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Genesis of catalysts for methanol synthesis

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The experimental data and hypotheses on the nature and structural peculiarities of the precursors and the active state of Cu–Zn-containing catalysts for methanol synthesis are considered.

1. Introduction

Catalytic methanol synthesis from CO, CO_2 and hydrogen is a key step of natural gas conversion to valuable organic compounds and polymers. The current world production of methanol is over 100 million tons per year. Although the activity of copper-containing catalysts in methanol synthesis has been known since the 1920s,[1] Zn–Cr catalysts were used for a long time, while Cu-containing catalysts only remained an object of laboratory research. In the 1960s, a technological breakthrough was made by ICI, which patented the process over a Cu–Zn–Cr catalyst[2] and later a Cu–Zn–Al catalyst and revealed coprecipitation as its production method.[3] This invention allowed one to reduce the synthesis temperature from 400 to 230 °C and the synthesis pressure from 200 to 50–100 bar. Due to the lower temperature, the selectivity of the process was dramatically improved. Starting from this point, the Cu–Zn-containing methanol synthesis catalysts have been studied intensively. In this research area, 20–30 articles per year were published in the 1990s, whereas this number increased to 60–70 articles per year in 2010–2013.

The catalysts that are exemplified in the patent[3] by ICI had the cationic composition Cu : Zn : Al = 60 : 30 : 10 and 75 : 19 : 6. Coprecipitation was performed from a nitrate solution by sodium carbonate at 85 °C and constant pH 7 and gave hydroxycarbonate, which was filtered off, washed and dried. Calcination of the precipitate at 300 °C gave oxide powder, which was pelletized and loaded to a catalytic reactor. The active state of the catalyst was achieved by reductive treatment in hydrogen or synthesis gas at 250 °C. This catalyst preparation procedure and the catalyst composition remained generally unchanged for almost 50 years. Several attempts were made to find other catalyst formulae; however, the copper–zinc pair seems to be obligatory in any highly active methanol synthesis catalyst. It is likely that the formation of mixed Cu–Zn hydroxycarbonate at a precipitation stage is strongly required for the good performance of the catalyst after calcination and reductive activation. For revealing plausible reasons for these requirements imposed on a catalyst precursor, we consider data on the active state of the Cu–Zn-containing catalysts.

2. Active state of a Cu–Zn-containing catalyst for methanol synthesis

The phase composition of a Cu–Zn-containing catalyst treated under reaction conditions reveals the presence of copper metal and zinc oxide phases. None of these phases alone has significant activity in methanol synthesis at 230 °C: zinc oxide was used as the methanol synthesis catalyst only at higher temperatures (400 °C) and copper metal has only little activity.[4] These findings forced Klier and co-authors to suppose that the active site of a Cu–Zn-containing catalyst is the Cu^+ cation stabilized in the tetrahedral position of ZnO and the active phase of the catalyst is therefore a substitutional solid solution of Cu^+ in ZnO. Indeed, XRD data showed that a ZnO phase of the catalyst contains up to 16% copper.[4(c)] The formation of a copper–zinc oxide solid solution was also confirmed by other studies (see Section 2). The presence of Cu^+ in the active state of Cu–Zn-containing catalysts was confirmed by several methods, including the combination of adsorptive decomposition of N_2O and LEIS[5(b)] and XANES.[6] The reaction mechanism proposed by the Klier group[4] suggests that a CO molecule is adsorbed on a Cu^+ site of mixed (Cu,Zn)O, while hydrogen is activated at a neighboring Zn^{2+} site. This mechanism gave a reasonable explanation of the necessity of the presence of CO_2 in the reaction feed: CO_2 prevents the overreduction of Cu^+ to copper metal. However, further studies showed

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that the methanol synthesis reaction rate depends linearly on the surface area of metallic copper,[7,8] while no direct correlation was found between the catalytic activity and the BET surface area. After these works, the metallic nature of the active site became the mainstream hypothesis, although the methods used for the measurement of specific copper surface area were argued[9] and new evidence pro Cu^+ active site model was reported in recent publications [*e.g.*, ref. 5(*b*)].

A correlation between the specific reaction rate and the surface area of metallic copper was confirmed by numerous studies; therefore, it was necessary to find some other reason for the obvious synergy between Cu and Zn. Chinchen and co-authors[7] reported that not only Cu–Zn-containing catalysts but also Cu/SiO_2, Cu/Al_2O_3, Cu/MnO and Cu/MgO follow nearly the same linear trend. Then, it could be admitted that the active site includes only metallic copper particles, and the role of ZnO is limited to maintaining a certain particle size and morphology of copper metal, *e.g.*, stabilizing highly dispersed metallic copper particles epitaxially bound to ZnO. Similar suggestions were made independently by several research groups.[10,11]

