

In celebration of the 60th birthday of Dr. Andrew K. Galwey

PHYSICOCHEMICAL AND CATALYTIC CHARACTERIZATIONS OF MATERIALS PREPARED FROM COPPER MALONATE BY THERMAL DECOMPOSITION OR CHEMICAL REDUCTION

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Abstract

Results of Carr and Galwey [1] concerning copper malonate (CM) decomposition in vacuo at 510 K prompted present studies on the utility of CM as a low-temperature precursor of oxide-supported copper catalysts. CM deposited upon metal oxides has been converted to copper particles by vacuum thermal decomposition or reduction with aqueous hydrazine. Using the dehydrogenation of isopropanol to acetone as a catalytic probe reaction, comparisons are made between levels of catalytic activity and selectivity induced in TiO₂, MgO and Ca(OH)₂ supports by copper deposited thereon. Effects of particle size, prerduction temperature, and support reducibility are described and evidence is given for a strong metal support interaction (SMSI)-like inhibition of activity of Cu/TiO₂ by prior high temperature reduction.

Keywords: catalysts, chemical reduction, copper malonate, kinetics, physicochemical and catalytic characterizations, thermal decomposition

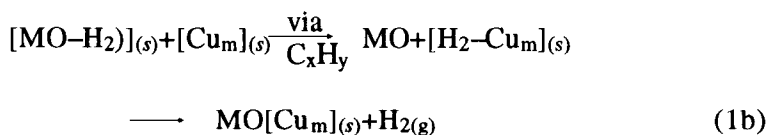
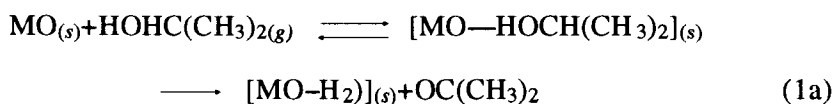
Introduction

The present work explores the possible applicability to catalyst preparation of results reported by Carr and Galwey [1] from their detailed studies of the thermal decomposition of copper malonate under continuous evacuation at 510 K. That work included characterization of the morphology of the decomposition product(s) by scanning electron microscopy (SEM), which revealed copper particles of fairly uniform size (0.1 to 0.3 μm) dispersed upon a filamentary carbonaceous residue. Kinetic analysis of plots of α , the fractional decomposi-

tion of copper malonate, *vs.* time of decomposition at 510 K under evacuation, led Galwey *et al.* [1] to conclude that the final stages of decomposition proceeded in a milieu involving a molten intermediate such as copper acetate. Shell formation, via bubbling of this decomposing intermediate, was invoked to explain the observed formation of the filamentary carbonaceous residue (C_xH_y). The reproduction of these observations in a second of our laboratories, including confirmation of 510 K as the relatively low temperature sufficing for production of copper particles, raised possibilities that the vacuum decomposition of copper malonate, previously dispersed upon metal oxide supports, might serve as a versatile low-temperature route to obtain various copper species finely dispersed thereon. Tests of these possibilities have involved comparison of the catalytic activities of ex-copper malonate (*xcm*) materials with those in the literature for oxide-supported copper materials prepared by more conventional methods [2, 3], and others obtained from colloidal copper hydrosols (*xcmhy*) [4]. The conversion used here as a probe of catalytic activity is the dehydrogenation of isopropanol vapour to acetone, $(-H_2)_{ip}$. Relevant information from previous studies in these laboratories upon this catalytic conversion [5, 6] included:

i) the fact that isopropanol vapour can reduce CuO or Cu₂O to metallic copper at temperatures >523 K, but that ongoing steady-state $(-H_2)_{ip}$ activity requires the coexistence of reduced copper and oxidised copper centres; and

ii) the likelihood of contributions by a dual-site, reverse-spillover type mechanism, involving isopropanol adsorption and activation upon support-related sites as per Eq. (1a), but with evolution of H₂ product into the gas phase dependent upon diffusion to and release from exposed metallic sites, as per Eq. (1b), [7]:



Also of interest in the present study were questions:

i) as to whether strong metal support interaction (SMSI)-like inhibition of catalytic activity of titania-supported copper, similar to that reported by Delk and Vavere [8], would occur after high temperature reduction (HTR); and

ii) whether presence of the filamentary carbonaceous residue, observed to accompany vacuum decomposition of copper malonate, might serve to promote

$(-H_2)_{ip}$ activity, or protect it against inhibitory factors. One possibility for promotion by the carbonaceous deposit was if it were to enhance Eq. (1b) above, i.e. reverse hydrogen spillover from IP activated on metal-oxide surface regions over to copper particles from whence H_2 product is desorbed in a rate-determining process. A possibility for protection by the carbonaceous deposit was that it might restrict HTR-induced migration of reduced metal oxide species onto copper particles, which otherwise could result in encapsulation/decoration of the metal particle surfaces and inhibition of $(-H_2)_{ip}$ activity. An inhibitory effect of that type, after HTR, was reported by Delk and Vavere [8] in respect of the hydrogenation of 2-methyl butanal to 2-methyl butanol over a conventionally prepared Cu/TiO₂ material. This was claimed by them to be the first example of such an inhibitory strong metal support interaction (SMSI) for a non-Group VIII metal. Recent work in our laboratories on the activity of TiO₂/Cu(*xcm*) material for the hydrogenation of acetone to isopropanol, $(+H_2)_{ac}$, confirmed that the $(+H_2)_{ac}$ catalytic activity of TiO₂/Cu(*xcm*) was indeed influenced by temperature of prior reduction, in ways symptomatic of an SMSI-type effect [4]: viz. good activity after low temperature reduction (LTR_{473 K}); loss of activity after high temperature reduction (HTR_{773 K}); but restoration of activity after a dual treatment of oxidation at 673 K plus LTR_{473 K}. Thus it was of interest to determine whether the TiO₂/Cu(*xcm*) materials would exhibit these symptoms of an SMSI-like effect, or whether they could be more resistant than conventionally-prepared material to inhibitory SMSI-like effects, by virtue of the carbonaceous co-deposit acting as a barrier-layer against migration of reduced TiO_x species onto the copper particles.

