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Thermal tuning of advanced Cu sol–gels for mixed oxidation state Cu/Cu_xO_y materials

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Roya Baghi, Geneva R. Peterson and Louisa J. Hope-Weeks*

In this report, we describe new conditions for the formation of copper gels and aerogels *via* epoxide addition to $CuBr_2$ in dimethylformamide (DMF). These $CuBr_2$-derived sols undergo a rapid gel transition and result in materials that have enhanced mechanical properties when compared with the gels derived from $CuCl_2$. Additionally, upon air-annealing, they convert to nanoscopic CuO at temperatures much lower than the $CuCl_2$ analogues. Moreover, annealing under nitrogen results in copper species with reduced oxidization states including Cu_2O and metallic Cu. The ratio of copper oxidation states can be controlled by simple modification of the thermal program used to anneal the materials. The thermal reduction of the copper is attributed to retained DMF ligands in the as-prepared aerogels which was confirmed by FTIR spectroscopy. These aerogel materials were characterized by powder X-ray diffraction (PXRD), physisorption, thermogravimetric analysis (TGA), and temperature programmed reduction (TPR).

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Introduction

Copper-based heterogeneous catalysts are key materials for environmentally-important reactions such as hydrogenation of carbon dioxide to methanol,[1] NO_x selective reduction,[2] CO oxidation,[3] and cross-coupling reactions.[4] These materials are usually supported on a substrate such as zinc oxide or aluminium oxide in order to increase their active surface area, improve their porosity characteristics, and influence their reactivity. Cutting-edge preparative methods in materials science have recently opened the possibility of preparing unsupported copper catalysts with high surface areas. For example, sol–gel methods have recently been explored as a route to unsupported porous copper materials,[5] and Cu nanoparticles have displayed excellent activity as heterogeneous catalysts for the Sonogashira coupling reaction.[6,7]

Many studies have investigated the relative catalytic activities of copper oxidation states for a given reaction. For example, Jernigan and Somorjai studied CO oxidation by copper and copper oxides[8] and reported that the catalytic activity of the copper species decreases in the order of Cu > Cu_2O > CuO. However, Huang indicated that Cu_2O exhibits the most activity for this reaction, but that non-equilibrium surface structures are important.[9] On the other hand, cupric oxide nanopowders (CuO) have been reported recently as efficient catalysts for CO oxidation whereas bulk CuO did not show any activity under analogous conditions.[10] The ambiguity of which is the "active oxidation state" may point to cooperative effects when mixtures of oxidation states are present and the importance of physical properties. As such, methods for the preparation of homogenous copper nanomaterials with controlled ratios of the oxidation states or of non-stoichiometric Cu_xO_y nanomaterials would provide interesting insights into the catalytic activity of copper heterogeneous catalysts.

Aerogels are a diverse class of porous materials prepared by the non-destructive removal of solvent from the pores of a gel, usually by critical point drying.[11] Here, we report a significantly improved facile method for the synthesis of unsupported copper-based sol–gels and aerogels which exhibit enhanced mechanical and physical properties. The resulting copper-based aerogels convert to unsupported, nanocrystalline CuO at relatively low temperatures. Additionally, residual organic material in the as-prepared aerogel can be utilized as a latent reductant during anaerobic annealing of this material to afford unsupported mixed oxidation state copper nanomaterials. The ratio of copper phases is easily tuned by adjustment of the thermal program.

Results and discussion

1 Synthesis and physical properties of Cu aerogels

The formation of copper(II) aerogels from copper(II) chloride in 2-propanol using propylene oxide as a proton scavenger and gelling agent has been reported previously.[5] However, these gels are fragile and crumble from their monolithic form easily. Moreover, sols from $CuCl_2$ undergo the sol–gel transition slowly and incompletely. The "epoxide addition" synthetic route to transition metal sol–gels is now well established.[12] In this approach, a metal salt solution is mixed with an epoxide which gradually basifies the solution leading to oxolation and olation

