

Direct production of hydrogen peroxide from CO, O₂, and H₂O over a novel alumina-supported Cu catalyst

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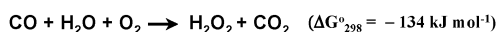
The direct production of hydrogen peroxide from CO, O₂, and H₂O over a novel catalyst system based on highly dispersed Cu supported on alumina has been demonstrated. Under optimized conditions, a high H₂O₂ formation rate of *ca.* 0.326 mmol (g cat.)⁻¹ h⁻¹ could be achieved.

Hydrogen peroxide is a clean oxidizing agent that is useful for highly selectively converting organic compounds into value-added products, as well as for industrial or municipal wastewater treatment and water disinfection.¹ Currently, the commercial production of H₂O₂ is mainly based on a multi-step process involving cyclic hydrogenation and oxidation of an alkyl anthraquinone in a complex working solution.² This high-energy consuming process often has disadvantages, such as the cost of the quinone solvent system and the elaborate treatments required to remove degradation products due to non-selective hydrogenation. Hence, it is highly attractive to develop more economical and “green” processes that can allow the direct synthesis of H₂O₂ from H₂ and O₂ or from CO, O₂ and H₂O. Although notable recent progress in this area is the use of noble metal based catalysts to achieve efficient production of H₂O₂ from mixtures of H₂/O₂,^{3–5} the latter process (Scheme 1) in particular has attracted recent interest due to its high safety.

During the past decade, a complex homogeneous palladium-ligand catalytic system that requires extra separation steps or acid additives has been extensively studied for the synthesis of H₂O₂ from CO, O₂ and water.^{6–8} Nevertheless, comparatively little attention has been paid to the development of new heterogeneous catalytic systems that can allow easy removal of the catalysts from reaction mixtures and recycling/reuse of catalysts.^{9,10} Catalyst systems based on supported noble metals, such as Pd/CaCO₃ or Ru/graphite, have recently been proposed for H₂O₂ synthesis from CO/O₂/H₂O,⁹ but the catalytic results in terms of H₂O₂ formation rate are far from satisfactory. More recently, Ma and co-workers reported a much cheaper catalyst system consisting of a rare earth modified alumina-supported amorphous alloy catalyst, Ni–La–B/Al₂O₃, for the catalytic production of H₂O₂ from CO/O₂/H₂O;¹⁰ moreover, it exhibited an activity only slightly inferior to that of the noble metal catalysts mentioned above.⁹ Here, for the first time, we report an alternative new heterogeneous catalyst system based on highly dispersed copper supported on alumina, which exhibits superior performance for the catalytic synthesis of H₂O₂ from CO, O₂ and water.

Table 1 shows the catalytic results for H₂O₂ production from CO/O₂/H₂O over several types of metal nanoparticles dispersed on alumina prepared by the wet reduction (WR) method, which has recently been shown to be an effective method for the preparation of various amorphous alloy catalysts for versatile hydrogenation applications.^{11,12} All the results presented in Table 1 were obtained using an autoclave with aqueous 0.01 M sulfuric acid as the reaction medium. It is remarkable that a much higher H₂O₂ formation rate could be achieved over the 1st row transition metal catalyst systems. Among these, the Cu/Al₂O₃ catalyst was the most active, giving a formation rate of *ca.* 0.236 mmol (g cat.)⁻¹ h⁻¹ for the H₂O₂ production at 273 K. Note that this result is drastically improved with respect to the patent value of 0.1 mmol (g cat.)⁻¹ h⁻¹ achieved over the Pd/CaCO₃ catalyst reported by Brill.⁹ As also shown in Table 1, the less active samples of alumina-supported Fe and Co particles present a much lower rate of H₂O₂ production. It should be noted that the present sample of Ni/Al₂O₃ shows a moderate activity of 0.075 mmol (g cat.)⁻¹ h⁻¹ for H₂O₂ formation at room temperature, which is comparable to that obtained over the amorphous alloy catalysts Ni–La–B/Al₂O₃.¹⁰ It is also clear from Table 1 that the rates of H₂O₂ formation over the alumina-supported noble metal catalysts (Au/Al₂O₃, Ru/Al₂O₃ and Pd/Al₂O₃) are extremely low. Although noble metals such as Pd and Au were reported to be superior candidates for the direct synthesis of H₂O₂ from H₂/O₂,¹³ the results listed in Table 1 suggest that neither Pd nor Au appears to be suitable material for direct H₂O₂ production from the CO/O₂/H₂O system. While further work is needed to fully understand why the performance of copper appears to be so much better than that of other metals, we suggest that the superior performance of the copper catalyst system is associated with a two-step reaction mechanism involving the initial step of the water gas shift (WGS) reaction (CO + H₂O = CO₂ + H₂) and subsequent reaction between the produced H₂ and O₂. In this respect, it is reasonable that the copper catalyst exhibits superior performance with respect to other metals for H₂O₂ synthesis, as it is known to be one of the most efficient systems for the WGS reaction.¹⁴

On the other hand, it was found that the catalytic activity of Cu/Al₂O₃ is greatly dependent on a number of important factors such as the reaction temperature, relative pressure of carbon monoxide with respect to O₂ and the choice of solvent as the reaction medium. Fig. 1 compares the formation rate of H₂O₂ over the present Cu/Al₂O₃ catalyst in a reaction medium consisting of 10 ml of 0.01 M H₂SO₄ and 40 ml of organic solvent or water at 273 K. Under the same reaction conditions, the organic solvents acetone, methanol, ethanol and *iso*-propanol were examined, along with pure water as a reference. Obviously, all organic solvents gave a much higher rate of



