted peaks used for quantification—blue line, additional deconvoluted peak—green line

both non-aged 70Cu/Zr/300 and 70Cu/Zr/350 samples, the BJH cumulative pore volume is the same and equal to 0.18 cm³/g. On the other hand, non-aged 70Cu/Zr/500 catalyst has slightly lower value of BJH cumulative pore volume (0.15 cm³/g). In this case, the visible maxima in PSD plots (Fig. 9A) above 18 nm are of lower intensity and there is no maximum in the PSD profile in the 3–5 nm range in comparison with 70Cu/Zr/550_1 h. Thus, this samples exhibits low BET specific surface area (18 m²/g).

The increase in zirconia content for non-aged samples (Fig. 10) leads to lower cumulative pore volume (0.15 cm³/g, 0.12 cm³/g and 0.12 cm³/g for 50Cu/Zr_300, 50Cu/Zr_350 and 50Cu/Zr_550, respectively) and flattened pore size distribution in comparison with non-aged 70Cu/Zr catalysts. The observed decrease in porosity results from catalysts sintering and corresponds with XRD analysis which shows an increase in crystal sizes of CuO with higher temperature of calcination.

The surface basicity of the catalysts was evaluated with CO₂-TPD. The obtained results for three series of catalysts are presented in Figs. 11, 12 and 13. To confirm that the observed low-temperature desorption CO₂ signals originate solely from the CO₂ introduced via pulses prior to the desorption stage, the blank TPD test was performed for samples calcined at 300 °C (line 1 in Figs. 11, 12 and 13). For the blank TPD test, the sample was only reduced and later heated up in the same manner as during typical TPD, meaning no CO₂ was introduced. In this case, a maximum of CO₂ signal was observed above 350 °C, which was higher than the calcination temperature of the samples (i.e. 300 °C) used in blank TPD tests. This suggests that the visible CO₂ signal from the precursor decomposition above 300 °C during TPD. The XRD analysis did not reveal any reflexes assigned

Fig. 12 CO₂-TPD profiles for blank TPD (1), 70Cu/Zr/300 (2), 70Cu/Zr/350 (3) and 70Cu/Zr/550 (4). Signal—black line, cumulative curve—red line, deconvoluted peaks used for quantification—blue line, additional deconvoluted peak—green line

Fig. 13 CO₂-TPD profiles for blank TPD (1), 50Cu/Zr/300 (2), 50Cu/Zr/350 (3) and 50Cu/Zr/550 (4). Signal—black line, cumulative curve—red line, deconvoluted peaks used for quantification—blue line, additional deconvoluted peak—green line

to the malachite phase in the samples after calcination at 300 °C, meaning that the amount of undecomposed precursor, being still present in this catalysts, is below the limit of detection by the conventional X-ray diffraction method. For blank TPD tests (line 1 in Figs. 11, 12 and 13), the lowest amount of CO₂ is released for the aged catalyst. On the other hand, it can be seen that for non-aged catalysts, the amount of CO₂ being released upon heating is higher. A further increase of CO₂ amount was observed for the catalysts with a higher content of ZrO₂ (50Cu/Zr).

For CO₂-TPD runs, all catalysts show broad desorption profile ranging from RT – 400 °C. In the case of catalysts calcined at 300 °C and 350 °C, the signal from CO₂

desorption overlaps with the signal assigned to CO₂ which is released due to malachite phase decomposition in the temperature range above 300 °C. To have better insight into the desorption process, the TPD profiles were deconvoluted. The observed peak maxima were assigned accordingly to the areas related with CO₂ desorption from weak (50–150 °C), medium (150–240 °C) and strong (> 240 °C) basic sites. It is known (Gao et al. 2013; Díez et al. 2000) that weak basic sites are related with the surface hydroxyl group, medium basic sites with Zr⁴⁺–O^{2–} pairs, and the strong basic sites with the low-coordination oxygen anions.

The quantitative analysis of deconvoluted TPD profile shows (Table 2) that aged catalysts possess the lowest concentration of surface basic sites. Additionally, the highest contribution (C) of weak basic sites is observed for these catalysts. In the case of the catalysts which were aged for 1 h, the increase in the temperature of calcination influences the formation of medium basic sites and lowering the contribution of weak basic sites. For non-aged catalysts, medium basic sites dominate and in this case for catalysts calcined above 350 °C strong basic sites are also formed according to the CO₂-TPD profiles.