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Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX, 79409, USA. E-mail: louisa.hope-weeks@ttu.edu; Fax: +1 806 742 1289; Tel: +1 806 742 4487

reactions at the metal centre.[12c] Under favourable conditions, these polycondensation steps create a continuous gel network. For the metal centres in the final gel, the exact nature and number of the inner sphere ligands (such as water, hydroxide, counterion, or solvent) are variable. The choice of precursor epoxide,[12c] solvent,[12b] and salt[12a] are all known to influence the gelation process as well as the chemical and physical properties of the resulting gels. The best combination of precursors is usually empirically determined. Consequently, we examined different solvents, epoxides, and copper salts to achieve a quick and facile synthesis of copper aerogels with improved mechanical properties. Among a variety of conditions, the best result was obtained by using copper(II) bromide in DMF and epichlorohydrin as the epoxide. In this system, the reactants undergo the sol–gel transition within 10 minutes of mixing at room temperature to afford a robust, opaque, turquoise-coloured gel. After washing the gel of residual reactants and critical point drying with carbon dioxide, a similar coloured monolith was isolated. The PXRD pattern of this as-prepared copper aerogel indicates that it is weakly crystalline and exhibits diffraction peaks which correspond to the $Cu_2(OH)_3Br$ phase (PDF no. 00-045-1309) (Fig. 1a). The analogous $Cu_2(OH)_3Cl$ phase was identified in the as-prepared $CuCl_2$-derived gels.[5]

The BET surface area of the as-prepared $CuBr_2$-derived aerogel was 232 $m^2\ g^{-1}$ compared with 313 $m^2\ g^{-1}$ for the $CuCl_2$-derived aerogel, which indicates that some loss of surface area accompanies the improved mechanical properties for the $CuBr_2$-derived aerogels. Additionally, the SEM images (Fig. 2) of the as-prepared $CuBr_2$-derived aerogel demonstrate a coral-like morphology with a homogenous network of pores in a variety of sizes, in strong contrast to the morphology of the $CuCl_2$-derived aerogels, which display clusters of joined spheres with large inter-particle voids.

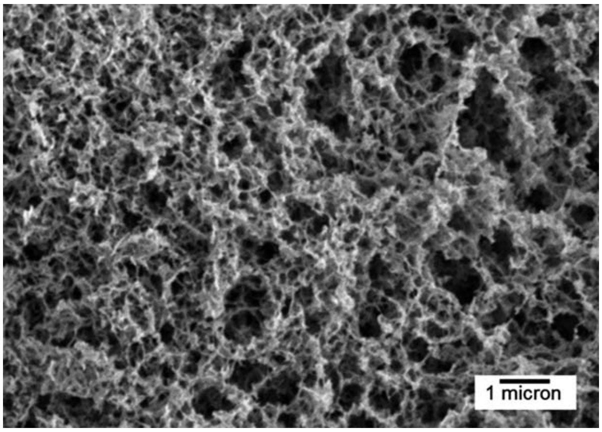

Fig. 2 SEM image of the as-prepared $CuBr_2$ derived aerogel.

2 Thermal degradation & aerobic formation of nano CuO

In addition to the faster sol–gel transition and improved mechanical properties, the use of $CuBr_2$ *in lieu* of $CuCl_2$ presents advantages in the thermal processing of the as-prepared aerogel materials. Thermogravimetric analysis of copper basic halides has been previously described[13] and indicates that the $Cu_2(OH)_3Br$ phase undergoes phase transitions at lower temperature than the analogous $Cu_2(OH)_3Cl$ phase. Specifically, the thermal decomposition of the copper basic halides proceeds through three steps. The first two steps are dehydroxylation with elimination of water and redox reaction to form Cu_2X_2 and X_2. Under inert atmosphere, Cu_2X_2 volatilizes, whereas under air the Cu_2X_2 is oxidized to CuO. The $Cu_2(OH)_3Br$ system undergoes the redox reaction to Cu_2Br_2 more readily than the chloride analogue, so the first two steps of the decomposition process take place simultaneously:

