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SELECTIVE PRODUCTION OF METHANOL FROM SYNGAS OVER $LaTi_{1-x}Cu_xO_3$ MIXED OXIDES

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Carbon monoxide hydrogenation was studied over partially substituted copper-containing $LaTi_{1-x}Cu_xO_3$ oxides and on copper supported on La_2O_3. The unsubstituted ($x = 0$) oxide was weakly active for CO hydrogenation, whereas all the other oxides were more active and exhibited high selectivity to methanol. Particularly, for substitutions $x = 0.5$–0.6, where the perovskite structure was observed, CO conversions close to 22% and selectivity close to 80% were found. Cu/La_2O_3 was, however, less active and yielded CO_2 and hydrocarbons as the major products. Using X-ray photoelectron spectroscopy it was determined that under reaction conditions copper exists as reduced species. The L_3VV X-ray induced Auger transition at 1849.2 eV observed for a representative $LaMn_{0.5}Cu_{0.5}O_3$ catalyst prereduced and used in CO hydrogenation at 573 K, suggests that Cu^+ species dominates in spent catalyst. These Cu^+ species are believed to be stable under reaction conditions in the perovskite structure, only a slight Cu enrichment occurs on the topmost layer of catalysts.

Keywords: CO hydrogenation, methanol production, Cu-containing mixed oxides, catalyst characterization

1. Introduction

The copper-containing catalysts employed in industry for the production of methanol from syngas ($CO + H_2$), commonly contain one or more host oxides. Since the discovery of the ICI process in the 1960's [1], the key development in methanol synthesis technology has been the catalyst. It has been observed that the Cu/ZnO catalyst can be promoted with alkali compounds [2,3] and transition or rare-earth metal oxides to increase the methanol yield or to shift the product distribution to higher C_2^+ alcohols [4–8].

Besides the classical Cu/ZnO system, other zinc-free catalysts have also been investigated. Alloys of copper with various rare-earth elements (CuRE) have been studied by Owen et al. [9] and by Nix et al. [10]. These authors found that exposure of the CuRE alloy to syngas mixture resulted in a catalyst consisting of copper crystals and a RE oxide phase in which copper was highly dispersed.

These catalysts were even more active, especially at lower temperatures, than the conventional $Cu/ZnO(Al_2O_3)$ formulation, due to the copper phase associated with the RE oxide.

A similar approach to the preparation of copper-based catalysts, active in the methanol synthesis from syngas, has been provided by solid state chemistry, through stabilization of copper in mixed oxides of well-defined crystalline structure, e.g. ABO_3 perovskites. The crystalline structure of perovskite oxides with its capability to accommodate many different cations [11] affords an interesting frame of reference to test the effect of substitution of B cations by copper in the perovskite on the catalytic behaviour. Accordingly to these ideas, Broussard and Wade [12] first and Brown Bourzutschky [13] have noted that substitution of Mn by Cu in $LaMnO_3$ shifted the product distribution from 100% hydrocarbons to methanol and small amounts of C_2^+ oxygenates.

In our laboratory we have recently synthesized coppercontaining perovskites of the type $LaM_{1-x}Cu_xO_3$ (M = Mn [14], Ti [15]) with the aim of understanding the effect of partial replacement of Mn or Ti by copper on the catalytic behaviour for CO hydrogenation. In this work we report activity data of $LaTi_{1-x}Cu_xO_3$ compounds for this reaction, under mild reaction conditions, and some characterization results by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) of the spent catalysts, in order to assess the chemical state and dispersion changes of Cu during operation.

2. Experimental

CATALYST PREPARATION

A series of $LaTi_{1-x}Cu_xO_3$ ($0 \le x \le 1$) compounds were prepared by amorphous citrate decomposition. For the synthesis, a concentrated solution of $La(NO_3)_3.6H_2O$ (Merck, p.a.) and $Cu(CH_3COO)_2.H_2O$ (Carlo Erba, reagent grade) was mixed with a Ti solution prepared from $(BuO)_4Ti$ (98% Ti, Aldrich Chemie) in desired proportions. Citric acid was added and the solution was evaporated at 343 K until dryness and then at 383 K for 16 h to produce a totally amorphous precursor. Finally, the product was calcined in air at 973 K for 5 h. For purposes of comparison, a 5% CuO/La_2O_3 catalyst was also prepared by impregnation of La_2O_3 with a $Cu(CH_3COO)_2.H_2O$ in excess of solution. After water removal at 343 K, the solid was dried at 343 K and then calcined in air in two steps: 623 K for 1 h and 773 K for 4 h.