Experimental

Materials preparation from copper malonate precursor (xcm)

Blue crystals of hydrated copper(II) malonate CH₂(COO)₂-Cu-nH₂O were prepared as described in [1]. For later comparison with oxide-supported materials, some preliminary studies were made on the levels of $(-H_2)_{ip}$ activity attainable with the material obtained by introducing samples of these blue crystals into an evacuable reactor and taking them through the same vacuum-decomposition sequence as that employed by Carr and Galwey viz. 200 min at 510 K plus 20 min. at 540 K. These are designated by *xcmv*. A second preparative route, based upon production of colloidal copper particles [9] by reduction of deoxygenated copper malonate solution with hydrazine at 350 K, was also tested. Shortly after such production of copper hydrosols, an addition of finely-divided metal oxide was made under N₂, with the objective of attaching

thereto those newly formed colloidal copper particles. $\text{MgO}/\text{Cu}(xcmhy)$, $\text{TiO}_2/\text{Cu}(xcmhy)$ and, $\text{Al}_2\text{O}_3/\text{Cu}(xcmhy)$, materials were obtained via this hydrosol route when powdered MgO (Aldrich), TiO_2 (Degussa P25), or Al_2O_3 (Degussa Aerosol), was added as the support. The initial step in a third preparative route to 'copper supported on metal oxides' involved incipient wetness to disperse copper malonate over the surface of those metal oxides and also CaO . Partly because of its relatively low solubility, the copper malonate did not readily lend itself to dispersion onto these oxide supports by this 'incipient wetness' procedure at coverages much in excess of one monolayer equivalent (m.e.). Amounts of copper retained by the materials at that stage were determined by digestion of aliquots of each precursor in acid, followed by atomic absorption measurements of copper in the resulting solutions. Quantities of such dispersed copper malonate precursors, (*dcm*), were converted into catalytic materials by a vacuum decomposition procedure identical to the conditions established by Carr and Galwey [1] – such materials are designated by *x dcmV* e.g. $\text{TiO}_2/\text{Cu}(x dcmv)$.

Materials characterization procedures

Microgravimetric measurements (Sartorius and Cahn vacuum microbalances), were used: firstly, to evaluate metallic copper surface-areas of $\text{MO}/\text{Cu}(x dcmV)$ materials from observations on the small increases in sample mass resulting from oxidation at 360 K by nitrous oxide of the exposed Cu^0 surface present on the oxide-supported materials after their in-situ pre-reduction in H_2 at 473 K [10, 11]; and secondly, to obtain temperature-programmed reduction (TPR) profiles for subsequent in-situ reduction by H_2 . For the $\text{MO}/\text{Cu}(x dcmhz)$ and $\text{MO}/\text{Cu}(xcmhy)$ materials, BET surface areas were obtained with Micrometrics equipment, and TPR profiles were measured under a flow of 3% $\text{H}_2/97\%$ Argon at 1 atm pressure. Information on morphology of copper in the various *xcm* materials was obtained by electron microscopy (SEM and TEM). Comparisons of the catalytic activities/selectivities of the various oxide-supported *xcm* materials were initially made at reaction temperatures, T_{rx} , in the range 453 ± 20 K, using a continuous-flow microcatalytic reactor system equipped for intermittent sampling and GC analysis of the exit gas flow after 1 s contact with the materials prepared as per the above. A steady flow of isopropanol reactant, premixed at constant vapour pressure (40 torr) with argon carrier-gas (720 torr) was maintained for on-stream times needed to reach pseudo steady-state conversions. Catalyst aliquots were subjected in-situ to desired oxidising and/or reducing pretreatments at temperatures T_{ox} and /or T_{rd} respectively prior to monitoring their catalytic activities for highly selective

dehydrogenation of isopropanol vapour to acetone, $(-H_2)_{ip}$, at 453 K. Whenever $T_{rx} > 473$ K was used, products also included a complex mixture of oligomeric C_6 and C_9 products having much higher boiling points. Off-line separation and identification of some components of these liquid oils was made using capillary GC plus MS.

Results and discussion

XCMV material without metal oxide support

The SEM photographs in Fig. 1 illustrate marked changes observed in the morphology of the unsupported *xcmv* material, upon subjecting the as-stored material (photo 1A) to increasingly severe oxidations (photos 1B–1D). Comparisons of photo 1B with photo 1A shows that mild oxidation caused individual copper particles of size ca. $0.2 \mu\text{m}$, originally well separated in photo 1A, to join together in pairs and triads as in photo 1B. Photos 1C and 1D show that more severe oxidation caused those small aggregates to come together into larger agglomerates, resulting in some cases in the ‘balling-up’ of the copper component (photo 1D). Such behaviour could be understood in terms of progressive erosion of the filamentary carbonaceous deposit as a consequence of repetitive $(2\text{CuO} + \text{Carbon} \rightarrow \text{CO}_2 + \text{Cu}^0)$ plus $(\text{Cu}^0 + 1/2\text{O}_2 \rightarrow \text{CuO})$ sequences in the presence of oxygen at >523 K, which appear feasible in view of literature reports of some surface oxidation of small copper particles even in air at room temperature [11], and also of the capability of the $\text{Cu}^{2+}/\text{Cu}^0$ couple to promote the oxidation of carbon [12]. In the present case, the resulting erosion of filamentary carbon support apparently led to retreat of the partially oxidised copper particles towards one another and in some cases to ‘balling-up’ [13]. Electron microprobe analysis on ‘balled-up’ entities confirmed copper as the major component rather than carbon. Serious doubts as to the value of such unsupported *xcmv* materials as practicable catalysts in net oxidising conditions were raised by these observations. However, it was known from previous work [5] that isopropanol vapour provided a reducing rather than an oxidising environment and some measurements were made, at $T_{rx}=423$ K, of the $(-H_2)_{ip}$ activities of *xcmv* aliquots which had received pretreatment sequences not involving exposure to O_2 at $T_{ox} > 423$ K. Listed in Table 1 under $\%S(-H_2)$ and $\%C(-H_2)$ respectively are values for the selectivity and extent of conversion of isopropanol vapour to acetone observed in the exit gas flow, both after 15 min on-stream and after attainment of pseudo-steady-state activity by ≈ 5 h on-stream.