Yoshihara and co-authors reported[10] that both methanol synthesis and CO_2 reduction to CO occur with a much higher rate over the Cu(110) single crystal surface than over Cu(100) or polycrystalline Cu foil. This structural sensitivity of the reaction was considered as an indication that the plausible reason of the uniquely high activity of the Cu/ZnO system is due to 'maintaining more of the metallic Cu in ultrathin islands that have (110)-like behavior'. The existence of such quasi-two-dimensional clusters in the reduced Cu/ZnO system was supposed earlier based on Cu/ZnO *in situ* EXAFS studies.[12] The hypothesis on the role of ZnO as a template for the stabilization of copper particles of preferable morphology gained additional confirmation when the Topsøe group[13] showed that the reduction potential of gas (*e.g.*, the H_2/H_2O or CO/CO_2 ratio) affected significantly wetting phenomena at the Cu/ZnO interface. Increasing reductive potential of the mixture (*i.e.* by increasing CO content) led to lowering the specific energy of the Cu/ZnO interface and flattening the metallic particles, which acquired a disk-like shape. Thus, by changing the CO/CO_2 ratio, it is possible to vary not only the specific surface area but also the proportion of metallic copper planes exposed to a reaction mixture. Such effects were observed neither for Cu/Al_2O_3 nor for Cu/SiO_2 systems. This allowed one to suggest an elegant explanation of kinetic data (including the necessity of both carbon oxides in the reaction feed for attaining high synthesis rates over Cu/ZnO),[11] which is often referred to as a 'wetting/nonwetting' model.

The formation of thin Cu^0 particles 3–10 nm in diameter, which are epitaxially bound to ZnO and strongly interacting with the support, was independently proposed for the Cu–Zn coprecipitated system upon its reduction in hydrogen at 500 K.[14] Epitaxial binding of metallic copper particles to ZnO was related to their genesis from mixed Cu–Zn oxide by a peculiar mechanism, which considered reversible redox substitution of hydrogen (as protons) for copper cations within their structural positions of zinc oxide. Destruction of these genetic links by dehydration of the reduced $Cu^0/(Zn^{2+},H^+)O$ system during its reduction at higher temperatures caused catalyst recrystallization and the loss of epitaxy. Later, the epitaxy between Cu and ZnO and the reversibility of copper reduction and its reoxidation to Cu^{2+} cations within mixed (Cu,Zn)O in a mildly oxidative or inert gas (helium) atmosphere were proved by *in situ* XRD, HR-TEM[15] (see Figure 1) and XANES-EXAFS.[16] The thickness of the epitaxial flat particles was estimated at only 3–4 lattice parameters of Cu^0 (1.2–1.6 nm). Recently, the mechanism of Cu^{2+} reduction from Cu-promoted wurtzite-like ZnO by redox substitution of hydrogen for copper cations was finally proved by *in situ* vibration spectroscopy (including inelastic neutron scattering).[17]

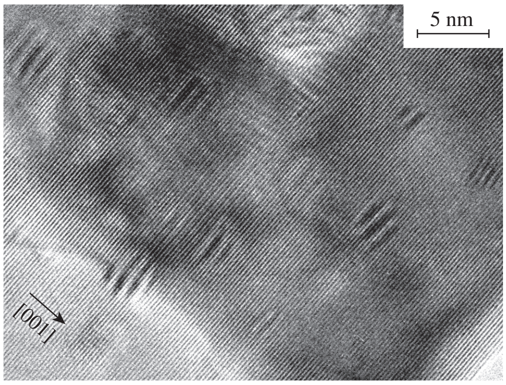

Figure 1 HR-TEM micrograph of metallic Cu nanoparticles epitaxially bound to ZnO (note the characteristic Moire fringes due to mismatch of interatomic distances in the epitaxial phases) in the Cu–Zn oxide after its reduction in hydrogen at 493 K. Reproduced from ref. 15 with permission from the PCCP Owner Societies.

The epitaxial binding of metal particles to the supporting oxide causes microstrains in the structures of metallic particles due to a mismatch of interatomic distances in these structures. Indeed, a significant microstrain was found in both the metallic Cu particles and ZnO by means of XRD profile analysis,[18] and epitaxy was considered as one of three main causes. The contribution of epitaxial strain to interface energy and wetting phenomena was supposed[19] to prevail for small copper particles with high adhesion to ZnO. The existence of a microstrain in metallic copper was correlated to enhanced catalytic activity in methanol synthesis.[18] Recent HR-TEM studies[20] provided additional support to this correlation and suggested that stacking faults of copper structure and the corresponding kinks and steps at the metallic surface are responsible for high activity in methanol synthesis due to the structural sensitivity of the reaction [activity of Cu(211) > > activity of Cu(111)]. The model of an active site[20] also includes Zn atoms on the surface of Cu at close vicinity of kink/step.

The data on structural sensitivity[10] were closely confirmed by Fujitani and co-authors,[21] however, they reported that the deposition of Zn on Cu(111) increases TOF by a factor of 13, which becomes 3.5 times higher than TOF over Cu(110) and 1.5 times higher than TOF over a real Cu/ZnO catalyst. Also, the further studies by Topsøe using the IR spectroscopy of adsorbed CO[22] evidenced that the Cu(110) surface dominates in a Cu/Al_2O_3 catalyst, whose catalytic activity was three times lower than that of Cu/ZnO. Revisiting a linear correlation between the reaction rate of methanol synthesis and the surface area of metallic copper, Fujitani and Nakamura[23] noticed that the observed dependence is only linear but not exactly proportional. Methanol yield approached zero at a Cu surface area of about 5 $m^2\ g_{cat}^{-1}$ for the Zn-free sample and the sample containing 90% Zn. Their experimental data were represented as specific activity (related to Cu surface area) of Cu/ZnO catalysts *versus* ZnO content (see Figure 2). From this plot, they deduced 'the additional effect of ZnO, that is, a significant promotion in the catalytic activity of the Cu surface by a factor of 13–22' and came to a conclusion about 'the formation of Cu–Zn alloy in the Cu particles ... leading to an increase in the specific activity in methanol synthesis.' Other studies considered the peculiar promotional role of Zn. However, note that consensus on this point has not been achieved yet; for more details, one may address to a report by Nakamura and co-authors[24] and a review by Waugh.[25]