All catalysts were tested in a single-pass, fixed bed, flow reactor. Feed gases were H_2 (99.995% volume, Argon Co.) and CO (99.97% volume, Matheson Co.), metered by means of Brooks mass flow controllers. Details about this configuration can be found elsewhere [16]. Organic products, CO, H_2 and H_2O were analyzed by gas-chromatography. All catalyst tests were run with synthesis gas of molar ratio $H_2:CO = 3$ at a GHSV (STP) of 3500 h^{-1}. Before synthesis gas exposure, the calcined catalysts were reduced in situ with a mixture of 20% H_2 in He in three steps: 473–573–623 K, maintaining half an hour each temperature. Once the catalyst was reduced, the temperature was set at 473 K and the synthesis gas admitted at atmospheric pressure; then temperature increased slowly up to 523 X and pressure up to 5 MPa. These conditions were maintained for 15 h on-stream, monitoring the effluent by gas chromatography at 30 min intervals. Subsequently, reaction temperature increased up to 573 K, and after a break in time of 3 h to reach steady state conditions, the first data point was taken.

X-ray photoelectron spectra (XPS) were obtained by using a Leybold LHS 10 equipped with a hemispherical electron analyzer and a Mg K_α X-ray ($h\nu = 1253.6$ eV) source. Although surface charging was observed in all samples, accurate binding energies (BE) could be determined by charge referencing with the La $4d_{5/2}$ peak at 101.4 eV or La $3d_{5/2}$ at 834.9 eV. X-ray diffraction patterns were obtained with a Philips PW 1716/30 diffractometer using nickel-filtered Cu K_α radiation over the range of 2θ angles 5–70° and the d-spacings were compared with the ASTM powder files to confirm sample identity. The BET areas were calculated from the N_2 isotherms at 77 K.

3. Results

X-RAY DIFFRACTION

X-ray diffraction (XRD) patterns of the calcined samples with nominal composition $LaM_{1-x}Cu_xO_3$ (M = Mn, Ti, and $0 \le x \le 1$) have been obtained. For the $LaMn_{1-x}Cu_xO_3$ series, diffraction lines were indexed to the perovskite structure in the composition range $0 < x < 1$, whereas for the fully substituted sample ($x = 1$) the only phases present were La_2CuO_4 and CuO [14]. This last result contrasts with literature findings. For instance, a pure $LaCuO_3$ phase has been reported by Demazeau et al. [17], whereas Gallagher et al. [18] and Vogel et al. [19] found a mixture of La_2CuO_4, perovskite and CuO phases in the preparation of Cu-rich $LaMn_{1-x}Cu_xO_3$ ($0.7 \le x \le 1.0$) compounds. The XRD patterns were even more complex for the $LaTi_{1-x}Cu_xO_3$ series. For the unsubstituted ($x = 0$) compound, lines which can be indexed as belonging to $La_2O_3.2TiO_2$, and $La_2O_3.2TiO_2$ and $La_2O_3.3TiO_{1.9}$ were observed. The absence of $LaTiO_3$ phase indicates that such structure is not obtained under the conditions of the synthesis. Many titanates of the type $MTiO_3$ (M = divalent cation) have been synthesised at moderate temperatures [20–22], however, as Ti^{3+} ions are present in $LaTiO_3$, the stabilization of these ions in air requires a very high calcination temperature. For $x = 0.2$ the dominant XRD peaks correspond to the same mixed oxides, but other weak peaks indexed as $2La_2O_3.3TiO_2$, CuO, and La_2CuO_4 oxide lines are observed. For substitutions in the range $0.3 \leq x \leq 0.8$ the perovskite structure is clearly distinguished; only very weak reflections indexed as CuO can be observed in the background. XRD patterns were also obtained for samples reduced at 973 K. For the $LaMn_{1-x}Cu_xO_3$ series the reduction products were La_2O_3, $La(OH)_3$, MnO and Cu. XRD peak intensities of MnO and Cu decreased and increased, respectively, with Mn substitution. Particularly, the bulk La_2O_3 phase was almost quantitatively transformed into the $La(OH)_3$ phase upon prolonged exposure to moisture of the fully substituted sample ($x = 1$). For the $LaTi_{1-x}Cu_xO_3$ catalyst series the reduction products are again more complex. The XRD pattern of $LaTiO_3$ after reduction is similar to that of the calcined sample. Reduction of substituted $LaTi_{1-x}Cu_xO_3$ ($0.3 \leq x \leq 0.6$) samples gave rise to the products La_2O_3, $La_2O_3.3TiO_{1.9}$ and Cu. Only for highly substituted ($x = 0.8$ and 1.0) samples were the $La(OH)_3$ and Cu phases observed.