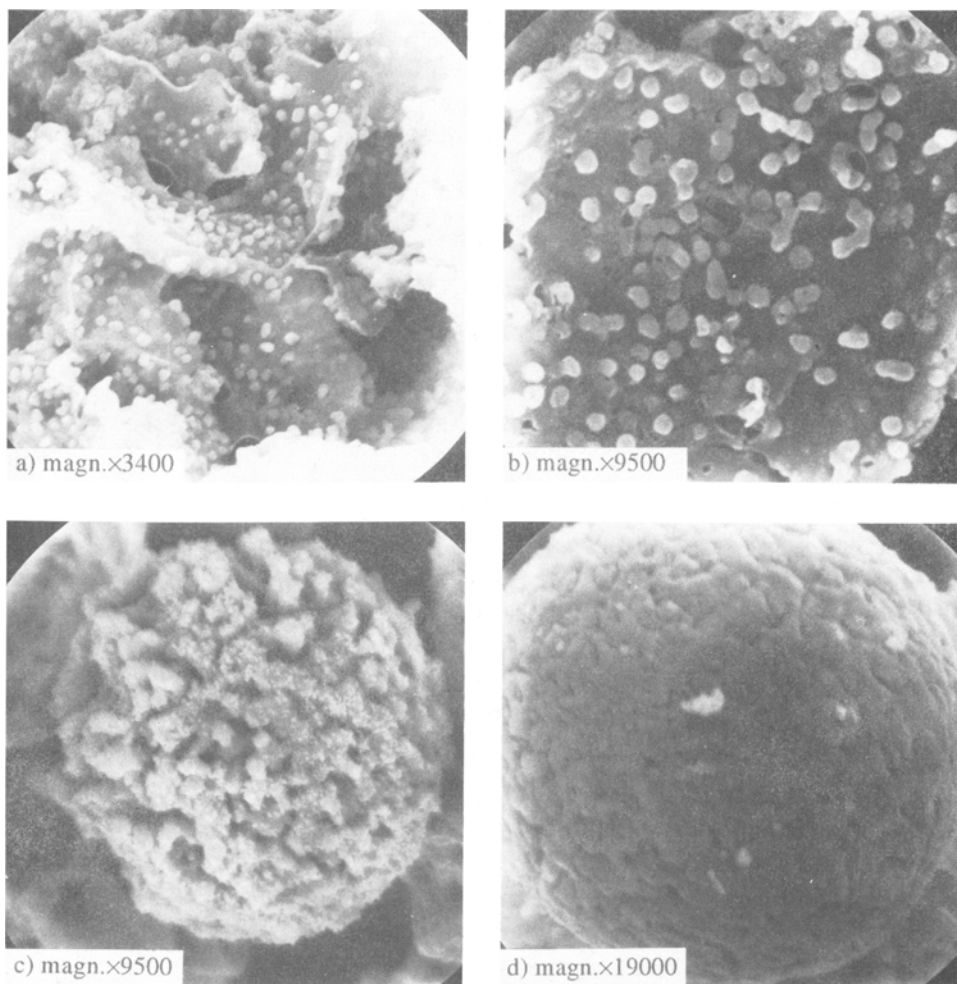


Fig. 1 SEM images of the *xcmv* material which resulted from decomposition in vacuum of unsupported copper malonate in the absence of any metal oxide support: Photo 1(a) material without further treatment (brighter, separate particles are copper at magn. $\times 3400$); Photo 1(b) after mild oxidation at 473 K showing linkages developing between particles; Photos 1(c) and (d) illustrating the progress towards 'balling-up' of the copper component after oxidations at 673 K followed by reduction at 573 K

A strong dependence upon pretreatment is evident only for the 15 min on-stream conversions. Values from chemical analyses for the percentages of carbon and hydrogen in aliquots of the unsupported *xcmv* material before and after the indicated treatments showed carbon to decrease to 8.6% (from 11.3% after

vacuum decomposition), and the %H to decrease to 0.4% (from 0.7%), no significant further change resulted from 1 h exposure to isopropanol vapour at 423 K. Only a small decrease in the %C (from 8.4 to 7.6) was caused by exposure to O₂ at 423 K. These pointers to composition of the unsupported *xcmv* material being little affected by the sequence of treatments in Table 1 were consistent with SEM observations showing persistence therein of morphology similar to those in Fig. 1A. Thus it seemed probable that the pretreatment-induced differences in initially-observed conversions of isopropanol vapour to acetone, evident within the second data column of Table 1, reflected the effect of factors other than morphological change. Redox-induced changes in the surface valence state of copper species, supported upon the carbonaceous residue, represented a likely alternative, since previous work from these laboratories demonstrated that, whilst very low initial $(-H_2)_{ip}$ conversions were observed over unsupported CuO, Cu₂O or Cu⁰ metal particles, large increases in such conversions could be attained following treatments which created a mixture of copper valence states at the surfaces [5, 6]. Qualitatively similar trends are evidenced by data in rows 2 and 3 of Table 1: only low initial conversions being shown after pretreatments likely to produce surfaces dominated either by Cu(II) or by Cu(O); whereas substantial pseudo-steady-state conversions emerge for each such material after 5 hr on-stream. The latter could be understood in terms of the on-stream formation of an active mixture of copper valence states. Conversely, the initially high conversions evident in data rows 1 and 4 may be understood on the basis that the corresponding pretreatments had already created such a mixture of copper valence states. A lower-limit estimate of ca. 0.002 s⁻¹ for an operational turnover frequency (TON) was arrived at on the basis of copper surface areas estimated from SEM and the pseudo-steady-state activities in Table 1.

Table 1 Comparison of $(-H_2)_{ip}$ activities of unsupported *xcmv* materials at $T_{rx} = 423$ K after various in-situ pretreatments in the microcatalytic reactor

Pretreatment sequence	Selectivity %S, and percentage conversion %C, of isopropanol to acetone			
	(i) after 15 min on-stream		(ii) after 5 h on-stream	
	%S(-H ₂)	%C(-H ₂)	%S(-H ₂)	%C(-H ₂)
4 h in N ₂ flow at 673 K	100%	37.0%	100%	35.0%
4 h N ₂ at 673 K + 0.5 h in O ₂ at 423 K	100%	4.0%	100%	52.0%
4 h N ₂ at 673 K + 1 h in H ₂ at 473 K	100%	1.7%	100%	34.0%
2 h O ₂ at 473 K + 1 h in N ₂ at 423 K + 1 h in H ₂ at 423 K	95%	56.0%	92%	48.0%