Cu–Zn alloy formation in a Cu/ZnO catalyst was first reported for a water-gas shift reaction catalyst.[26] A theoretical thermodynamic analysis performed by Spencer[27] for the methanol synthesis condi-

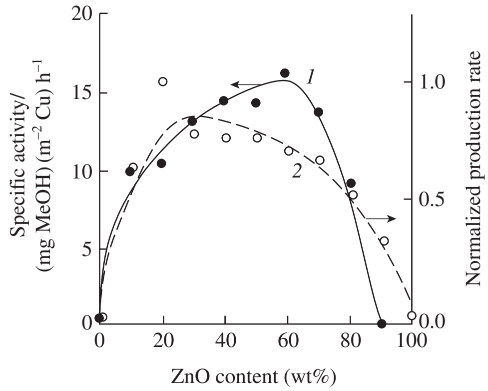

Figure 2 Relation of specific activity of Cu–Zn methanol synthesis catalysts to ZnO content according to (*1*) ref. 23(*b*) and (*2*) ref. 18.

tions highlighted that ZnO reduction is favourable in the presence of metallic copper particles when α-brass forms. The chemical potential of metallic zinc in a dilute brass alloy linearly depends on the logarithm of its atomic fraction. Therefore, even at rather low temperatures and moderate CO/CO_2 ratios characteristic of the conditions of methanol synthesis, some of zinc cations are reduced and dissolved by metallic copper (or α-brass) particles. The equilibrium atomic fraction of Zn^0 in the bulk of metallic particles was estimated to be small (*ca.* 0.1% for methanol synthesis conditions), however significant due to the effect of surface segregation.[27(c)] Indeed, it is well known that the additive with a lower specific surface energy (*i.e.*, a surfactant) concentrates at the surface. Since the specific surface energy of metallic zinc (*ca.* 0.92 J m^{-2}) is much less than that of metallic copper (*ca.* 1.76 J m^{-2}), the surface concentration of Zn could be up to four orders of magnitude higher than that in the bulk (depending on temperature and crystal face). For Cu(111) at 500 K, the surface segregation ratio estimate is 78 and the surface concentration of Zn can be several percent. This theoretical report summoned up numerous experimental works, which aimed to detect metallic zinc atoms in the bulk and at the surface of copper particles in the active Cu–Zn-containing catalyst and tried to relate the methanol synthesis activity with zinc sites at the surface of α-brass.

The XRD studies of Cu/ZnO catalysts reported that the lattice constant of a metallic phase generated after the reduction of a catalyst in hydrogen exceeds the constant of Cu^0, which may indicate the formation of bulk brass. According to Nakamura *et al.*,[24] the lattice parameter exceeded 3.64 Å, which corresponds to >13% Zn, when the Cu/ZnO catalysts containing more than 40 wt% ZnO were reduced at a low temperature of 523 K. Similar concentrations of Zn in a metallic phase were reported for the Cu/ZnO catalyst reduced at 573 K.[26] Guenter and coauthors[18] emphasized that, even at lower ZnO contents, a considerable lattice expansion of metallic phase by 0.14% (from 3.6150 to 3.620 Å) was observed, which corresponds to about 5% Zn in Cu. This high concentration of Zn in the alloy was not confirmed by other methods: the *in situ* K–Cu EXAFS studies of Cu/ZnO treated up to 573 K in dry and wet syngas[28] did not show any shift of the Cu–Me distance from 2.56 Å (for Cu–Cu in metallic copper), unlike the catalyst treated in syngas at 873 K, for which the formation of bulk Cu–Zn alloy can be clearly deduced from EXAFS analysis. Despite that, significant changes in the vibration frequency of adsorbed CO were detected for mildly reduced (at 573 K) catalysts, which were interpreted as the formation of surface Cu–Zn alloy. For the Cu–Zn–Si system,[6] the formation of metallic Zn was clearly detected by *in situ* K–Zn XANES after reduction at 573 K, while *in situ* K–Cu EXAFS analysis proved appearance of Cu–Zn distance of 2.58 Å from Cu atom; reduction at 673 K increased the amount of metallic Zn in the alloy. The enrichment of the alloy surface in Zn was deduced from experimental data.

Although the formation of bulk alloy at moderate temperatures typical of methanol synthesis (<573 K) might be debated, the migration of Zn from a ZnO phase to the surface of metallic particles has now to be considered as a solid fact. Jansen and co-authors[5] used low-energy ion scattering (LEIS) to estimate the atomic fraction of Zn^0 at 2% for the surface layer of the $Cu/ZnO/SiO_2$ catalyst reduced at 473 K (increasing to 19% after reduction at 673 K), while the most of the metallic copper surface was concluded to be covered with ZnO clusters (55% at 473 K and 77% at 673 K). According to these LEIS data, the fraction of ‘free’ metallic copper surface is only 300 ppm after reduction in H_2 at 673 K. ZnO coverage was considered beneficial for catalytic methanol synthesis. Substantial decoration of metallic copper particles by Zn-containing oxide overlayer is the only explanation for an extraordinary high intensity of the surface plasmon resonance band of metallic copper and its shift to lower energies by 1000 cm^{-1}, which were reported for the Cu/ZnO catalysts reduced at 508 K.[29] Moreover, the entire coverage of the metallic nanoparticles with a disordered oxide overlayer having a thickness of *ca.* 1 nm is shown by HR-TEM for Cu–Zn–Al catalysts, which are referred to as ‘conventionally prepared, most-active $Cu/ZnO/Al_2O_3$ catalysts’.[20]