X-RAY PHOTOELECTRON SPECTROSCOPY

Fig. 1 shows the copper core level spectra for the spent catalysts. The binding energies (BE) for O 1s and the principal Cu 2p and Ti 2p peaks are summarized in table 1. From this table, it results that the BE values of Cu 2p electrons are very similar from sample to sample and somewhat lower than that of Cu^{2+} ions. Identification of the chemical state of copper was complicated since the BE for Cu^0 nd Cu^+ are almost the same, appearing ca. 1.3 eV below that of Cu^{2+} ions. Cupric ions can easily be distinguished by the appearance of shake-up satellite structures by ca. 9.8 eV above the principal Cu 2p peaks of the photoelectron spectrum. As can be seen, for substitution $x = 1.0$, and to a lesser extent for $x = 0.6$, shake-up satellite peaks are observed. The presence of Cu^{2+} ions in $LaCuO_{2.5}$ ($x = 1.0$) catalyst after prereduction and use is not surprising. As revealed by the XRD pattern, Cu crystallites were clearly distinguished which is also in agreement with the reddish colour of the catalysts. The presence of both Cu^0 and Cu^{2+} ions is expected because the reduction at 573 K only eliminates the CuO phase,

$$CuO + La_2CuO_4(LaCuO_{2.5}) + H_2 \rightarrow Cu^0 + La_2CuO_4 + H_2O$$

while the La_2CuO_4 phase appears to be stable up to ca. 673 K. In order to monitor the changes undergone by copper upon H_2-reduction and use, the Cu/La surface atomic ratios have been calculated. In this calculation, intensities of Cu 2p and La 4d peaks averaged for the number of scans, published atomic sensitivity factors [23], and a correction to account for the efficiency of the detector have been used. In fig. 2 the XPS Cu/La atomic ratios of $LaTi_{1-x}Cu_xO_3$ samples are plotted against the stoichiometric ones. It is observed that the Cu/La ratio increases with x, but deviates slightly from the stoichiometric composition, i.e., the surface Cu/La ratios become larger than x. Similarly, the XPS Cu/La ratio for the lanthana-supported copper catalyst is essentially the same than the

