Effect of Zn Substitutions in $YBa_2Cu_3O_{6+x}$ Phases on Reactivity during the Ammoxidation of Toluene

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Zn substitution in Y–Ba–Cu–O phases influences the catalytic ammoxidation of toluene. The activity for formation of both benzonitrile and CO_2 at low and high O_2 pressures, respectively, decreases strongly with increasing Zn content up to 4%. Above this substitution level, the activity, however, increases slightly. Characterisations of the surface by XPS and of the bulk by XRD analysis, indicate the presence of overlayers on the catalysts. In these overlayers, irrespective of the Zn content of catalysts, Cu¹ states predominate at low O_2 pressure and Cu¹¹ at high pressure. These states are associated with selective and non-selective properties, respectively. The activity of the catalysts shows a general tendency to increase with surface copper concentrations as found from XPS studies. However, strong deviations from linearity indicate that the activity of the overlayer is greatly influenced by the bulk acting as a support.

The recently discovered $YBa_2Cu_3O_{6+x}$ phases¹ and their substituted analogues are amongst the most studied materials. Their catalytic effects in reactions such as oxidation, ammoxidation and oxidative dehydrogenation are beginning to receive attention.²⁻⁶ Study of the reactivity of these materials as new catalysts in oxidation reactions is justified not only by the fact that they act as oxygen reservoirs, but also by the necessity to understand more about their physical and chemical properties, and how they are interrelated.

The crystal chemistry and structure of these compounds are well known,⁷⁻¹⁰ and the earlier catalytic studies were performed using mainly non-substituted phases. Substitution in the $YBa_2Cu_3O_{6+x}$ phases is important in order to elucidate the many properties of these materials. When Y^{3+} is substituted with other lanthanides such as Nd, Sm, Eu, Gd, Dy, Ho, Er etc., negligible changes in the catalytic and superconductivity properties^{6,11} are observed. Substitution in the Cu sites is an interesting alternative as most properties are influenced strongly; e.g. substitution by Ni or Co substantially decreases superconductivity.¹² In a recent investigation of toluene ammoxidation over YBa₂Cu₃O_{6+x} with $x \approx 0$, and its Co substituted analogues,¹³ Cu sites were established as the active sites. The replacement of Cu by Co, led to a decrease in reactivity and selectivity. Even at high O2 pressure the activity of the $YBa_2Cu_3O_{6+x}$ for CO_2 formation exceeded those of the Co-substituted analogues despite the fact, that Co is an active component for total combustion.¹⁴

Zn in comparison to Co is much less active for oxidation processes,¹⁵ thus its substitution in $YBa_2Cu_3O_{6+x}$ would lead to a decrease in the number and possibly properties of the active Cu sites. Based on neutron diffraction studies, it is known that Zn primarily substitutes for Cu on the Cu sites located adjacent to the Y planes and leads to a very significant change in physical properties.^{16,17} These can influence surface and near-surface states which are of importance for oxidation reactions. Consequently, in the present investigation, toluene ammoxidation was studied over Zn-substituted analogues in combination with XPS studies of the surface composition.

Experimental

 $YBa_2(Cu_{1-y}Zn_y)_3O_{6+x}$ with $x \approx 0$ and $y \approx 0-16\%$ (hereafter referred to by their atom % Zn substitution) were prepared

from stoichiometric amounts of high-purity $BaCO_3$, ZnO, Y_2O_3 and CuO by the methods described elsewhere.¹⁷ The B.E.T. surface areas of the samples were within 0.3–0.5 m² g⁻¹ and did not change during use.

The catalytic activity of each sample was tested in ammoxidation of toluene. For each experiment, ca. 350 mg of fresh sample was diluted with quartz and heated in an isothermal plug-flow reactor to a reaction temperature of 400 °C in N₂. The preheated mixture of reactants was then passed over the catalyst bed and the O₂ partial pressure was varied from 0 to 42.5 kPa while keeping the pressures of toluene and NH₃ constant at 0.77 and 2.58 kPa, respectively. At each O₂ pressure reaction was carried out until a steady state was confirmed by three consecutive measurements 15 min apart. At zero pressure of O2, however, only two consecutive measurements were made to avoid decomposition of samples. Samples for XPS investigations were taken after use at 2.15 and 42.5 kPa O₂ pressures, respectively, by rapidly cooling in N_2 . These conditions are henceforth referred to as low- and high-pressure conditions, respectively. Over all catalysts studied, benzonitrile, CO₂ and trace amounts of CO, were the only products observed. The analysis of toluene and products was carried out on a Varian Vista 6000 gas chromatograph following procedures and conditions described elsewhere.¹⁸