The catalytic hydrogenation activity of the entirely decorated metallic nanoparticles needs more commenting. It is a common knowledge that, for some Ni/TiO_2 systems, the decoration of Ni particles by titania oxide clusters and the consequent decrease in the specific surface area of metallic nickel did not result in a proportional decrease in catalytic activity,[30,31] which was related to enhancement of the specific catalytic activity (TOF) of free metallic surface (strong metal-support interaction or SMSI). However, there are examples of Ni/(Mg–Al–Si-vermiculite) systems that contain entirely decorated metallic nickel particles and, nevertheless, exhibit significant catalytic activity in CO hydrogenation and methane reforming processes.[32] Similarly to SMSI Ni/TiO_2 systems,[33] these Ni/chlorite-vermiculite catalysts are absolutely inactive in graphite-like carbon formation both in pure CO and in pure methane. The decoration of nickel with an oxide overlayer is responsible for its passivity in these processes, which require a free metallic nickel surface for graphite phase crystallization. Therefore, the entire shielding of metallic particles by the oxide overlayer cannot be considered as an *a priori* indication to their inertness in the catalytic hydrogenation of carbon oxides.[34]

Experimental data indicate that Cu–Zn-containing catalysts upon their reduction and under methanol synthesis conditions are an extremely complicated system containing metallic nanoparticles that strongly interact with the oxide support. Both the metallic nanoparticles and the oxide support have mixed (Cu–Zn) composition and defect structure. Epitaxial binding and wetting of the oxide with a metallic phase and the wetting of metallic nanoparticles with disordered oxide overlayer are characteristic of Cu–Zn catalysts in the reducing medium. Significant microstrain and extended defects (stacking faults) are intrinsic to metallic nanoparticles and the oxide support. Cu and Zn in all possible oxidation states were found in this system. The analysis of such a sophisticated system is complicated by numerous real and model systems under study, giving slightly different results and a variety of activation procedures and reaction conditions applied in the experiments.

It is very plausible that these effects are critical for the occurrence of methanol synthesis, whereas the others are less important. Therefore, various models for the methanol synthesis active sites were proposed, which took into account some of the peculiarities, while neglecting (after a proper discussion) the others. Fujitani and co-authors[24] concluded that metallic Cu–Zn sites of surface alloy are responsible for CO_2 hydrogenation, while the interface between metallic Cu and ZnO clusters (Cu–O–Zn site) is active in the synthesis of methanol from CO. Then, the role of CO_2 in methanol synthesis from CO consists in maintaining the necessary oxidation of surface Cu–Zn alloy for further CO activation. The effects of epitaxy and hydrogen spillover were considered as less important in comparison to the role of alloying. Yurieva and co-authors[14,35] considered metallic copper as a site for CO_2 hydrogenation and oxygenic sites at the copper surface (Cu–O–Cu site) being responsible for CO activation, zinc oxide support epitaxial to copper particles serving as a depot of H^+, which hydrogenates the adsorbed CO and formate species on the surface of metallic copper. In other words, this model considers epitaxial binding and hydrogen spillover as important effects and disregards the alloying effect. The role of ZnO as a reservoir for atomic hydrogen was also proposed by Burch *et al*.[36] Recent studies on the kinetics of hydrogen interaction with Cu/ZnO[17] confirmed the reactivity of protons accumulated in ZnO; however, they evidenced that this is not the major reaction route to methanol due to high activation energy of redox activation of hydrogen. Guenter and co-authors[18] emphasized the key role of microstrain, while considered the surface ZnO clusters and epitaxial binding as ancestor effects, which cause the microstrain. Further development of this research resulted in a recent model by Behrens and co-authors,[20] where $Zn^{\delta+}$-promoted stepped surfaces of Cu [*e.g.* (211) or (522)] related to the stacking faults of Cu^0 are proposed as the main active sites with reference to an SMSI-like effect causing the partial charging of Zn. Cu/ZnO epitaxy was not regarded in this study.

Model systems using atomic-layer deposited Cu/ZnO, Zn/Cu/ZnO, ZnO/Cu and other models were studied,[37,38] and provided an intriguing insight into structural and chemical interactions within chemically pure model samples, which proved 'unexpected large complexity of the Cu/ZnO interface'. It was also concluded that 'clearly additional work is required to obtain a good understanding of this rather complex system'. It is worthy to comment that the transfer of these results to real Zn–Cu-containing catalysts is not straightforward since the procedures used for the preparation of these model systems are very much different from traditional catalyst preparation (*e.g*., precipitation followed by thermal treatment).