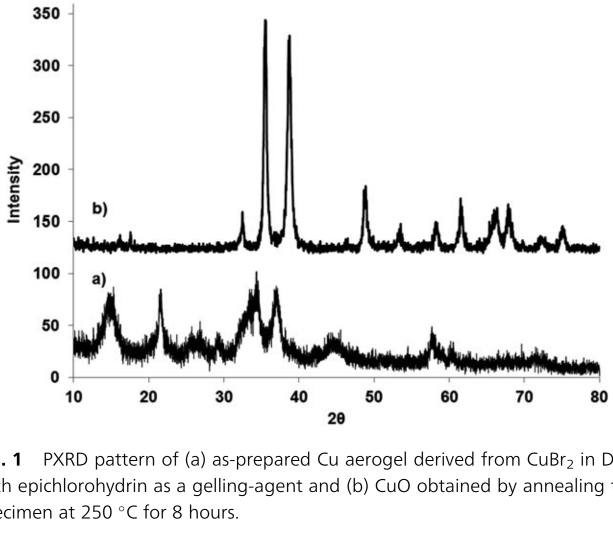

Fig. 1 PXRD pattern of (a) as-prepared Cu aerogel derived from $CuBr_2$ in DMF with epichlorohydrin as a gelling-agent and (b) CuO obtained by annealing this specimen at 250 °C for 8 hours.

$$2Cu_2(OH)_3Br \rightarrow 3CuO + \tfrac{1}{2}Cu_2Br_2 + \tfrac{1}{2}Br_2 + 3H_2O$$

For the $CuBr_2$-derived aerogel under investigation here, thermogravimetric analysis under nitrogen generally follows this literature pathway for $Cu_2(OH)_3Br$ (Fig. 3). The first mass loss observed from 130 to 265 °C can be attributed to the dehydroxylation and the redox reaction to liberate Br_2, and the second mass loss from 300 to 400 °C corresponds to volatilization of

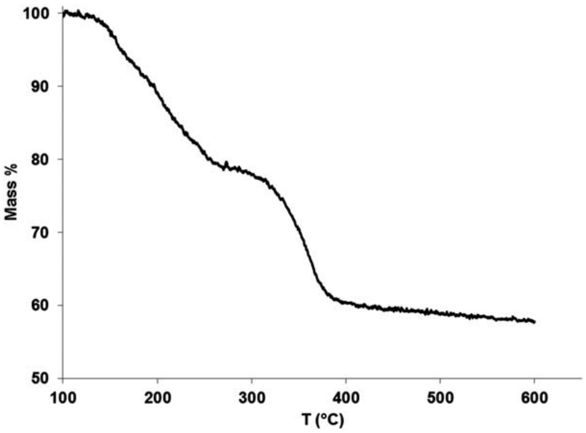

Fig. 3 Thermogravimetric profile of the as-prepared $CuBr_2$-derived aerogel under nitrogen flow.

Cu_2Br_2. The observed weight losses are 22% and 20%, respectively, which are both lower than the calculated mass losses of 26% and 28%. Both of these calculated mass losses depend upon the stoichiometric quantity of bromide in the material. If the Cu-aerogels are bromide-deficient relative to the $Cu_2(OH)_3Br$ formula, then the mass losses would be lower, as observed here. This situation is consistent with the somewhat amorphous nature of the $CuBr_2$-derived aerogel which likely possesses inexact stoichiometry relative to the pure $Cu_2(OH)_3Br$ phase.

The as-prepared aerogel was annealed under static air to afford CuO, as shown in Fig. 1b (PDF no. 00-044-0706). The phase was completely changed to CuO after annealing for 8 hours at only 250 °C compared with 450 °C required for complete conversion of the $CuCl_2$-derived aerogels. This mild annealing resulted in a surface area of 47 $m^2\ g^{-1}$ and an average particle size of 11 nm, as calculated from the (111) reflection of the PXRD pattern (Fig. 1b). Overall, these results indicate that the as-prepared $CuBr_2$-derived aerogel generally possesses similar chemical properties to pure $Cu_2(OH)_3Br$ including its aerobic thermal decomposition pathway.

Temperature programmed reduction (TPR) analysis was performed on the CuO sample calcined at 250 °C using a mixture of 5% hydrogen and 95% nitrogen to investigate the reduction behaviour of this material (Fig. 4). The TPR curve exhibits a single peak indicating a one-step reduction mechanism, directly from CuO to metallic Cu without formation of the Cu_2O intermediate. This thermal behavior is consistent with the report of Ahmadi *et al.*[14] that indicates that reduction of nano-CuO particles follows a one-step mechanism whereas micro-CuO produces two reduction peaks indicating a two-step mechanism with formation of Cu_2O as an intermediate. Consequently, both our physical (PXRD) and chemical (TPR) analyses confirm the nanoscopic nature of this easily-prepared, unsupported CuO.