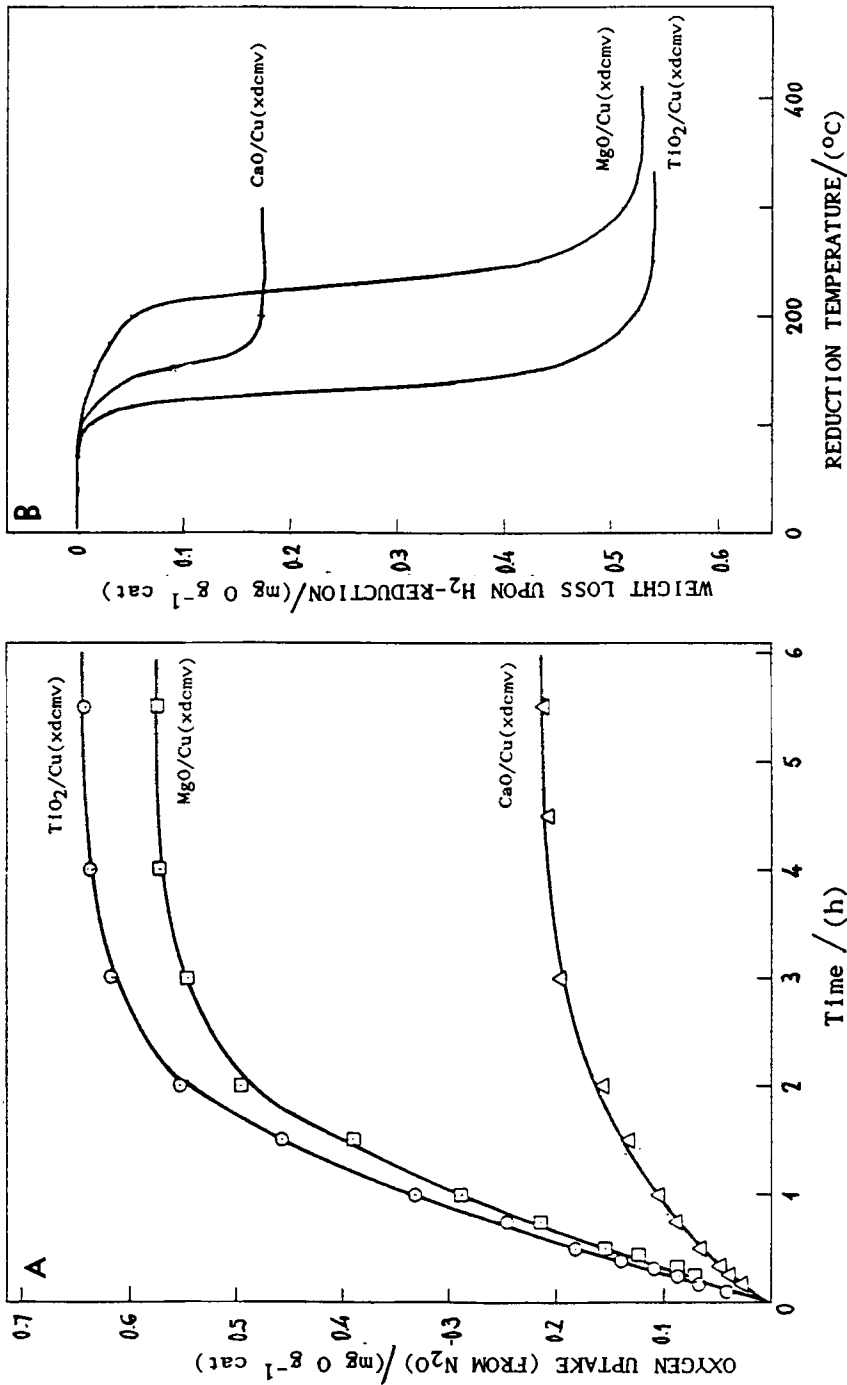


Fig. 2 In-situ mass changes observed for the indicated *x dcmv* materials following their decomposition in vacuum, plus the following treatments within the vacuum microbalance: (A) Isothermal exposure to nitrous oxide at 363 K for the indicated times; (B) temperature programmed reduction of the N₂O-oxidised materials in flowing H₂

Metal-oxide supported XDCMV materials

Figure 2 summarises microgravimetric data relating to changes in mass of $\text{TiO}_2/\text{Cu}(x\text{dcmv})$, $\text{MgO}/\text{Cu}(x\text{dcmv})$ and $\text{CaO}/\text{Cu}(x\text{dcmv})$ materials, subsequent to their in-situ preparation on a Cahn vacuum-microbalance from precursors made by aqueous impregnation of the metal oxide with copper malonate at a surface loading of ca. 0.5 monolayer equivalents. Duration of the in-situ vacuum decompositions was similar to that adopted by Carr and Galwey [1]. Subsequently, and without exposure to atmosphere, each sample was contacted with $P_{(\text{N}_2\text{O})} \sim 200$ torr and Fig. 2A shows the time-profiles for increases in sample mass resulting from $2\text{Cu}^0_{(\text{s})} + \text{N}_2\text{O}_{(\text{g})} \rightarrow \text{Cu}_2\text{O}_{(\text{s})} + \text{N}_2_{(\text{g})}$. In each case, the profile in Fig. 2A levels off to a plateau at contact times >5 h, signifying completion of this surface reaction [10]. Values for the limiting mass of oxygen uptake (per g of material) allow calculation of the following metallic copper surface area of the materials (m^2 of copper surface area per g of material): $\text{TiO}_2/\text{Cu}(x\text{dcmv}) = 3.4$; $\text{MgO}/\text{Cu}(x\text{dcmv}) = 2.9$; $\text{CaO}/\text{Cu}(x\text{dcmv}) = 1.03$. Upon in-situ evacuation and cooling of the samples, information on temperature profiles for reduction (TPR) of Cu_2O , produced at equivalent dispersions on these materials by the N_2O treatment, was obtained by introducing H_2 into the microbalance system, increasing the temperature and measuring the progressive decreases in mass as Cu_2O was reduced back to metallic copper. Those results are summarised in Fig. 2B. Comparison between the maximum mass-loss shown therein as attainable by H_2 -reduction, with the maximum loss-increase attained in Fig. 2A for the same material under oxidation by N_2O , shows satisfactory agreement and lends confidence that both mass-changes derive mainly from redox processes involving copper, rather than from changes in the carbonaceous residue known to accompany vacuum decomposition of copper malonate. From visual comparisons of the shapes of the temperature profiles for H_2 -reduction of the three materials in Fig. 2B it would appear that such reduction proceeds most readily for $\text{TiO}_2/\text{Cu}(x\text{dcmv})$, less readily for $\text{CaO}/\text{Cu}(x\text{dcmv})$, and much less readily for $\text{MgO}/\text{Cu}(x\text{dcmv})$, (witness 408, 423, and 503 K as respective temperatures for attaining 50% of the corresponding maximum mass-loss). An important implication of these observations, in relation to results in a later section showing differing influences of severity of prior reduction upon $(-\text{H}_2)_{\text{ip}}$ activity of these materials at $T_{\text{rx}} = 473$ K, is that MgO evidences by far the greater probability of retaining some fraction of copper species in oxidised form at that temperature.