XPS investigations were performed on a Kratos XSAM 800 instrument. The samples removed in N₂ were mounted and inserted into the vacuum system in high-purity Ar. An Al anode (1486.6 eV) was used and the slit width was set at 40° and the analyser operated at 40 eV pass energy at high magnification. Charging effects were corrected for by adjusting the main C 1s peak to a position at 285.0 eV. Analysis of spectra was carried out with the DS 800 system. Sensitivity factors used in the quantitative analysis were obtained by calibration using some YBa₂Cu₃O₇ samples and were for O 1s 1.0, Y 3d 1.15, Ba 4d 1.54 and Cu $2p_{3/2}$ 2.65. The vacuum was initially in the 10^{-8} Torr† range due to sample outgassing, but later, it was in the 10^{-10} Torr range.

XRD analysis of fresh material and samples used at high O_2 pressures was performed using a Philips X-ray powder diffractometer equipped with a diffracted beam monochro-

 $[\]dagger 1 \text{ Torr} = 133.322 \text{ Pa.}$

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mator, Cu-K α radiation and a 4 kW X-ray generator (PW 1730) operated at 40 kV and 20 mA.

Results

Activity Measurements

In Fig. 1, the rates of formation of benzonitrile over the catalysts are shown as a function of O_2 pressure. Irrespective of the Zn content of the catalysts, benzonitrile was exclusively formed at low O_2 partial pressure (<10 kPa). The shape of the curves observed is quite similar. The rates for CO_2 formation over the samples as O_2 pressure was varied from 0 to 42.5 kPa, are shown in Fig. 2. Zn substitution lowers the activity for benzonitrile and CO_2 formation as previously observed for Co-substituted analogues.¹³ The sharp transition in activity observed as O_2 pressure approaches 8.65 kPa is no longer dramatic.

Comparison of rates of formation of products at low and high pressures of O_2 as a function of Zn content is shown in Fig. 3(a) and (b), respectively. At low Zn substitutions <4%, the activity for benzonitrile drops dramatically, but increases again for higher Zn substitutions >4%. Also included is the data for the 16% Zn catalyst which deviates from the general trend observed. For formation of CO_2 , at low O_2 pressure, the rate decreased with increase in Zn content of samples. However, at high pressure, Fig. 3(b), a similar trend as in the case of benzonitrile, Fig. 3(a), is observed. Data for the 16%



Fig. 1 Rate of formation of benzonitrile over various catalysts as a function of partial pressure of O_2 . \blacksquare , 0% Zn; \square , 1.67% Zn; \spadesuit , 3.3% Zn; \triangle , 4% Zn; \bigcirc , 6.67% Zn; \blacktriangle , 8% Zn



Fig. 2 Rate of formation of CO_2 over various catalysts as a function of partial pressure of O_2 . Symbols as in Fig. 1



Fig. 3 Comparison of rates of formation of products at O_2 pressure of, (a) 2.15 kPa and (b) 17.5 kPa, as a function of % Zn content of catalysts. \blacksquare , Benzonitrile; \Box , carbon dioxide

Zn catalyst also deviates from the general pattern of dependence and this catalyst showed formation of surface ZnO according to XPS analysis.

Fig. 4 shows the variation of the selectivity for benzonitrile formation as a function of partial pressure of O_2 . At low O_2 pressures the catalysts are selective for benzonitrile, while at high O_2 pressure the selectivity for carbon oxides, especially CO_2 , approaches 100%.

X-Ray Diffraction Analysis

The X-ray diffraction patterns of some of the catalysts before and after use at 42.5 kPa pressure of O_2 are given in Fig. 5. No new phases are formed during use, except for the 16% Zn catalyst that shows a slight increase in X-ray lines suggesting formation of ZnO. The characteristics of the samples and the negligible amounts of impurities found are given in Table 1. From the values of the *c* axis which were found to be within 11.78–11.80 Å, x values of *ca*. 0.2–0.35 were estimated for the fresh samples using the relationship published by Rao.⁹



Fig. 4 Variation of selectivity to benzonitrile with partial pressure of O_2 . Symbols as in Fig. 1