3 Anaerobic production of mixed oxidation state Cu

Interestingly, in the case of the $CuCl_2$-derived aerogels, a mixture of Cu_2O and CuO phases were formed after annealing at 350 °C, even though this Cu(I) oxide phase is not predicted as an intermediate by the literature thermal decomposition route.[13] This result suggests alternative decomposition pathways for the Cu-aerogel materials compared with the pure $Cu_2(OH)_3X$ phases. It is known that aerogel materials from the epoxide addition method possess inexact chemical formulas and even a substantial amount of residual organic material.[12a] Leventis *et al.* have recently explored the reduction of copper and iron derived aerogels by using a co-gelled organic component to mimic smelting reactions under inert atmosphere.[15]

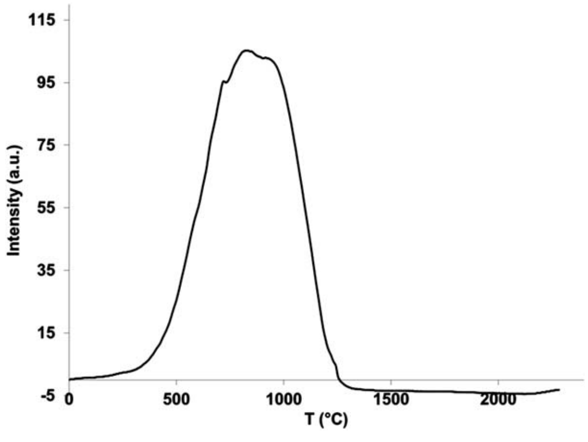

Fig. 4 Temperature programmed reduction (TPR) of the CuO aerogel in 5% H_2 95% N_2 stream at a constant thermal ramp of 5 °C min^{-1}.

In order to probe the capability of the $CuBr_2$-derived aerogel to likewise afford reduced copper intermediates as observed for the $CuCl_2$-derived aerogels, a series of aerobic annealing conditions were investigated (Table 1). However, the only decomposition products observed from aerobic annealing are Cu_2Br_2 and Cu(II) oxide. Based upon this information, annealing of the $CuBr_2$-derived aerogels was conducted under nitrogen atmosphere in order to investigate the possibility of Leventis-style nano-smelting (Table 2).

The annealing of the as-prepared $CuBr_2$-derived aerogel under inert atmosphere resulted in the formation of a mixed oxidation state copper oxide material (Fig. 5). To further understand the effect of annealing conditions on the oxidation state of the final product, a series of conditions were investigated to explore the influence of time and temperature in these phase transitions. The results are summarized in Table 2 and Fig. 5. All annealed phases were highly crystalline, as indicated by the flat baselines of the PXRD patterns, which show no amorphous background. Examination of these patterns reveals that very subtle changes in the thermal treatment of this single aerogel precursor can produce dramatic changes in the final phase compositions. A mixture of species ($CuO/Cu_2O/CuBr$) was obtained after brief annealing at 400 °C for 2 hours. Increasing the time and temperature led to products with lower oxidation states. Annealing at 450 °C for 7 hours resulted in a mixture of Cu metal and Cu_2O as the major phases with a small amount of residual CuO. This mixed oxidation state copper material

Table 1 Static air annealing conditions, $CuBr_2$-derived aerogel

Target temp. (°C)	Ramp rate (°C min^{-1})	Dwell time (h)	Observed phases
400	10	2	CuO
275	2	2	CuO/CuBr
275	2	6	CuO/CuBr
275	2	8	CuO
250	2	8	CuO

Table 2 Inert atmosphere annealing conditions, $CuBr_2$-derived aerogel

Target temp. (°C)	Ramp rate (°C min^{-1})	Dwell time (h)	Observed phases
400	10	2	$CuO/Cu_2O/CuBr$
400	2	7	$CuO/Cu_2O/Cu/CuBr$
450	2	4	$Cu_2O/CuBr$
450	2	6	$Cu/Cu_2O/CuBr$
450	2	7	$Cu_2O/Cu/CuO$ (minor)