Readily measurable selective conversions of isopropanol vapour to acetone were achieved over these metal-oxide supported $x\text{dcmv}$ materials at $T_{\text{rx}} = 473$ K, despite that fact that their mass % copper content was only ca. one-fiftieth of that in unsupported $x\text{cmv}$ residues. Table 2 lists values obtained for the

pseudo-steady-state rates of such $(-\text{H}_2)_{\text{ip}}$ conversion, attained in a continuous-flow microcatalytic reactor system at 473 K under identical reaction conditions, for *xdcmv* deposits upon TiO_2 , MgO , CaO and ZnO after the pretreatments listed in the first column.

Table 2 Comparisons of pseudo-steady-state rates for $(-\text{H}_2)_{\text{ip}}$ conversions at $T_{\text{rx}} = 473$ K, over 100 mg of various metal-oxide supported ~1% Cu (*xdcmv*) materials

Pretreatments		$(-\text{H}_2)_{\text{ip}}$ rates as $\mu\text{mol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$			
		MgO/Cu	CaO/Cu	TiO ₂ /Cu	ZnO/Cu
(i)	Argon flow at 473 K	41	58	65	75
(ii)	H ₂ at 473 K after (i)	130	–	225	80
(iii)	H ₂ at 673 K after (i)	203	–	17	–

A notable contrast in the table is that between the responses of the activity of $\text{TiO}_2/\text{Cu}(\text{xdcmv})$ and of $\text{MgO}/\text{Cu}(\text{xdcmv})$ to those pretreatments: activity of the latter increases steadily through rows 1 to 3, whereas the former shows a sharp drop in row 3 after prereduction at 673 K. Such a contrast was not unexpected in view of the above-mentioned greater stabilization of oxidised copper species on $\text{MgO}/\text{Cu}(\text{xdcmv})$ and of our earlier proposal that significant ongoing $(-\text{H}_2)_{\text{ip}}$ activity requires the coexistence of copper in oxidised and in reduced forms [5, 6]. Additional observations not inconsistent with that proposal included:

i) insignificant levels of $(-\text{H}_2)_{\text{ip}}$ activity at 473 K for the various metal oxide supports in the absence of dispersed copper;

ii) activity levels an order-of-magnitude lower over metal oxide *xdcmv* precursor not taken through the vacuum decomposition step. However, an enhancement to $660 \mu\text{mol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$ was noted in the $(-\text{H}_2)_{\text{ip}}$ activity of $\text{TiO}_2/\text{Cu}(\text{xdcmv})$ whenever it was subjected, after treatment of Table 2, to 'reoxidation at 673 K plus reduction at 473 K'. This pointed towards the intervention of additional factors, including the possibility of beneficial removal by $T_{\text{ox}} = 673$ K of a blocking carbonaceous co-deposit from vacuum decomposition of copper malonate. This led us to utilise reduction of Cu^{2+} by hydrazine as an alternative route to systems featuring metal oxide support in close contact with reduced copper species but without the complication of carbonaceous co-deposit. Results from these approaches are described in the following sections.

Metal oxides in contact with copper particles from copper hydrosols

Higher wt% copper contents of up to 30% could be obtained by this method and facilitated characterizations of $\text{TiO}_2/\text{Cu}(xcmhy)$ materials by XPS, AES, and TEM techniques, as already reported elsewhere [4]. They demonstrated the formation of large aggregates, comprising both the added TiO_2 particles (primary particle size ca. 30 nm) and copper particles originated as a hydrosol by hydrazine reduction of aqueous copper malonate. Analysis of XPS and AES spectra from the 'as-stored' $\text{TiO}_2/\text{Cu}(xcmhy)$ materials confirmed a strong predominance of Cu^{2+} in the surfaces of accessible copper particles. Following H_2 -reductions – which covered a similar range to that of reaction temperatures used in obtaining catalytic results below – the XPS and AES spectra demonstrated a strong persistence of Cu^{2+} species, together with some Cu^0 [4].

Selective dehydrogenation activity

Preliminary catalytic studies at $T_{rx} = 453$ K on the 'as-stored' $\text{TiO}_2/\text{Cu}(xcmhy)$ materials in the present study demonstrated that dehydrogenation to acetone with >98% selectivity was the sole conversion detectable with flame ionization detection. However, profiles for the variation in extent of this conversion with time-on-stream at $T_{rx} = 453$ K showed marked dependences upon duration of hydrogen pretreatment at 473 K. For example, untreated, as-stored aliquots exhibited very high initial conversions (>80%) which decreased very sharply during the first 3 h on-stream and settled eventually to a pseudo-steady-state conversion of ~18% after 15 h on-stream, whereas aliquots pre-reduced in H_2 for 3 h for 15 h displayed relatively flat profiles with pseudo-steady-state conversion of 33% and 8%, respectively. Such observation of lowest pseudo-steady-state conversion with samples which had received a 15 h pre-reduction at 473 K suggested that this had caused significant aggregation of copper particles. Comparisons were made, using the N_2O technique, of the exposed copper metal surface areas upon aliquots of $\text{TiO}_2/\text{Cu}(xcmhy)$ subjected to prior reductions at increased T_{rd} . Plot A of Fig. 3 illustrates how the number of surface-exposed Cu^0 species, thus detected upon TiO_2 11%/Cu(*xcmhy*) aliquots, increased to a maximum for a sample pre-reduced at ~400 K, but declined after H_2 pretreatments at 478 or 573 K. Plot B illustrates a similar trend observed experimentally for dependence of the pseudo: steady-state activity for $(-\text{H}_2)_{ip}$ conversion at $T_{rx} = 453$ K, upon temperature of H_2 pretreatment of the same material. An appropriately pretreated TiO_2 blank, without copper, was inactive for $(-\text{H}_2)_{ip}$ at 453 K. Comparisons, under differential conditions, between the pseudo-steady-state conversions achieved at $T_{rx} = 453$ K over 20 mg aliquots of

TiO₂/Cu(*xcmhy*), having copper loadings of 6, 11, 17 and 25% by mass, showed a progressive increase in $(-H_2)_{ip}$ activity for those copper loadings. Taking those observations into account, together with the strong similarity between plots (a) and (b) of Fig. 3, leads to a conclusion that surface-exposed Cu⁰ is an essential component of sites active for the highly selective dehydrogenation of isopropanol to acetone at 453 K over TiO₂/Cu(*xcmhy*). Present data do not provide information on questions as to whether, or which, other valence states of copper may cooperate with Cu⁰ in the sites active for $(-H_2)_{ip}$. However, results published elsewhere [4] of our XPS and AES studies upon TiO₂/Cu(*xcmhy*) materials after H₂ reductions at various temperatures indicate that such mixed-valence character of the active sites for $(-H_2)_{ip}$ should not be discounted, since those surface studies pointed to the coexistence of Cu⁺ species together with Cu⁰, even after reductions at 523 K.