An important difference of real catalysts from models created by vacuum methods, which is now generally disregarded by the majority of researchers, is a significant proportion of admixing anions in the composition of real catalysts. Indeed, hydroxyls and carbonates are present in the composition of oxide precursors. The role of these anions should not be underestimated by considering them just as residual admixtures. For Cu^{2+} species, which are the Jahn–Teller d^9 cations, the presence of anionic admixtures may affect the energetics of Cu^{2+} in the oxide state by changing the local neighborhood symmetry to more favorable flat square or tetragonally distorted octahedron. The presence of anionic admixtures in the Cu–Mg oxide system was shown to affect dramatically the local structure of Cu^{2+} cations in mixed oxide and alter the kinetics of copper reduction.[39] The partial removal of admixing anions also changes the kinetics of Cu^{2+} reduction from mixed (Cu,Zn)O.[17]

Concluding the above discussion on the active state of the Cu–Zn-containing methanol synthesis catalysts, we have to assert that the active component is an extremely complicated system, which includes defective metallic particles that are at least partially decorated by an amorphous oxide overlayer and strongly interact with the supporting defective ZnO phase. Such intimate interaction of Cu, Zn and Cu–Zn species may only be possible as a result of their genesis from mixed Cu–Zn oxide phases. It seems natural to suppose that studying the structure of mixed Cu–Zn oxide phases could give important information for better understanding the nature of the active state of the methanol synthesis catalysts.

3. Oxide precursor of the Cu–Zn-containing catalyst for methanol synthesis

Two mixed oxides can form in the Cu–Zn oxide system: a Cu^{2+} solution in zincite, ZnO (wurtzite-like hexagonal structure, Me^{2+} located in tetrahedra) and a Zn^{2+} solution in tenorite-like CuO (monoclinic prismatic structure, Me^{2+} located in tetragonal coordination close to flat square). For Al-containing and Cr-containing catalysts, these cations can be dissolved in ZnO or CuO phases, at that a spinel-like $Me^{2+}Me^{3+}_2O_4$ phase may form at high loading of Al^{3+} and/or Cr^{3+}.

Before discussing in detail the solid solutions based on ZnO and CuO, let us briefly review data on spinel-like oxide precursors. In the 1970s, some patents described the presence of copper–zinc–aluminum spinel as a preferable phase in the catalyst composition ('preferred extents of such spinel formation are over 30%, especially in the range 50–95%'),[40] the main benefit of a higher content of spinel is lengthening of the catalyst life in methanol synthesis. Indeed, the catalysts with significant content of Cu–Zn–Al spinel have excellent stability, showing no decrease in specific activity after thermal shock at 623 K.[41] However, the activity of these catalysts is manifold lower as compared to catalysts which contained less Al^{3+} and no or little of spinel phase.[42] Similar properties (high stability at the expense of activity) were observed in the Cu–Zn–Cr catalyst with a spinel-like structure.[43] This can be reasonably related to a very high stability of Zn^{2+} cations in the tetrahedral positions of a $Zn(Al,Cr)_2O_4$ spinel phase, which hinders their reduction and migration to the bulk or surface of metallic copper particles. Spinel-like oxide appears in the catalyst only at a considerably high Al^{3+} content of 15 at%,[44] which exceeds the Al concentration in commercial catalysts for methanol synthesis.

Returning back to the mixed Cu–Zn oxides based on wurtzite-like and tenorite-like structures, one may notice that a tenorite structure does not render any tetrahedral cationic positions, which are preferred by Zn^{2+}, while the tetrahedra of ZnO are strongly unfavorable for Jahn–Teller Cu^{2+} cations. By that reason, no more than 1% Cu^{2+} can dissolve in well-crystallized ZnO,[45] and from 1.2[46] to 3%[47] Zn^{2+} can dissolve in tenorite. Meanwhile, the mixed oxides prepared by decomposition of mixed hydroxycarbonates show much greater solubility limits (see Figure 3). It was reported[44,48] that 4–6% Zn^{2+} can dissolve in CuO. Up to 10% Cu^{2+} in ZnO can give monophase samples,[14(a)] while the concentration of Cu^{2+} in ZnO is about 17 at%, if the total Cu^{2+} content of the hydroxycarbonate precursor is about 50 at%, and a tenorite phase formed simultaneously to zincite.[44] The co-doping of ZnO by Al^{3+} (refs. 42, 44) or Cr^{3+} (ref. 49) can increase Cu^{2+} solubility even further: for Cu–Zn–Al catalysts with 10 at% Al, the solubility of Cu^{2+} in zincite shifts to about 20 at% in monophase ZnO samples and to 40 at% in the two-phase (CuO + ZnO) catalysts with high Cu loading. Such a high solubility of Cu^{2+} in ZnO can be attributed to the effect of anionic admixtures.

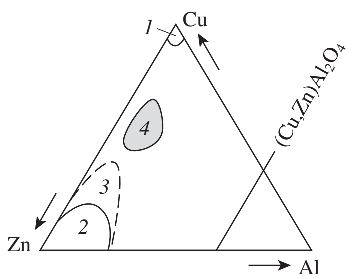

Figure 3 Ternary diagram of anion-modified Cu–Zn–Al oxides: (*1*) monophase a.m.-mixed oxide with tenorite structure, (*2*) monophase a.m.-mixed oxide with zincite structure, (*3*) composition of a.m.-mixed oxide with zincite structure in two-phase system (co-existing with CuO phase) based on the data of ref. 44; (*4*) typical composition of commercial methanol synthesis catalysts.

Indeed, the oxides structure originating from the decomposition of hydroxycarbonates at moderate temperatures (below 700 K) still contains OH^- and CO_3^{2-} anions.[50] Evolution of these admixing anions only occurs at higher temperatures and is often accompanied by oxide recrystallization. These admixing anions are not just the residual anions; however, they modify the structure of the catalyst, *e.g.*, they can change the local symmetry of a cation, as it was discussed above. Therefore, the solubility of Cu^{2+} in anion-modified (a.m.) ZnO is much greater than that in ideal zincite.