For non-aged catalysts calcined at 550 °C, there is decreased amount of CO₂ desorbed (Tot_{des}) compared to the amount of CO₂ introduced (Tot_{ads}) via pulses during the adsorption stage. One can say that in this case, some fraction of CO₂ is still bonded to the surface of these catalysts while heating up to 400 °C. This means that for aged catalysts calcined at 550 °C, the contribution of strong basic sites is higher than that calculated as well as total basicity. For other catalysts, the observed discrepancies between the amount of adsorbed CO₂ and desorbed CO₂ are due to experimental error related mainly with difficulties in integration of long-tailed CO₂ pulse responses.

Average Cu⁰ particle size (P_{Cu}) and metallic copper dispersion (D_{Cu}) obtained via N₂O pulse chemisorption are presented in Table 1. The value for CuO crystal sizes based on Rietveld refinement is much lower than P_{Cu} for all synthesized catalysts. This means that during reduction at 250 °C prior to the introduction N₂O pulses, the Cu particles sinter. Especially, surface Cu particles are more prone to agglomerate and sinter due to the low Hüttig temperature of copper (Twigg and Spencer 2001). According to Table 1, it is clear that the presence of small CuO crystallites in the catalyst leads to a lower value of P_{Cu} and higher D_{Cu} . On the other hand for aged catalysts, the increase of the CuO crystal size with temperature of calcination does not result in change in the values of P_{Cu} and D_{Cu} , whereas the loss of BET specific surface area for these catalysts is pronounced. According to Li et al. (2001), copper dispersion depends on two competitive phenomena. First is the segregation of CuO from the ZrO₂ matrix, which is undergone when transformation of amorphous ZrO₂ proceeds, leading to a higher

Table 2 Catalyst basicity—quantitative analysis

Catalyst	Weak sites		Medium sites		Strong sites		$Tot_{des}^a/\mu\text{mol}$	$Tot_{ads}^b/\mu\text{mol}$	Basicity ^a / $\mu\text{mol/g}$
	$T_{max}/^\circ\text{C}$	$CI/\%$	$T_{max}/^\circ\text{C}$	$CI/\%$	$T_{max}/^\circ\text{C}$	$CI/\%$			
70Cu/Zr/300_1h	90	49	165	51	—	—	4.2	3.5	43
70Cu/Zr/350_1h	88	39	153	61	—	—	3.7	3.2	37
70Cu/Zr/550_1h	81	39	145	61	—	—	3.5	3.8	36
70Cu/Zr/300	74	16	162	84	—	—	6.1	5.7	60
70Cu/Zr/350	72	11	162	72	332	17	5.3	5.1	51
70Cu/Zr/550	85	29	169	71	—	—	3.0	4.8	27
50Cu/Zr/300	67	7	183	93	—	—	5.6	4.9	55
50/Cu/Zr/350	68	7	200	65	330	28	5.2	5.5	52
50Cu/Zr/550	105	11	194	76	350	13	5.3	7.0	52

T_{max} temperature of maximum desorption rate for deconvoluted peaks, C basic site contribution, Tot_{des} total amount of CO_2 desorbed during TPD, Tot_{ads} total amount of CO_2 adsorbed

^aBased on TPD signals up to 350 °C

^bBased on consumed CO_2 pulses

copper surface area. The monoclinic to tetragonal phase transformation starts at 400 °C at the surface regions and then proceeds into the bulk as the temperature of calcination is increased. The XRD analysis for aged samples did not reveal any reflexes of m- ZrO_2 . Nevertheless, at the early stage of ZrO_2 phase transformation, the concentration in the surface region of m- ZrO_2 was low. Therefore, the absence of m- ZrO_2 in the subsurface region cannot be ruled out, since crystallites of ZrO_2 might be less than 4 nm in size which is below the detection limit of the XDR technique. The second factor is the increase in copper particle size with increased temperature of calcination, resulting in lowering the surface copper area. In the case of aged samples, both stabilization effect of ZrO_2 and copper particle growth can take place simultaneously, leading to constant values of surface copper area and copper dispersion.

For catalysts which were not aged, the increase in P_{Cu} and decrease in D_{Cu} were observed with increase in the temperature of calcination. In this case, the surface copper stabilization is not observed. The addition of ZrO_2 leads to catalysts of higher value of P_{Cu} which is in agreement with the CuO crystal sizes determined by XRD.