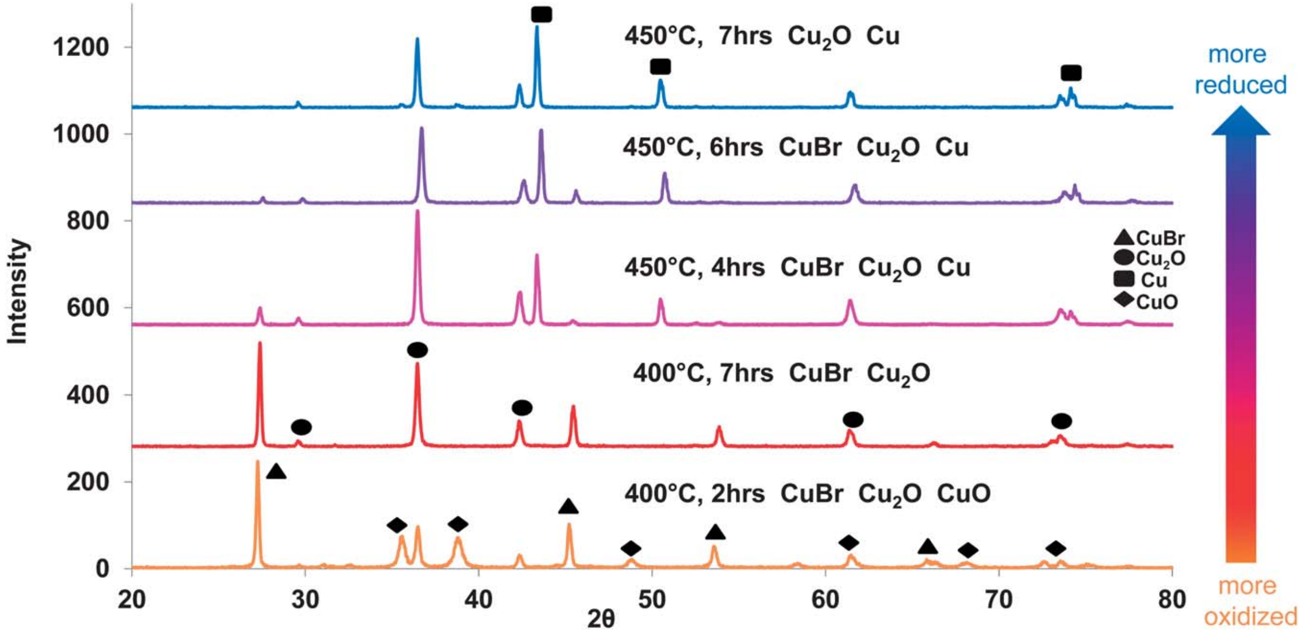

Fig. 5 PXRD patterns of the Cu aerogel material after various annealing programs.

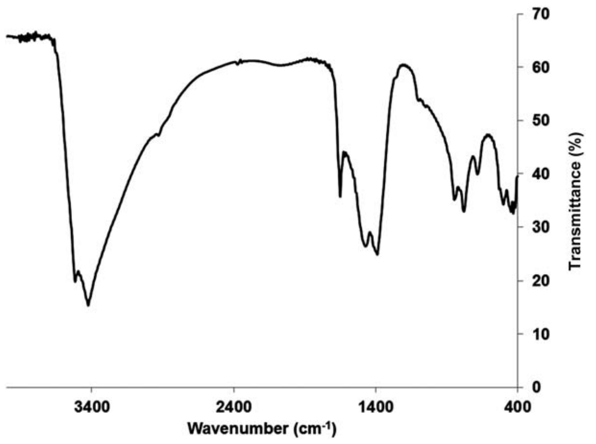

Fig. 6 FTIR spectrum of the as-prepared $CuBr_2$-derived aerogel, prepared as a KBr pellet.

possessed a surface area of 10 $m^2\ g^{-1}$ as a result of grain growth and densification during extended annealing. Importantly, within a window of only 50 °C and 5 hours annealing time, substantial changes in the ratios of oxidation states can be accessed.