Note that the temperature of calcination strongly affects the structure and properties of Cu–Zn oxides: after calcination at 625 K, oxide phases are anion-modified; however, anionic admixtures evolve at above 700 K causing the sintering or even recrystallization of oxides with the decomposition of mixed oxide to separate CuO and ZnO phases, see *e.g.*, data on Cu–Zn[51] and $Cu_{0.7}Zn_{0.3}Al_{0.1}$.[52] Minyukova *et al*.[49] correlated the temperature of evolution of anionic admixtures to the value above which the catalytic activity decreased (*i.e.*, to the thermal stability threshold of the catalyst).

The structure of Cu^{2+} in anion-modified ZnO was studied using monophase anion-modified Cu–Zn oxides by means of XRD, HR-TEM, ESR, UV-VIS diffuse reflectance spectroscopy, EXAFS, *in situ* FTIR and inelastic neutron scattering (INS) in a series of publications.[15–17,29,53,54] XANES studies[16] did not find Cu^+ cations in a.m.-ZnO, all the Cu cations are in Cu^{2+} state. UV-VIS reflectance spectroscopy evidenced that Cu^+–O–Cu^{2+} inter-valent band is observed only in the samples calcined at high temperatures (1000 K). According to findings of ESR,[53(a)] UV-VIS DRS,[53(b)] HR-TEM,[15,54] and EXAFS,[16] Cu^{2+} cations in ZnO structure form small flat clusters with tetragonally distorted octahedral coordination, which can be located in the stacking faults of ZnO structure along (001) plane. Figure 4 shows the HR-TEM image of the a.m.-(Cu,Zn)O and the scheme of a plausible geometry of a Cu^{2+} cation in a stacking fault. The planar defects of ZnO structure are preserved even after reduction. During the reoxidation, copper atoms return back to the extended stacking faults of ZnO as the clusters of flat-square coordinated copper cations. *In situ* FTIR and INS data proved the presence of hydroxyl and carbonate anions in the a.m.-Cu,ZnO and highlighted their effect on the interaction of hydrogen with the a.m.-Cu,ZnO oxide.[17]

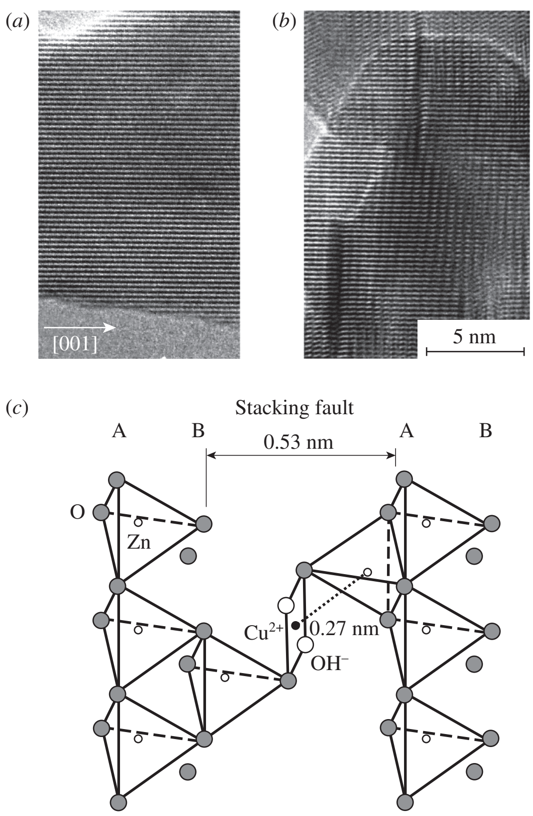

Figure 4 HR-TEM data: (*a*) a.m.-ZnO, (*b*) a.m.-(8% Cu, 92% Zn)O sample, (*c*) plausible scheme of the Cu^{2+} cation stabilized in the planar defect of ZnO. A and B are the layers of the hcp ZnO. Reproduced with permission from ref. 16(*b*). © Elsevier, 2006.

Solubility of Zn^{2+} in a.m.-CuO is not so high and is limited by 4–6 at%. Zinc cations are supposed to 'occupy defect positions in the tenorite lattice',[48] limit of zinc content is related to a concentration of defects in CuO. Elucidation of the local structure of Zn^{2+} in CuO is still waiting for thorough research.

The role of Al^{3+} promotion of both the Zn^{2+} dissolution in CuO and the Cu^{2+} dissolution in ZnO is related with increasing the amount of defects in these oxides. At low Al : Zn ratios of < 10%, Al resides on the tetrahedral Zn sites in the ZnO wurtzite-type lattice.[55,56] The difference in charge of Al^{3+} and Zn^{2+} evidently creates defects in ZnO and increases Cu^{2+} solubility, as it was mentioned above. The recent study[57] pointed out two other plausible effects of Al in Cu–Zn–Al catalysts: 'geometric effect of dilution of Cu^{2+} on an atomic level in the precursor phase' and 'electronic promotion effect', which affects redox properties, *i.e.* increases Zn^{2+} reducibility. Promotion by Ga^{3+} and Cr^{3+} has similar, however smaller impact to the activity. It was noted, that these promoters create donor levels and enhance the n-type semiconductivity of ZnO, addressing to a Schottky-junction model of methanol synthesis site.[58] On the contrary, promotion by Mg^{2+} decreases the Cu–Zn catalyst activity, this was related to making the ZnO support less reducible. This supposition, however, cannot explain high stability (including thermal stability) of Al- and Cr-promoted methanol synthesis catalysts. It is quite possible that Me^{3+} cations can be involved in decorating oxide clusters, stabilizing them, and preventing reduction of Zn^{2+} in the decorating surface overlayers.