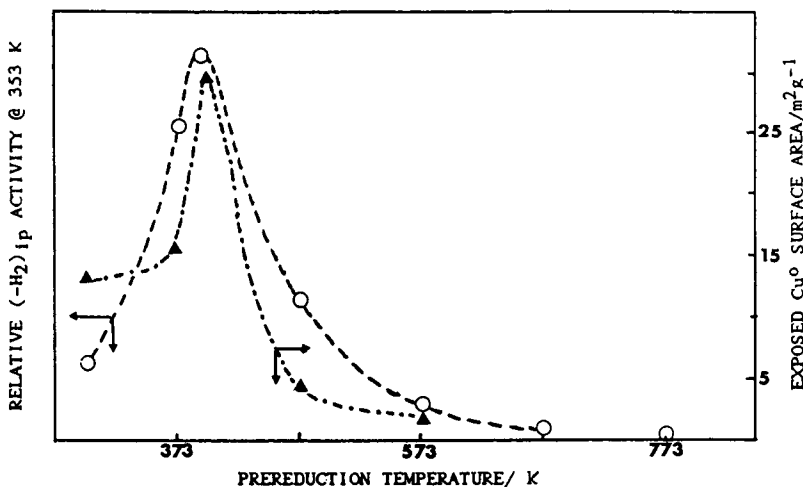


Fig. 3 Comparison between the dependences upon severity of prior H₂-reduction observed experimentally over TiO₂/Cu(*xcmhy*) aliquots for (i) exposed Cu⁰ surface area detected by N₂O; (ii) steady-state catalytic activity for selective dehydrogenation of isopropanol at $T_{rx} = 453$ K

Profiles of product-yield vs. time-on-stream in isopropanol vapour at 453 K were compared for variations in percentage conversion to acetone over MO/Cu(*xcmhy*) material when the metal oxide support was TiO₂, or MgO, or Ca(OH)₂ or ZnO. Such profiles made clear the requirement for long on-stream times (≈ 16 h) before attainment of pseudo-steady-state $(-H_2)_{ip}$ activities, except with ZnO as support. In separate experiments with MO/Cu(*xcmhy*) materials prepared with copper loadings in the range 3 to 20%, such pseudo-steady-state conversions were found to increase in proportion to copper loading upon

TiO₂, MgO and ZnO, whereas with CaO a maximum occurred for CaO/10% Cu(*xcmhy*). Consequently, estimates of turnover number (TON) per second per exposed Cu^o species, attainable on these MO/Cu(*xcmhy*) materials, were compared for 10±2% by mass copper loadings. TON values estimated for (-H₂) over the MO/Cu(*xcmhy*) materials (by dividing (-H₂)_{ip} rates as measured under differential conditions by the number of exposed Cu^o species, evaluated from reaction with N₂O) varied in the sequence TiO₂/Cu at 0.31>MgO/Cu at 0.25>ZnO/Cu at 0.14>CaO/Cu at 0.04. In view of the relatively small difference between the TON values over basic (MgO and ZnO) or acidic (TiO₂) supports, it could be concluded that the acidity/basicity of these metal oxide supports did not exert a strong influence upon (-H₂)_{ip} activity at 453 K.

An interesting experimental finding in published work [4] was evidence that HTR_{773 K} brought about an SMSI-like inhibitory effect upon catalytic activity of TiO₂/Cu(*xcmhy*) for the hydrogenation of acetone to isopropanol at *T_{rx}* = 448 K. This led us to test whether prior HTR_{773 K} would likewise inhibit the (-H₂)_{ip} activity of Cu^o-containing sites of the TiO₂/Cu(*xcmhy*) material. LTR_{473 K} was selected as a suitable starting treatment for the aliquot used for such tests. This selection was influenced both by present observations that this sufficed to complete most of the copper aggregation effect, and by prior TPR observations that it sufficed to rapidly reduce copper oxide particles upon TiO₂ supports [4].

Results from the catalytic runs made to test for an SMSI-like inhibition are summarised in Fig. 4 which compares profiles of rate of conversion vs. time-on-stream for the level of (-H₂)_{ip} activity displayed by an aliquot of TiO₂/13%Cu(*xcmhy*) after each of the following pretreatment sequence: pre-reduction in H₂ at 473 K (plot a); pre-reduction at 773 K (plot b); reoxidation at 673 K followed by LTR_{473 K}, plot c. The fact that activity is seen to be strongly inhibited by HTR_{773 K}, (plot b), but restored to activity by *T_{ox}* = 673 K + LTR_{473 K} means that behaviour of the TiO₂/Cu (*xcmhy*) material is phenomenological consistent with those two criteria for SMSI. Since reducibility of the titania support is often regarded as essential for the establishment of SMSI states by HTR [14], it was of interest to test whether MgO/Cu(*xcmhy*) material, featuring an oxide support much more difficult to reduce than TiO₂, would also have its (-H₂)_{ip} activity strongly inhibited by HTR_{773 K}. Such experiments with MgO/Cu(*xcmhy*) demonstrated the absence of any significant HTR-induced inhibition of its (-H₂)_{ip} activity. The contrast with results in Fig. 4 for TiO₂/Cu(*xcmhy*) is consistent with the greater reducibility of TiO₂ being an important factor in the greater susceptibility of TiO₂/*xcmhy* to HTR₇₇₃-induced inhibition of (-H₂)_{ip} over that material.