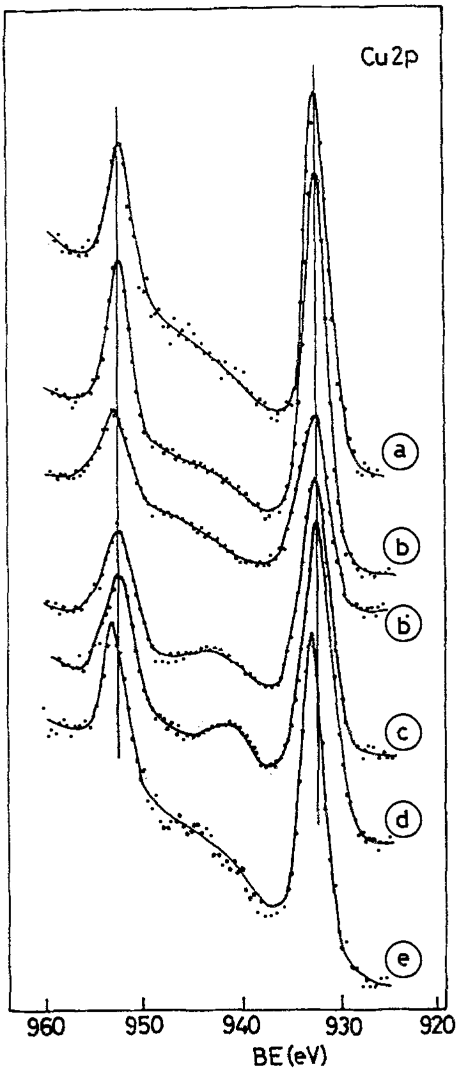

Fig. 1. Copper 2p core level spectra of various $LaTi_{1-x}Cu_xO_3$ oxides, taken after reduction at 573 K and used for reaction. (a), $LaTi_{0.8}Cu_{0.2}O_3$; (b), $LaTi_{0.5}Cu_{0.5}O_3$; (b′), $LaMn_{0.5}Cu_{0.5}O_3$; (c), $LaTi_{0.4}Cu_{0.6}O_3$; (d), $LaCuO_3$; (e), Cu/La_2O_3.

$x = 0.2$ sample, though the latter catalyst has a lower bulk Cu content. All these results indicate that surface of $LaTi_{1-x}Cu_xO_3$ catalysts becomes slightly Cu-enriched during reduction and use in reaction. However, for Cu/La_2O_3 catalyst it seems that big Cu crystals build up on top lanthana surface.

CATALYTIC ACTIVITY

Catalytic activity data for CO hydrogenation as a function of the substitution degree (x) are summarized in table 2. The results reported are the values obtained

Table 1
BE (eV) of core electrons in spent catalysts

Catalyst	O 1s	Cu $2p_{3/2}$	Ti $2p_{3/2}$	La $4d_{5/2}$
$LaTiO_3$	529.6	–	457.4	101.4
$LaTi_{0.8}Cu_{0.2}O_3$	529.2	932.8	457.3	101.4
$LaTi_{0.5}Cu_{0.5}O_3$	529.6	933.0	457.2	101.4
$LaTi_{0.4}Cu_{0.6}O_3$	529.9	933.1	457.3	101.4
$LaCuO_3$	530.4	932.5	–	101.4
Cu/La_2O_3	531.2	933.6	–	101.4

Table 2
Activity and product distribution for all catalysts

Catalyst	x_{CO}(%)	Selectivity (%)					
		MeOH	CO_2	CH_4	C_2H_6	DME	C_2^+OH
$LaTiO_3$	0.6	31	31	29	–	9	–
$LaTi_{0.8}Cu_{0.2}O_3$	12.7	39	34	9	6	10	2
$LaTi_{0.5}Cu_{0.5}O_3$	22.4	78	13	5	1	1	2
$LaTi_{0.4}Cu_{0.6}O_3$	21.0	83	10	4	1	1	2
$LaCuO_3$	21.3	73	15	7	2	1	1
Cu/La_2O_3	7.7	18	38	25	10	9	–

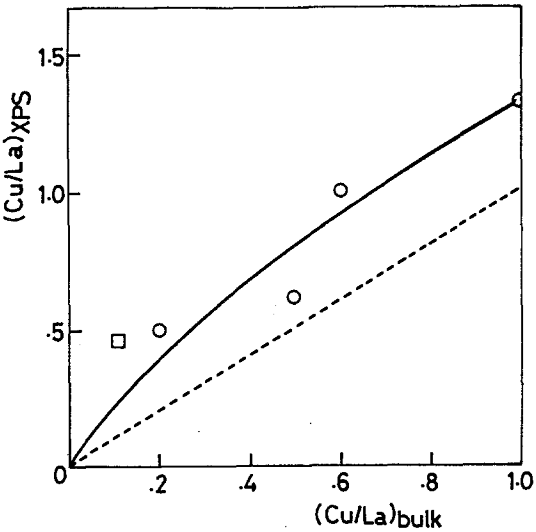

Fig. 2. Dependence of the bulk Cu/La atomic ratios on the surface Cu/La ratios as measured from X-ray photoelectron spectra. Square refers to the Cu/La_2O_3 catalyst. Dashed line corresponds to the stoichiometric composition.