In the range of industrially important catalyst compositions, both the oxides with tenorite and with wurtzite structure constitute the catalyst, while spinel-like structures seem to be undesirable. Both co-existing oxides are mixed Cu–Zn–Al oxides, *i.e.* the solid solution of Cu and Al in ZnO and the solid solution of Zn and Al in CuO. Highly active catalysts can be produced if the temperature of calcination is not very high (below *ca.* 700 K), which means that the oxide precursors are anion-modified oxides. The role of anion admixtures may consist in increasing mutual solubility. Several effects of Al^{3+} promoter can be proposed, however, it is quite clear that Al_2O_3 is not a merely structural promoter. Mixing of cationic components on the atomic level needs deep chemical interaction at the early catalyst preparation stages, co-precipitation method perfectly matches this purpose giving the mixed hydroxycarbonates of Cu–Zn–Al.

4. Hydroxycarbonate precursors of the Cu–Zn-containing methanol synthesis catalyst

Precipitation from a mixture of nitrate solutions was initially suggested by ICI patents, now it is still the main and the most studied method for preparation of Cu–Zn–Al methanol synthesis catalysts. The conditions of precipitation are usually chosen within the range of pH 6.8–7.5, $T = 60-80$ °C. A systematic scanning of 49 $Cu_{0.7}Zn_{0.3}Al_{0.1}$ samples prepared at various pH and temperature[52] showed that these conditions make it possible to achieve the optimal catalyst activity. A variety of mixed hydroxycarbonates may form during co-precipitation procedure and further aging of the precipitate. Most studies report the presence of malachite (or zinc-malachite) $[Cu_2CO_3(OH)_2]$, aurichalcite $[(Cu,Zn)_5(CO_3)_2(OH)_6]$ and hydrozincite $[Zn_5(CO_3)_2(OH)_6]$ phases in the uncalcined catalysts. In some publications it was noted that the other hydroxy-

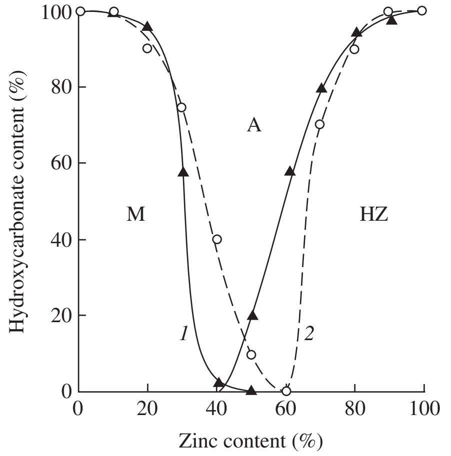

Figure 5 Composition of Cu–Zn hydroxycarbonates in the precipitate as a function of Zn^{2+} content according to data of (*1*) ref. 23(*b*) and (*2*) ref. 51. M – (zinc-)malachite, A – aurichalcite, HZ – (copper-)hydrozincite.

carbonates, like georgeite[59] and azurite,[59(b)] may form under certain conditions. To produce the latter, it was necessary to recrystallize georgeite in an autoclave at 40 bar of CO_2 and seeds of azurite. Thus, although this precursor may be interesting for research it does not relate to the Cu–Zn–Al catalyst discussed in this review. Rosasite [$Cu_2CO_3(OH)_2$] is metastable[60] and, therefore, cannot form in the co-precipitated system. In the aluminum-enriched samples hydrotalcite-like structures[44(b),57] and zaccagnaite ($Zn_4Al_2[(OH)_{12}CO_3]\cdot 3H_2O$)[55] were found.

Figure 5 summarizes the data[23(b),51] on the impact of Cu : Zn ratio in the initial solution on the phase composition of precipitate formed. Only three structures are present in these catalysts: (Zn-)malachite, aurichalcite and (Cu-)hydrozincite. Data of Millar *et al*. are close to earlier reported data by the Porta group,[61] while differ from those of Fujitani and co-authors.[23(b)] The maximal content of Zn in zincian malachite was found to be 27–28%.[55,57,60]

Spencer and co-authors emphasized that aurichalcite and malachite phases have a common ancestor: XRD amorphous hydroxycarbonate, georgeite, which may form in Cu–Zn and Cu–Zn–Al systems as an intermediate phase. However, it is unstable under typical preparation conditions (60–80 °C): Cu : Zn = 2 : 1 georgeite rapidly transforms to the mixture of high-Zn aurichalcite and low-Zn malachite. Upon ageing at 60 °C this mixture was found to transform further to high-zincian malachite.[59] Ageing conditions seem being one of the parameters responsible for the difference seen in Figure 5, since Fujitani and co-authors aged the suspension of precipitate at ambient temperature.