Fig. 5 X-Ray diffraction patterns of some fresh and used catalysts. (a) 0% Zn before use; (b) 0% Zn after use; (c) 4% Zn before use; (d) 4% Zn after use; (e) 8% Zn before use; (f) 8% Zn after use; (g) 16% Zn before use; (h) 16% Zn after use

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 Table 1
 Phase composition of samples before and after use^a according to XRD

	main	phase	impurities		
sample	before	after	before	after	
0% Zn 4% Zn 8% Zn 16% Zn	tetragonal tetragonal tetragonal tetragonal	tetragonal tetragonal tetragonal tetragonal	Y ₂ BaCuO ₅ ^b none BaCuO ₂ ^b unknown ^b	Y ₂ BaCuO ₅ ^b none none unknown ^b	

a After use at 42.5 kPaO₂ pressure. ^b Very low concentration.

XPS Analysis

Table 2 lists the binding energies (E_b) for the various core levels measured for fresh samples and after use at different conditions. The Cu $2p_{3/2}$ and Cu $L_{2,3}M_{4,5}M_{4,5}$ lines showed large differences, while Zn $2p_{3/2}$ and Zn LMM lines were almost unaffected. The differences for O 1s and various Y and Ba lines were very small. The XPS data were quantified and the atom % excluding oxygen were calculated. The main differences were observed in the concentration of Zn and Cu, and are shown in Table 3. The Y/Ba ratio for fresh catalysts was generally constant irrespective of Zn content, but showed a slight increase after use.

Ba 4d and Y 3d Spectra

In Fig. 6 are shown Ba 4d representative spectra for a sample freshly prepared and after use at high O_2 pressures. The curve form and position for used samples, Spectrum (b), suggests predominance of a single Ba species, most likely that present in the surface layer.¹⁹ Subtraction of this species from the spectrum for the fresh sample, Spectrum (a), produces a difference spectrum (c), which is representative of the bulk states.¹⁹ Attempts to calculate a difference spectrum for the Y 3d spectra failed due to small splitting between the 3d components.

O 1s Spectra

Fig. 7 shows O 1s spectra for fresh and used catalysts. The O 1s spectra are dominated by a component at *ca*. 531.5 eV similar to those of hydroxide and carbonate compounds, such as $Ba(OH)_2$, $BaCo_3$ and $Y(OH)_3$.¹⁹ A smaller contribution is made by a component at *ca*. 529 eV, representing the bulk O 1s state.¹⁹ Small variations are observed in the relative contributions to the spectra of the carbonate and hydroxide components with increasing Zn content, spectra (*a*)–(*d*). Fig. 8 shows the difference spectra, obtained by subtracting spectra in Fig. 7. The O 1s binding energies for (*a*), (*b*) and (*c*), are 529.1, 528.7 and 528.1 eV, respectively. For

Table 2 Binding energies and half widths, in brackets, (eV) of various core levels^{*a*} for $YBa_2(Cu_{1-y}Zn_y)_3O_{6+x}$ catalysts

y (%)	O 1s	Y 3p	Y 3d	Ba 3d	Ba 4d	Cu 2p	Cu LMM ^b	Zn 2p
016	531.3-531.4	299.9-300.4	157.2–157.7	779.7–779.9	89.2-89.3	933.5-933.8	917.0-917.7	1021.5-1021.6
fresh	(2.3 - 2.5)	(1.9 - 2.9)	(3.3 - 3.8)	(2.2 - 2.6)	(2.2 - 4.7)	(3.1-3.6)	(5.5-6.0)	(1.4-1.7)
0–16	531.6	300.3-300.4	157.2-157.4	780.0-780.1	89.6-89.7	933.0-933.1 ^d	916.4-916.5	1021.7-1021.9
used	(2.3 - 2.6)	(1.7 - 3.0)	(3.4-3.8)	(2.3 - 2.4)	(4.3)	(1.9 - 2.1)	(3.2-3.9)	(1.9 - 2.3)
0-16	531.4-531.5	300.3-300.4	157.3-157.7	779.8-780.0	89.4-89.6	933.5-933.6	918.1-918.3	1021.5-1021.8
used ^e	(2.5-3.4)	(1.5 - 2.9)	(3.4-3.8)	(2.2 - 2.4)	(2.2 - 4.3)	(2.6 - 3.3)	(2.9 - 3.7)	(1.9 - 2.2)
Cu ₂ O	530.9	. ,		. ,	. /	932.9ª	916.4	, ,
2	(2.3)					(1.6)	(2.9)	
CuO	530.0					934.0	917.7	
	(1.7)					(3.4)	(3.2)	
ZnO	530.4						. ,	1021.6
	(2.4)							(2.0)

^{*a*} Y $3p_{3/2}$, Y $3d_{5/2}$, Ba $3d_{5/2}$, Ba $4d_{5/2}$, Cu $2p_{3/2}$, Zn $2p_{3/2}$. ^{*b*} L_{2,3}M_{4,5}M_{4,5} kinetic energy. ^{*c*} Used at low O₂ pressure. ^{*d*} No satellite. Otherwise a satellite at *ca*. 942 eV. ^{*c*} Used at high O₂ pressure.