Table 3
Intrinsic rates of methanol production

Catalyst	μmol MeOH/g cat·s	μmol CO ads/g cat	(g MeOH/m^2 Cu·h)×10^3
$LaTi_{0.5}Cu_{0.5}O_3$	1.56	219.3	23.5
$LaTi_{0.4}Cu_{0.6}O_3$	1.52	49.8	97.3
Cu/La_2O_3	0.12	378.6	1.0

after the catalysts had been on-stream for 3 h. The conversion level of CO strongly depends on the Cu substitution, attaining the highest values in the composition range $0.5 \leq x \leq 1.0$ and the lowest for $x = 0$. As both BET areas and metallic copper areas of the catalysts varied with Cu substitution, the intrinsic activities (or efficiency) have been calculated. Activities for the production of methanol were also normalized with respect to the Cu area of the prereduced catalysts (table 3). For the $LaTi_{1-x}Cu_xO_3$ catalyst series, the intrinsic activity passed through a maximum at $x = 0.6$, then decreased sharply for composition $x = 0.5$. Moreover, the La_2O_3 catalyst has an extremely low intrinsic activity as compared to those of $LaTi_{1-x}Cu_xO_3$ compounds.

The product distribution was also influenced by Cu substitution. Methane, ethane, dimethyl-ether and alcohols were the principal organic products. Carbon dioxide was also observed in the products. Table 2 summarizes the product distribution observed at a fixed set of reaction conditions. Unsubstituted $LaTiO_3$ produced CH_3OH, CO_2 and CH_4 with selectivities by about 30%, and substantially lower proportion of dimethyl-ether. Upon incorporation of Cu, the alcohols selectivity increased whereas that of methanation decreased. The overall selectivity pattern markedly varied for $0.5 \leq x \leq 1.0$. Interestingly, for $x = 0.5$ and 0.6 selectivity to methanol ranged from 78 to 83%, while that of CO_2 varied from 13 to 10%; other minor products for balance.

The product distribution obtained with the Cu/La_2O_3 catalyst resulted quite disimilar to that of the perovskites $x = 0.5$ and 0.6. In particular, methanol selectivity decreased markedly whereas CO_2, CH_4, C_2H_6, and C_2H_6O followed an opposite trend. It is also clear from table 2 that the product distributions of $LaTiO_3$ and Cu/La_2O_3 catalysts are similar. Moreover, none of them produces higher alcohols even though the conversion level of CO is ca. twelve times higher in the latter.

4. Discussion

The activity results presented in this study reveal that $LaM_{1-x}Cu_xO_3$ (M = Ti, Mn) compounds are highly active and selective in CO hydrogenation, methanol being the major hydrogenation product. As expected, the unsubstituted $LaTiO_3$ compound was almost inactive for the reaction. When Cu was substituted by Ti (or Mn), the CO hydrogenation activity increased drastically with increasing Cu substitution. These findings are similar to that reported early by Broussard and Wade [12] for a $LaM_{0.5}Cu_{0.5}O_3$ (M = Mn,Ti) perovskite and by Brown-Bourzutschky et al. [13] for $LaMn_{1-x}Cu_xO_3$ catalyst series. The methanol synthesis rate was observed to pass through a maximum at substitution $x = 0.6$. For this catalyst the methanol synthesis rate was 9.7×10^{-2} g/h.m^2, which is similar to the one found by Sheffer and King [3] for a 1.2 mol% K promoted unsupported Cu catalyst using similar reaction parameters. All these facts indicate clearly the importance of copper for both activity and selectivity toward methanol.