The following aspects of recent literature point, however, to a need also to consider whether the foregoing results may not equally well be accounted for in terms of active sites for $(-H_2)_{ip}$ featuring Cu^+ , possibly paired with another copper species [15]:

i) an inference, drawn from differences noted by XPS between HTR induced changes in thin-layer Cu/TiO_2 model systems from those in Rh/TiO_2 and Pt/TiO_2 model systems, that surfaces in the Cu/TiO_2 system were not subject to the same encapsulation/decoration-type effects as the Group VIII metal systems [16];

ii) conclusions from XPS and AES studies which show that Cu^+ species account for ca. 50% of surface and near-surface copper species on powdered Cu/TiO_2 materials even after prereducations to 550 K [4, 18];

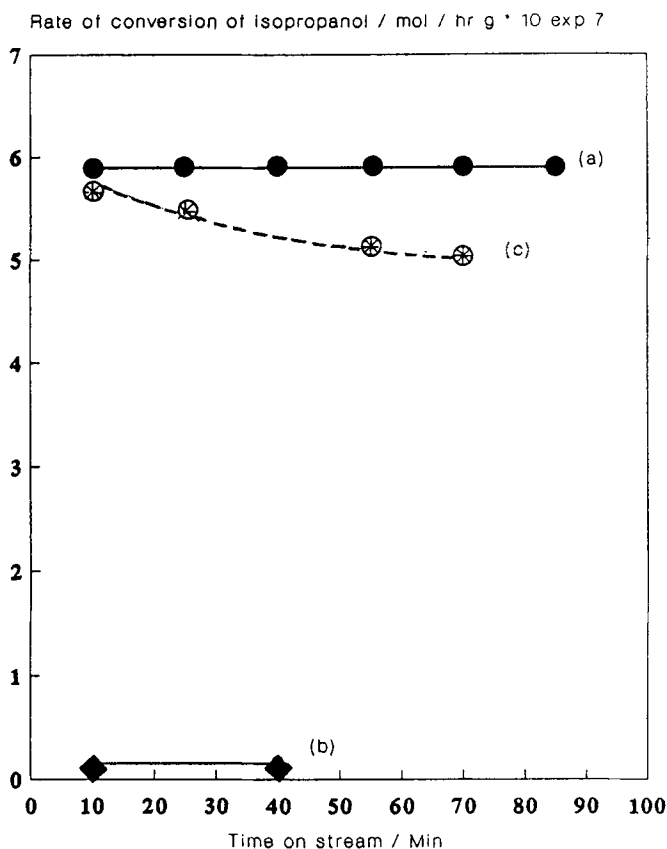
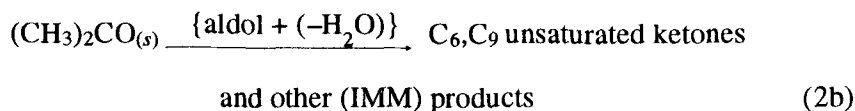
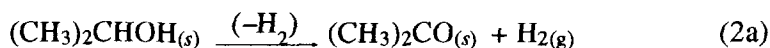


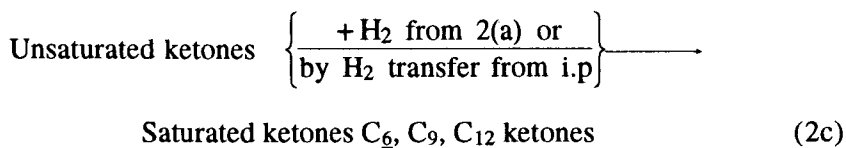
Fig. 4 Illustrations of the influence of prior differing pretreatments upon the selective dehydrogenation activity of $TiO_2/Cu(xcmhy)$ at $T_{rx} = 453$ K; (a) after LTR at 473 K; (b) after HTR at 773 K; (c) after reoxidation at 673 K and second LTR at 473 K

iii) high hydrogenation activity reported for Cu/Al₂O₃ and tentatively attributed to centres similar to the Copper(I)-hydride centres known to exhibit such activity in homogeneous catalysis [18]. Against that background, a hypothesis which merits further study is that the rate-determining step in (-H₂)_{ip} activity over LTR TiO₂/Cu(*xcmhy*) at 453 K may proceed upon active sites featuring both Cu⁰ and Cu⁺ centres. These sites may be rendered inactive upon complete conversion to (Cu⁰)_n by HTR_{773 K}, but regenerated by T_{ox} at 673 K + LTR_{473 K}.

Catalytic activity for oligomer formation

The 100% selectivity towards acetone product, which characterised the (-H₂)_{ip} catalytic activities of the MO/Cu(*xcmhy*) materials at T_{rx} Ω0≤453 K, did not persist over TiO₂/Cu(*xcmhy*) when T_{rx} was raised above 473 K. Instead, a progressive decline in selectivity towards acetone was observed whilst evidence emerged, as T_{rx} was increased from 473 to 573 K, for an increased conversion to products having increased boiling points and molecular masses, (IMM). Initially these products appeared as a liquid oil which could be collected at a cool section of the exit line from the flow reactor. Off-line GC/MS indicated it to contain a complex mixture of C₆H₁₂O, C₉H₁₈O and C₁₂H₂₄O oligomeric products. Recent work from these laboratories [4] using acetone vapour as the sole reactant over Cu/TiO₂ catalysts pointed to the operation of an aldol-condensation-based mechanism for formation of C₆, C₉ and C₁₂ oligomeric products which in that case were predominantly α, β-unsaturated ketones. Operation of such an aldol-condensation-based mechanism upon the acetone formed as primary product of isopropanol dehydrogenation remains the most probable route to oligomeric products in the present work. However, the apparent predominance of saturated ketones in the C₆, C₉ and C₁₂ oligomeric products from isopropanol implies an efficient reduction process operating in conjunction with aldol condensation and dehydrogenation steps. Possible sources of the requisite hydrogen include the H₂ accompanying the primary dehydrogenation step (cf. Eq. (2a)) or direct hydrogen-transfer from unreacted isopropanol vapour (cf. Eq. (2c)).





Overall our observations are consistent with only Eq. (2a) being significant over $\text{TiO}_2/\text{Cu}(xcmhy)$ at $T_{rx} \leq 453$ K, whereas conversions as per Eqs (2b) and (2c) became important at higher temperatures.

Efforts were made to determine the selectivity towards (IMM) products displayed by $\text{TiO}_2/\text{Cu}(xcmhy)$ materials and whether other $\text{MO}/\text{Cu}(xcmhy)$ materials displayed similar selectivity/activity. These experiments involved maintaining the exit-line and CSV of the continuous-flow, microcatalytic reactor system, at much higher temperatures in efforts to keep all end-products from Eq. (2b) over the various $\text{MO}/\text{Cu}(xcmhy)$ catalysts in the vapour phase, so that they might be carried to the GC for on-line separation and quantitative analysis. However, complete on-line separation of the complex mixtures of IMM products was beyond the capabilities of the packed column in the GC. Conse-