Table 3 Data for satallite and main line^{*a*} of $Cu 2p_{3/2}$ and Zn atom % for various $YBa_2(Cu_{1-y}Zn_y)_3O_{6+x}$ catalysts

		binding energy/eV			Cu ^{II} (%)	Cu ^{II}	
y (%)	intensity ratio sat./main line	sat.	main line	- Zn (%)	(Y + Ba + Cu + Zn)	Cu	$r_{tol}/(\mu mol m^{-2} min^{-1})$
0	0.50	942.4	933.9	0	42	0.77	_
0, used ^{b}	0.60	942.1 (4.9)	933.8 (3.6)	0	48	0.92	230
0, used ^c	0		933.2 (2.1)	0	(68) ⁴	0	15
1.67, used ^b	0.56	941.8 (5.0)	933.5 (3.9)	1.1	45	0.86	100
4.0	0.50	942.3 (5.2)	933.8 (3.7)	1.6	37	0.77	
4.0, used ^{b}	0.57	942.3 (5.1)	933.6 (3.6)	2.7	39	0.88	58
4.0, used ^{c}	0		933.0 (1.9)	1.3	$(67)^{d}$	0	8
6.70, used ^b	0.60	942.1 (5.1)	933.7 (3.7)	1.9	39	0.92	77
8.0	0.47	942.4 (5.2)	933.7 (3.6)	2.1	32	0.72	_
8.0, used [*]	0.58	942.1 (5.1)	933.7 (3.5)	2.9	38	0.89	100
8.0, used ^{c}	0	_	933.1 (1.9)	2.0	(62) ^{<i>a</i>}	0	12
Cu ₂ O	<i>ca</i> . 0	-	932.9 (1.6)			0	
CuO	0.65	942.4 (5.1)	934.2 (3.6)		100	1.00	—

" Fitted with Gaussian components." Used at high O2 pressure. Used at low O2 pressure. (%).

16% Zn catalyst a second component at 530.5 eV in the difference spectrum is obtained. This value suggests formation of ZnO.²⁰ O 1s spectra for catalysts used at high O₂ pressure were similar to each other and a representative is shown in Fig. 7(e). These spectra were in general slightly different from those of the fresh catalysts, Fig. 7(c). Difference spectra gave single O 1s components between 529.5 and 529.7 eV, Fig. 8(d). Catalysts used at low O₂ pressure did not show this difference, but slightly narrowed peaks with increased intensity around 531 eV. Subtraction of spectra of catalysts used at low O₂ pressure from those used at high pressure, gave difference spectra with peaks at 529.9–530.1 eV, e.g. Fig. 8(e). These positions compare well with those of CuO given in Table 2.

Cu 2p Spectra

Fig. 9 shows Cu 2p spectra for fresh and used catalysts, Cu₂O and CuO. The Cu 2p spectra for Cu^{II} state are associated with strong satellite features, whereas for Cu^{II} state, satellite features are absent,²¹⁻²³ Fig. 9(f) and (g). The small structure at 942 eV and asymmetry observed in the main line of Fig. 9(f), are due to a contribution from surface CuO.²¹ Fig. 9(a) for fresh 0% Zn catalyst shows the predominance of the Cu^{II} state, but the Cu^I state is also present in this catalyst as could be noticed from the satellite/main line intensity ratio, which is less than 0.65 obtained for pure CuO, Table 3. Catalysts used at high O₂ pressure, *e.g.* Fig. 9(b), showed higher Cu^{II} concentration, whereas those used at low pressure, *e.g.* Fig. 9(c), showed complete absence of the satellite peak. The narrow main line at lower E_b indicates the presence of only the Cu^{II} state.