The reducibility of synthesized catalysts was investigated by means of temperature-programmed reduction with hydrogen (H_2 -TPR) and the results are presented in Figs. 14, 15 and 16. For all catalysts, the reduction stoichiometry (Cu/H_2) is slightly above one, meaning that all CuO is reduced to metallic copper during TPR. The observed differences in H_2 consumption (Table 3) are related with differences in concentration of CuO in the obtained catalysts. The ICP analysis shows that for aged 70Cu/Zr/, the CuO/ ZrO_2 ratio (wt%) is 7.3, while for non-aged 70Cu/Zr/550 and 50/Cu/Zr, the ratio (wt%) is 3.8 and 1.6, respectively. The observed differences are related with lower value of ZrO_2 concentration in synthesized samples. The maximum reduction rate

Fig. 14 H_2 -TPR profiles for 70Cu/Zr/300_1 h (1), 70Cu/Zr/350_1 h (2) and 70Cu/Zr_550_1 h (3)

(T_{max}) occurs at lower temperature for all catalysts than for standard CuO ($T_{max} = 338$, not shown), resulting from copper–zirconia interaction. Based on the broad shape of the TPR profile, one can say that at least two copper species are present in the obtained catalysts. To distinguish between different copper species, the TPR signals were deconvoluted into two or three Gaussian peaks in all cases. The number of deconvoluted peaks can suggest that there are at least two or three types of CuO phases in the synthesized samples.

Only minor changes can be seen in TPR peaks for aged and non-aged catalysts which were calcined at 300 °C and 350 °C. In this case, the position of the deconvoluted peaks was similar. On the other hand, the increase of calcination temperature to 550 °C results in significant changes in the TPR profile shapes for all samples. The deconvoluted

Fig. 15 H_2 -TPR profiles for 70Cu/Zr/300 (1), 70Cu/Zr/350 (2) and 70Cu/Zr/550 (3)

Fig. 16 H_2 -TPR profiles for 50Cu/Zr/300 (1), 50Cu/Zr/350 (2) and 50Cu/Zr/550 (3)

maxima shift toward higher reduction temperature. This effect is more pronounced for the non-aged catalyst which exhibits the deconvoluted peak at 294 °C and 307 °C for 70Cu/Zr/550 and 50Cu/Zr/550, respectively. Peaks which occur at higher temperature are attributed to the reduction of bulk CuO species, whereas the low-temperature peaks are due to dispersed and well-dispersed CuO species (Zhan et al. 2014). The observed changes in the deconvoluted peak numbers suggest that the ratio of dispersed and well-dispersed CuO species changes due to the synthesis condition.

The observed changes in the TPR profiles and in the value of $T_{\max}$ result from copper dispersion. With increased metallic copper dispersion, there is pronounced decrease in the

Table 3 Reducibility of synthesized catalysts

Catalyst	$T_{\max}/^{\circ}\text{C}$	H_2 consumption/ $\text{mmol H}_2/\text{g}$	Reduction stoichiometry
70Cu/Zr/300_1 h	258	10.0	1.1
70Cu/Zr/350_1 h	267	10.5	1.2
70Cu/Zr/550_1 h	262	10.1	1.1
70Cu/Zr/300	257	8.9	1.0
70Cu/Zr/350	272	9.0	1.0
70Cu/Zr/550	293	9.8	1.1
50Cu/Zr/300	271	6.8	1.1
50Cu/Zr/350	269	6.7	1.1
50Cu/Zr/550	307	7.1	1.1

Fig. 17 Influence of metallic copper dispersion (D_{Cu}) on maximum reduction rate ($T_{\max}$)

value of $T_{\max}$ (Fig. 17). For aged catalysts, copper dispersion is the same, regardless of the temperature of calcination. This means that there is the same ratio of surface copper species to bulk copper species in these catalysts. Therefore, only minor changes in the value of $T_{\max}$ are observed. The increased dispersion means that there is a higher ratio of surface copper species to bulk copper species. The surface copper species are reduced at lower temperature, while reduction of bulk copper species requires higher temperature. Considering this, the segregation of copper species and their stabilization on the surface of the catalysts facilitate the reduction.

Conclusions

The influence of aging time, temperature of precursor calcination and catalysts' composition on ZrO_2 polymorphism, catalyst reducibility, basicity and copper dispersion was investigated. It can be stated that the above-mentioned catalyst parameters are closely related with the synthesis method. There is an observed stabilization effect of surface copper species for aged CuO/ZrO_2 catalysts, which is due to the subsurface ZrO_2 transformation from tetragonal to monoclinic. For non-aged catalysts, this effect is not present and a decrease in copper dispersion is observed with increased temperature of calcination. This is in agreement with the TPR profile. The value of T_{max} practically does not change for aged catalysts, no matter the temperature of calcination. This means that aged catalysts calcined at 300 °C, 350 °C and 550 °C possess the same surface copper species concentration. In the case of non-aged catalysts, the increased content of ZrO_2 results in increased temperature of reduction. This is due to lower copper dispersion, meaning that a bulk of the copper species dominates. One can say that increased temperature of precursor calcination leads to higher basicity of catalyst surface, which can play a crucial role in catalytic reactions involving CO_2 .

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Compliance with ethical standards

Conflict of interest On behalf of all the authors, the corresponding author states that there is no conflict of interest.

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