In order to substantiate the hypothesis that these reduced copper species result from smelting-type reactions with retained organic material in the aerogel matrix, elemental analysis was obtained for the as-prepared aerogel material which revealed the presence of 6.33% carbon, 1.79% hydrogen, and 1.34% nitrogen. Additionally, an FTIR spectrum of the as-prepared aerogel was acquired which supports the presence of retained DMF molecules in the aerogel matrix (Fig. 6). The spectra obtained for the as-prepared aerogel exhibits OH vibrations near 3400 cm^{-1} which correspond to those observed for the pure $Cu_2(OH)_3Br$, which has been reported previously.[16] In addition, the as-prepared aerogel also displays bands near 1400 cm^{-1} which are attributable to coordinated DMF molecules. Retention of DMF in the Cu sol–gel matrix is perhaps not surprising in view of the good capability of DMF to act as a ligand and the affinity of copper for nitrogenous bases.

Experimental

Copper bromide (Alfa Aesar), epichlorohydrin (Acros) and dimethylformamide (DMF, Fisher) were all used as received. All syntheses were performed under ambient conditions. PXRD analyses were performed on a Rigaku Ultima III diffractometer using Cu Kα radiation. The BET surface area was determined from N_2 adsorption/desorption data collected at 77 K on a NOVA 4200e model surface area/pore size analyzer (Quantachrome Instrument Corp.). Seven data points were selected in the relative pressure region of 0.05–0.3 P/P_0. The morphology of the gel was studied by scanning electron microscopy (SEM) Hitachi S-4300 scanning electron microscope. TPR was carried out with a ChemBET TPR/TPD Analyzer (Quantachrome Instrument Corp.). Thermogravimetric analyses were conducted with a Shimadzu TGA-50 Thermogravimetric Analyzer under N_2 (50 ml min^{-1}). For TGA experiments, the thermal program raised the specimen to 100 °C at a ramp rate of 10 °C, held the sample at 100 °C for one hour to remove residual volatile materials, and then raised the specimen to 600 °C at a ramp rate of 5 °C. Specimens for FTIR spectroscopy were prepared as KBr pellets using ~10 mg of as-prepared aerogel in ~150 mg of KBr. FTIR spectra were collected on a Hitachi FTIR-8400.

Copper sol–gels were prepared by addition of epichlorohydrin (2.75 ml, 0.03 mol) and H_2O (0.24 ml, 0.013 mol) to a solution of $CuBr_2$ (0.7371 g, 0.0033 mol) dissolved in DMF (5 ml) to yield a dark black-green solution. Following combination of all the reagents, the solution was stirred for a few seconds and then poured into 6 dram shell vials as moulds which were capped and left undisturbed to gel. After 10 minutes the gel started to form and the solution turned lighter green and opaque. Sol–gels were allowed to age 24 h, and then were washed with DMF and acetone (3 times each solvent, 24 h each time). The gel samples were then dried in a SPI-DRY model critical point dryer using carbon dioxide to generate aerogels.

Conclusions

In this study, unsupported Cu-based aerogels were successfully prepared using the epoxide addition method from a copper bromide salt. The counter-ion (Br rather than Cl), the solvent (DMF rather than 2-propanol), and the epoxide (epichlorohydrin rather than propylene oxide) all contribute to a faster gel time and greater mechanical strength.

The as-prepared $CuBr_2$-derived aerogels produce PXRD patterns consistent with poorly crystalline $Cu_2(OH)_3Br$ and share many properties with the pure $Cu_2(OH)_3Br$ phase including a low thermal threshold for the aerobic formation of crystalline CuO. Both PXRD and TPR confirm the nanoscopic nature of this unsupported CuO material.

Despite similarities to the $Cu_2(OH)_3Br$ phase, the weakly-crystalline as-prepared aerogel possesses important differences in composition and structure, as illustrated by thermal analyses, PXRD, FTIR, elemental analysis, and annealing studies. These analyses indicate the presence of residual organic material within the aerogel network structure, which is attributed to the replacement of some bromide ligands by DMF ligands. This organic component enables the formation of mixed oxidation-state Cu materials by smelting-type reactions under inert atmosphere. Subtle changes to the thermal program allow control of the ratio of the oxidation states. Altogether, this work illustrates the potential to design sol–gel materials with latent reactivity that can be unlocked by careful thermal processing and paves the way for studies regarding the catalytic activity of different copper heterogeneous catalysts.

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