Cu LMM Auger Spectra

The Cu $L_{2,3}M_{4,5}M_{4,5}$ Auger spectra were also determined for the various catalysts and for reference Cu₂O and CuO. For fresh catalysts an intermediate electron kinetic energy of *ca.* 917.0–917.7 eV, and a broad featureless peak different from those of copper oxides were obtained, see Table 2. Catalysts used at high O_2 pressure gave sharp Auger peaks at higher kinetic energy, *ca.* 918.1–918.3 eV, which are similar to that of CuO. Those used at low O_2 pressure, gave Auger peaks shifted to 916.4–916.5 eV, identical to Cu₂O. Cu⁰ is not formed as no sharp peak at 919.0 eV²¹ was observed.

Discussion

XRD Analysis

Y-Ba-Cu-O phases are prepared by heating mixtures of metal oxides and/or salts under appropriate conditions, thus, an important issue concerns the purity and stability of the final materials. From the XRD results presented in Fig. 5 and Table 1, it is seen that the samples prepared contain contaminants only in very low concentrations. It is also noticeable that up to 8% Zn substitution, XRD studies do not show bulk decomposition of catalyst upon use in ammoxidation. All the catalysts retained their original tetragonal structure. Similar results were obtained in an earlier study of the nonsubstituted material.² For the 16% Zn catalyst larger changes are observed. This may be associated with the fact that the Zn content is close to the limit of substitution which is ca. 16%,17 hence segregation of ZnO can possibly occur. Consequently, the results for this catalyst should be considered in light of its non-ideal composition.

XPS Analysis

XPS analysis of Y-Ba-Cu-O phases^{19,24,25} has shown that their surfaces are contaminated with degradation products such as BaCO₃, Y(OH)₃, Y₂BaCuO₅, CuO, arising from reaction with atmospheric water and CO₂. In the present investigation, similar results are observed for both freshly prepared samples and those used at various conditions. These are noticeable in Table 2 for surface states with E_b of 157.5 eV for Y $3d_{5/2}$, 779.9 eV for Ba $3d_{5/2}$ and 89.4 eV for Ba J. CHEM. SOC. FARADAY TRANS., 1991, VOL. 87



Fig. 6 Ba 4d spectra for (a) a representative fresh catalyst, (b) used catalyst, and (c) their difference. (d) is obtained by smoothing (c) by (31, 2)

 $4d_{5/2}$, which are typical of the contaminants mentioned above.¹⁹ However, contributions from the bulk states are also observed as is evident from the difference spectrum in Fig. 6(c) and the O 1s difference spectra with $E_{\rm b} \approx 529$ eV, Fig. 8. Concerning Cu states, fresh samples show predominance of Cu^{II} state, although existence of Cu^I states can be concluded from the satellite/main line intensity ratio which is less than the ratio for CuO. This observation is consistent with the results of other investigators.²⁶ For used samples, the major difference is in the oxidation states of the copper observed. Almost 100% Cu^I and Cu^{II} states are observed after use at low and high O₂ pressure, respectively, indicating that the surface structure is quite different from that of the bulk. However, considering that the Ba 4d photoelectron has almost three times as much kinetic energy as the Cu 2p and must be collected from a rather thicker layer, the formation of a surface layer containing either Cu^I or Cu^{II} can be imagined to be limited to a very thin overlayer ca. a few tens of angstroms. With these results and those of the XRD discussed above we conclude that a thin overlayer is formed over Y-Ba-Cu-O phases and that during reaction this overlayer is fully developed and protects the material from further decomposition.



Fig. 7 O 1s spectra for fresh and used catalysts. (a) 0% Zn, fresh catalyst; (b) 4% Zn, fresh catalyst; (c) 8% Zn, fresh catalyst; (d) 16% Zn, fresh catalyst; (e) 8% Zn, used at high O₂ pressure; (f) 8% Zn, used at low O₂ pressure