Owing to the small differences in the BE of Cu 2p levels of Cu^0 and Cu^+, the differentiation among these species by XPS alone becomes extremely difficult, if not impossible. This is feasible only through observation of the L_3VV X-ray induced Auger transition of copper. The modified Auger parameter α_A, defined by the equation,

$$\alpha_A = h\nu + KE_{LMM} - KE\ Cu\ 2p_{3/2}$$

is generally used. KE_{LMM} and KE Cu $2p_{3/2}$ are the kinetic energies of the L_3VV X-ray induced Auger emitted electrons and the Cu $2p_{3/2}$ photoemitted electrons, respectively. The X-ray induced Auger spectrum for a representative $LaMn_{0.5}Cu_{0.5}O_3$ catalyst prereduced and used in the CO hydrogenation at 573 K is shown in fig. 3. This catalyst was found to have the Cu L_3VV peak at 1849.2 eV, which agrees well with that at 1848.8 eV observed by Sheffer and King [3] for a prereduced and synthesis gas-exposed unsupported CuK0.36 catalyst, and that at 1848.9 eV found by Karwaci et al. [24] for cuprous oxide. Hence, as no other peak is observed in fig. 3 at energies as high as 1851.0 eV, [24], where both Cu^0 and Cu^{2+} species are expected to appear, it can be concluded that Cu^+ is the dominant copper species in the spent catalyst.

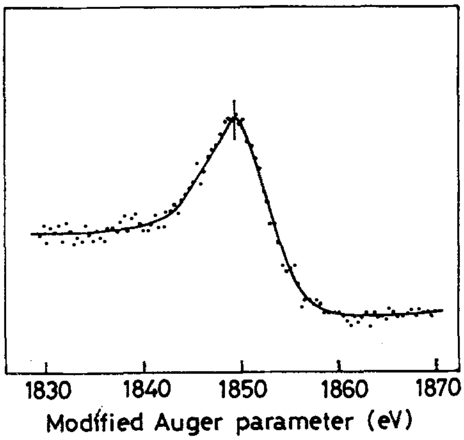

Fig. 3. L_3VV X-ray induced Auger transition for the $LaMn_{0.5}Cu_{0.5}O_3$ catalyst prereduced at 623 K and then used in CO hydrogenation at 573 K. The spent catalyst was transferred into the spectrometer under iso-octane to prevent oxidation of copper by air.

On the basis of this spectroscopic analysis, and considering that substitutions of M by Cu in the range $x = 0.5-1.0$ in $LaM_{1-x}Cu_xO_3$ compounds result in active and selective catalysts toward methanol synthesis, one would infer that Cu^+ locations should be responsible for methanol synthesis. Methanol synthesis activity has been correlated with the presence of cuprous ions in Cu/ZnO [25] and Cu/Cr_2O_3 [5] catalysts. In both cases, the host oxide stabilizes Cu^+ species by substitutional or interstitial occupancy in the ZnO lattice in the former case, and by solid-state reaction in the latter. The mechanism by which the perovskite lattice stabilizes Cu^+ ions can be envisaged by studying some bulk properties of the perovskite crystal. As it has been observed, TPR profiles of $LaMn_{1-x}Cu_xO_3$ [14] and $LaTi_{1-x}Cu_xO_3$ [15] catalyst series demonstrated that Cu^{2+} ions placed in the perovskite lattice become to be reduced at temperatures much higher than in CuO. Consequently, sintering of the resulting reduced copper phase is retarded with respect to the reduced bulk CuO or conventional supported catalysts.

The quite different catalytic behaviour of Cu/La_2O_3 catalyst and $LaTi_{1-x}Cu_xO_3$ compounds suggests that under the reaction conditions the structure and probably the chemical state of copper are disimilar. As observed by XRD and XPS, the used Cu/La_2O_3 catalyst possesses large Cu crystallites deposited on lanthana. The formation of hydrocarbons very likely occurs on metallic Cu. Since CO does not dissociate over Cu [26], reaction probably proceeds via hydrogenation of CO to form H_xCO intermediates, which then undergo dissociation to form CH_y species. Even though the dominant copper species in the used Cu/La_2O_3 catalyst is Cu^0 as concluded from the high proportion of hydrocarbons in the product distribution, the presence of a small part of ionic copper on the surface of Cu^0 crystals, or in close contact with them, cannot be excluded since it seems a requirement for the methanol synthesis.

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