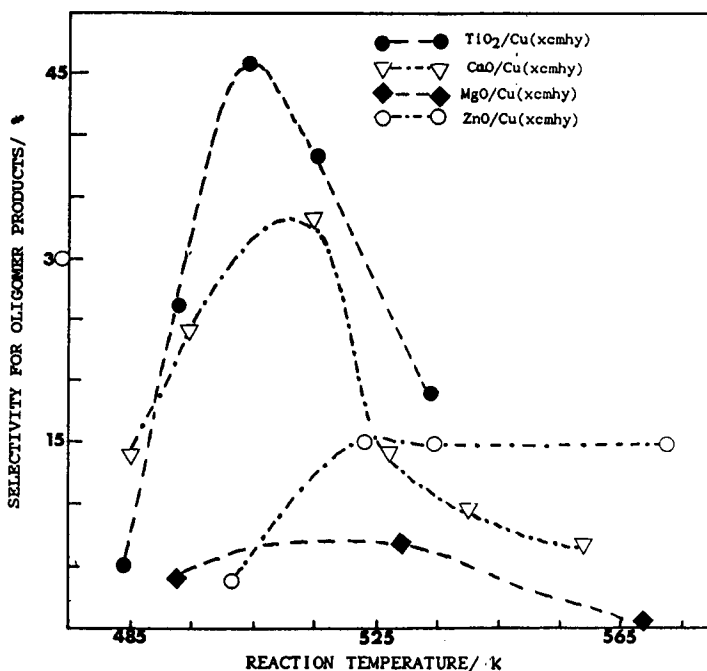


Fig. 5 Semiquantitative comparisons for the indicated $\text{MO}/\text{Cu}(xcmhy)$ materials of the T_{rx} range over which significant selectivity for production of C_6 – C_9 oligomers from isopropanol was observed (based on loss of isopropanol to non-volatile products)

quently, total area under the several incompletely resolved GC features originating from IMM products (well separated from features of acetone, isopropanol and any propene product) represented the best available measure of the relative abilities of the various MO/Cu(*xcmhy*) materials in catalysing the oligomerization process at $T_{rx} > 473$ K. Results of such semi-quantitative comparison of percentage selectivities towards IMM products at T_{rx} 485–575 K are summarised in Fig. 5 which illustrates the following:

i) within that temperature range, acetone accounted for 3/4 of the additional overall conversion of isopropanol over $TiO_2/Cu(xcmhy)$, whereas, at higher T_{rx} , amounts of propene and cracking-products increased rapidly;

ii) position, height and width of this 'IMM-window', within which T_{rx} -range oligomeric products could be formed via Eq. (2b) with good selectivity, varied with the metal-oxide support. Thus with TiO_2 and CaO supports, this window extended $T_{rx} = 513 \pm 15$ K, with ZnO it occurred at only low level for $T_{rx} = 525$ –610 K and for MgO, it remained at a much lower level across that entire T_{rx} range;

iii) maximum values of selectivity towards IMM products were 46% for CaO/Cu at 505 K; >33% for TiO_2/Cu at 515 K; >17% for ZnO/Cu at 525 K; >7% for MgO/Cu at 530 K.

These indications of the attainment of higher IMM selectivities over CaO/Cu(*xcmhy*) and $TiO_2/Cu(xcmhy)$ than over the corresponding MgO-supported material are surprising and worthy of further study in view of a literature preference for MgO [19, 20] as a catalyst for acetone oligomerization, in the absence of added copper.

Conclusions

Comparisons between the catalytic activities for selective dehydrogenation of isopropanol vapour to acetone at $T_{rx} \leq 453$ K over oxide-supported copper materials prepared from copper malonate precursor [i.e. MO/Cu(*xcm*)] indicate that prior dispersion of the malonate onto the support followed by chemical reduction with hydrazine [e.g. $TiO_2(xcmhy)$] resulted in the best dispersion and activity. In other preparative methods, the carbonaceous residue left after thermal decomposition of CM in vacuo exerted net inhibiting effect.

Participation of Cu^0 centres in the sites active for selective dehydrogenation at $T_{rx} \leq 453$ K over $TiO_2/Cu(xcmhy)$ is indicated by the closely similar dependences upon severity of prior reductions at T_{rd} 353–453 K observed at 473 K for initial ($-H_2$) activity and for metallic copper surface area by N_2O . Prior reduction at high temperature (HTR₇₇₃ K) inhibited such ($-H_2$) activity, whilst

subsequent reoxidation at 673 K, followed by LTR₄₇₃, restored activity. Although those observations appear consistent with HTR-induced creation of an inhibitory strong metal support interaction (SMSI) effect upon the $(-H_2)_{IP}$ activity of $TiO_2/Cu(xcmhy)$, they do not exclude an alternative explanation, viz. that the active sites are mixed-valent in character involving both Cu^0 and Cu^+ centres. Further work will be needed to resolve this interesting question.

Onset of activity for secondary conversions of the acetone product from isopropanol dehydrogenation onwards to C_6 and C_9 oligomers was observed whenever T_{rx} was increased above 483 K. Selectivities for production of such condensation-products having increased molecular mass (IMM) varied with the nature of the metal oxide support in the $MO/Cu(xcmhy)$ materials, higher selectivities being achieved at 515 ± 10 K for TiO_2/Cu and CaO/Cu than for ZnO/Cu or MgO/Cu . Composition of the IMM products was qualitatively similar to those reported in the literature to result from aldol-condensations of acetone over MgO and other basic metal oxides.

* * *

The authors acknowledge expert assistance from the electron-microscopic and chemical-analysis units in their respective organizations. They are also grateful for financial support for MON, CP, NH and ZW from the postgraduate support scheme of UCC. Assistance from Dr. J. O'Reilly (Cara Partners) and Dr. K. McNamara (Irish Distillers) in the resolution and identification of oligomeric products by capillary GC-MS is also gratefully acknowledged.

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Zusammenfassung — Die Resultate von Carr und Galwey [1] über die Zersetzung von Kupfermalonat (CM) in Vakuum bei 510 K veranlaßte uns zur Darlegung von Untersuchungen über die Verwendbarkeit von CM als Niedrigtemperatur-Präkursor für oxidgestützte Kupferkatalysatoren. Auf Metalloxid geschichtetes CM wurde durch thermische Vakuumzersetzung oder durch Reduktion mit wäßrigem Hydrazin in Kupferpartikel überführt. Unter Verwendung der Dehydrogenierung von Isopropanol zu Aceton als zu katalysierende Probereaktion wurden Vergleiche zwischen der katalytischen Aktivität und Selektivität von Kupfer auf TiO_2 , MgO und Ca(OH)_2 angestellt. Es wird der Einfluß von Partikelgröße, Vorreduktionstemperatur und Reduzierbarkeit des Trägermaterials beschrieben und ein Beweis für eine SMSI-artige (starke Metall-Trägermaterial Wechselwirkung) Hemmung der Aktivität von Cu/TiO_2 bei vorangehender Hochtemperatur-Reduktion erbracht.