Model of the Y-Ba-Cu-O Catalysts and their Reactivity

The overlayer as already discussed may contain various segregated products including copper oxides and Y₂BaCuO₅. The influence of these compounds is of importance and has been considered in our earlier studies. In toluene ammoxidation over a Y₂BaCuO₅ sample,⁶ we found the activity and selectivity towards benzonitrile formation to be low. A major observation was that a sharp transition in activity as a function of O₂ partial pressure was not noticed for Y₂BaCuO₅ as is the case for Y-Ba-Cu-O. Our recent study²⁷ also showed major differences between copper oxides and Y-Ba-Cu-O phases, e.g. the rate for formation of benzonitrile over Y-Ba-Cu-O passed through an optimum as a function of partial pressure of O_2 , whereas over copper oxides this rate showed different behaviour. This study, also showed that although the formation of benzonitrile and CO₂ could be associated with Cu^I and Cu^{II} states, respectively, correlation of activity to surface concentrations of Cu species could not fully account for the observed reactivity. In the present investigation, this is also found to be the case as could be noticed from comparison of rates with concentrations of Cu species, Table 3. These results suggest influences by bulk material. Influences of bulk oxygen contents of the Y-Ba-Cu-O on reactivity was also observed in our earlier studies.^{2,6,27} It was found that $YBa_2Cu_3O_6$, was more active and selective than YBa₂Cu₃O₇, nominal compositions, when used under identical reaction conditions. This was the case even though XPS analysis did not show significant differences between their surface compositions. However, analysis of the bulk oxygen content revealed large differences. Therefore, it seems that the reactivity of $YBa_2Cu_3O_{6+x}$ and its substituted analogues can be modelled to that of a supported active phase with strong influence from the support. In this case, the overlayer is the active phase, while bulk Y-Ba-Cu-O acts as the support.

The reactivity of all the samples has several features in common as could be observed from Fig. 1 and 2. At low O_2



Fig. 8 O 1s difference spectra for fresh and used catalyst obtained by analysing spectra in Fig. 7. (a) 7(b)-7(a); (b) 7(c)-7(a); (c) 7(d)-7(a); (d) 7(e)-7(c); (e) 7(e)-7(f)

pressures, benzonitrile is selectively formed, whereas at high pressures, CO_2 is the selective product with the 0% Zn sample showing the highest activity in both cases. Zn substitution affected considerably the transition from selective to non-selective reaction.

The fact that benzonitrile and CO_2 are selectively formed at low and high O_2 pressures, respectively, can be explained by the site-isolation theory of Callahan and Grasselli.^{28,29} This requires the number of oxygen species surrounding the hydrocarbon to be limited and of appropriate bond energy in order to avoid complete oxidation. With increase in O_2 pressure, the number of surface oxygens increases and favours combustion. However, in earlier investigations,^{6,13,27} similar dependences as in Fig. 1 and 2 were explained on the basis that at low O_2 pressure, Cu^1 sites are associated with the formation of benzonitrile, whereas at high pressures, Cu^{II} sites are transformed to higher oxidation states leading to transition of the reaction mechanism from selective to non-



Fig. 9 Cu 2p spectra for fresh and used catalysts, including reference copper oxides. (a) 0% Zn, fresh catalyst; (b) 0% Zn, used at high O₂ pressure; (c) 0% Zn, used at low O₂ pressure; (d) 8% Zn, used at high O₂ pressure; (e) 8% Zn, used at low O₂ pressure; (f) Cu₂O; (g) CuO

selective oxidation, as the nature of surface oxygen species changes from O^{2-} to $O^{-,6,30,31}$ This explanation is consistent with the XPS analysis that showed existence of Cu¹ and Cu^{II} states at low and high O₂ pressures, respectively.

Influence of Zn Substitution on Structure and Reactivity

Zn substitution in the lattice of Y-Ba-Cu-O affects its structure and properties.^{16,17} These influences may not be restricted to bulk properties, but can also be reflected in the behaviour of the surface overlayer. The reactivity of the overlayer can be influenced by Zn substitution which in general decreases the number of Cu species, which is a more active species for oxidation. Also, the number of Cu species available for reaction can depend on dispersion, crystallisation or segregation of Zn phases. Thus, at low Zn concentration, Zn may be well dispersed at the surface reducing the number of active Cu species. At higher Zn concentrations, crystallisation

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or segregation can occur increasing the number of active Cu species. Support for this behaviour is found by considering the variation of surface Zn content as it was obtained from XPS data, cf. Table 3. Thus, the variation of dispersion of Zn can explain the minimum in rate with Zn content which was observed for the formation of both benzonitrile and CO_2 at low and high O_2 pressures, respectively. An additional factor which could be of importance is that Zn substitution in the bulk can affect the surface structure. The change from selective to non-selective region with increase in O_2 pressure is, as was discussed above, a consequence of change of Cu valence.

Considering the influence of segregated phases or cooperation between phases,³² such an effect will not only be reflected in the activity level but possibly also in the selectivity. From the plot shown in Fig. 4, it is seen that selectivity for benzonitrile formation over the samples is basically the same, hence synergy effects from segregated phases, seem to be absent.

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