Two structures are observed in the range of commercial catalyst compositions: aurichalcite and malachite. Fujitani and co-authors correlated the fraction of aurichalcite precursor to the activity of Cu–Zn catalysts in methanol synthesis and concluded that formation of aurichalcite structure is advantageous for methanol synthesis.[23(b)] Similar conclusions were made earlier by Fujita *et al*.[62] and by the Yurieva group.[63] In the works of the Yurieva group it was shown that ex-Zn-malachite catalysts have rather high specific activity, however low stability due to sintering of metallic copper, while thermal stability of both ex-aurichalcite and ex-hydrozincite catalysts is much better. This was related to a.m.-$Cu_xZn_{1-x}O$ oxide formation during decomposition of these structures. Also, Millar and co-authors[51] reported that (Cu-)hydrozincite and aurichalcite precursors give superiorly high dispersed and intimately mixed anion-modified CuO and ZnO particles (Plyasova *et al*. observed epitaxy between CuO and ZnO crystals even after decomposition of 10% Cu–ZnO solid solution caused by overheating the sample at temperatures above thermal stability of anionic admixtures[14(a)]). According to data of Millar *et al.* zincian malachite precursors provide catalysts with large CuO and ZnO crystals. Thus, different groups suppose that aurichalcite structure is the preferable precursor of the Cu–Zn methanol synthesis catalyst.

Ternary Cu–Zn–Al system is more complicated. First of all, hydrotalcite-like hydroxycarbonates may form at Al^{3+} content of above 15 at%[44] or even 6 at%.[57] According to the recent study by Behrens and co-authors,[57] the introduction of 2.5 at% of Al^{3+} to Cu : Zn = 70 : 30 system resulted in a significant decrease in the aurichalcite content, at 3.3–4.0% of Al^{3+} the Al-doped zincian malachite was the only crystalline phase in the precursor. Thus, doping by Al^{3+} significantly increases Zn^{2+} solubility in malachite structure. This dilution of Cu^{2+} cations results in smaller size of CuO crystallites after decomposition of the precursor and more dispersed metallic copper in the active state. The activity of the catalyst increases by 79% upon introduction of 3.3% of Al and the precursor of this most active catalyst was monophase Al-promoted zincian malachite. Similar effect was observed for Ga^{3+} and Cr^{3+} promoted catalysts. Promotion of activity by introduction of Al^{3+}, Ga^{3+} and Cr^{3+} was reported earlier by Fujitani.[23(a)] Also, the results of this work of Behrens and co-authors correlate with the earlier observations that aluminum and, especially, chromium improve stability (including thermal stability) of the Cu–Zn-containing catalysts.[41,42] So, these promoters oppose the main drawback of malachite-based catalysts.

Increasing the Al content to 6% and more led to appearance of hydrotalcite structure and further increase of its fraction in the precursor. Decomposition of Cu–Zn hydrotalcites affords spinel-like Cu–Zn–Al structures (which composition may deviate from stoichiometric spinel $Cu_{1-x}Zn_xAl_2O_4$).[44(b)] Cu–Zn–Al spinels are rather active in water gas shift reaction, however, their activity in methanol synthesis is fair.[42]

5. Conclusions

The active state of Cu–Zn-containing methanol synthesis catalysts is an extremely complicated system, which includes defective metallic particles that are at least partially decorated by amorphous oxide overlayer and strongly interact with the supporting defective ZnO phase. Both the metallic nanoparticles and the oxide support have mixed (Cu–Zn) composition and are defective. Epitaxial binding and wetting of the oxide with metallic phase as well as wetting of metallic nanoparticles with disordered oxidic overlayer are characteristic of Cu–Zn catalysts in the reducing medium. Significant microstrain and extended defects (stacking faults) are intrinsic to metallic nanoparticles and oxidic support. Cu and Zn in all possible oxidation states are reported to be found in this system. Al^{3+}, Ga^{3+} and Cr^{3+} promoting cations are not merely structural promoters, however, directly affect the specific activity of the active sites. It is very plausible that some of these features are crucial for the occurrence of methanol synthesis, while the others are less important. However, nowadays there is no common opinion what structural and chemical peculiarities of the active state of Cu–Zn-containing catalysts determine their high catalytic activity in methanol synthesis.

The intimate interaction of Cu, Zn and Cu–Zn species may only be possible as the result of their genesis from mixed Cu–Zn oxide phases. Solubility of Zn^{2+} in CuO and, especially, Cu^{2+} in ZnO can be dramatically increased by anionic modification of the mixed oxide structure. Evolution of anionic admixtures due to overheating the mixed oxide beyond the threshold of their thermal stability (*ca*. 650–670 K) leads to decomposition and recrystallization of mixed oxides, causing the decrement of the catalytic activity in methanol synthesis. Promotion of the oxide structures by small quantities of Al^{3+}, Ga^{3+} or Cr^{3+} cations can further expand solubility ranges and thermal stability of the catalyst.

The most natural way for production of anion-modified mixed oxide is decomposition of mixed hydroxycarbonates at moderate temperatures. In binary Cu–Zn system, Cu–hydrozincite and aurichalcite precursors are advantageous with respect to Zn-malachite, since they lead to formation of more dispersed and intimately mixed anion-modified Cu–Zn oxides with zincite and tenorite structures. Promotion by Al^{3+} or Ga^{3+} not only increase solubility of Zn in malachite precursor, but their action oppose the drawbacks of the catalysts derived from Zn-malachite. Thus, Al-promoted zincian malachite is one of the most advantageous precursors for methanol synthesis catalysts.

The composition and the method of preparation of the Cu–Zn–Al methanol synthesis catalysts are almost unchanged during last 50 years and close to the initially proposed by ICI. However, the structure of the catalyst and its active state, as well as the mechanism of methanol synthesis are still the challenges worthy of further investigation.

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