Scheme 1

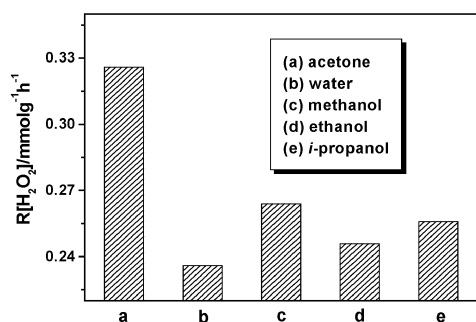
Table 1 Formation of H₂O₂ from the reaction of CO/O₂/H₂O over various alumina-supported catalysts^a

Catalyst	Prep. method	T/K	P _{CO} :P _{O₂}	R[H ₂ O ₂] ^b /mmol (g cat.) ⁻¹ h ⁻¹
Cu/Al ₂ O ₃	WR	273	1:1	0.236
	WR	273	3:1	0.178
	WR	273	1:3	0.202
	WR	293	1:1	0.177
	GR ^c	273	1:1	0.150
Ni/Al ₂ O ₃	WR	273	1:1	0.095
	WR	293	1:1	0.075
Co/Al ₂ O ₃	WR	273	1:1	0.055
	WR	293	1:1	0.045
Fe/Al ₂ O ₃	WR	273	1:1	0.023
	WR	293	1:1	0.016
Ru/Al ₂ O ₃	WR	273	1:1	0.005
Au/Al ₂ O ₃	WR	273	1:1	0.002
Pd/Al ₂ O ₃	WR	273	1:1	0.002

^a Reaction conditions: total pressure = 4 MPa, reaction medium = water, 0.01 M of sulfuric acid, reaction time = 3 h. ^b Average rate of H₂O₂ formation over 3 h experimental time. ^c The reduction of the copper catalyst by gas phase reduction in H₂/Ar at 250 °C for 3 h.

H₂O₂ production than the aqueous reaction medium. Acetone appears to be the best organic media by affording a remarkably high H₂O₂ production rate of *ca.* 0.326 mmol (g cat.)⁻¹ h⁻¹, although the use of acetone as a solvent may result in additional safety concerns due to the possible formation of explosive organic peroxides in the reaction system. It was recently shown that the catalytic activity of a palladium catalyst system for direct H₂O₂ synthesis from a H₂/O₂ mixture is greatly dependent on the reaction medium,⁵ where the rate of production of H₂O₂ from H₂ and O₂ has been suggested to be strongly influenced by the mass transfer rate of the gas into the liquid reaction medium. Thus, the dramatic increase in reaction efficiency upon the proper choice of organic solvent in the present case also confirms the presence of mass transfer limitations in the H₂O₂ synthesis from the CO/O₂/H₂O mixture.^{15,16}

From these experiments, it was found that the choice of solvent was the most important factor to achieve a high rate of H₂O₂ formation from CO, O₂, and water over the Cu/Al₂O₃ catalyst, which is a consequence of enhanced solubility of the CO and O₂ reactant gases in the reaction media.⁵ Under optimized conditions, CO/O₂/H₂O could be transformed efficiently into H₂O₂, with the highest rate attained being 0.326 mmol (g cat.)⁻¹ h⁻¹ for H₂O₂ formation. This result is much superior to that for noble metal catalysts reported in the literature,⁹ showing attractive potential for practical applications. On the other hand, it should be noted that the Cu/Al₂O₃ prepared by gas phase reduction (GR) is less active for H₂O₂ production than the wet reduced sample (see Table 1). TEM

**Fig. 1** Comparison of different reaction media used with 0.01 M sulfuric acid ($V_{\text{solvent}}:V_{\text{H}_2\text{O}} = 3$), $P_{\text{CO}} = 2$ MPa, $P_{\text{O}_2} = 2$ MPa, reaction temperature 273 K, reaction time 3 h.

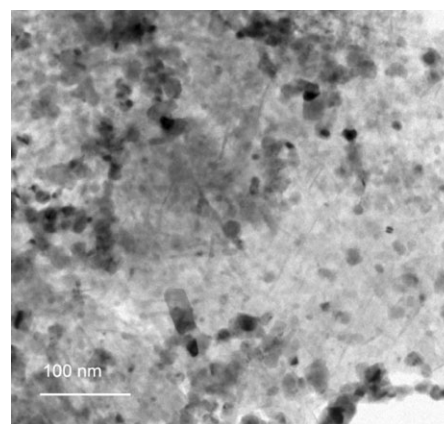
analysis of the two samples reveals that this is probably due to the low dispersion of the Cu particles deposited on alumina when prepared by the GA method. As shown in Fig. 2, Cu nanoparticles (the darker spots as verified by EDX) with an average diameter of *ca.* 12 nm were highly dispersed on the surface of alumina by the wet reduction method, in contrast to a much larger particle size of 20 nm (not shown) for Cu nanoparticles deposited on alumina prepared by the GR method. Therefore, it appears that the size of the Cu particles deposited is also an important factor to achieve a high rate of H₂O₂ formation from CO/O₂/H₂O over the Cu/Al₂O₃ catalyst.

In summary, we have successfully demonstrated that the direct production of hydrogen peroxide from CO, O₂, and water can be effectively achieved over a novel alumina-supported Cu catalyst prepared by a chemical reduction method. Although the mechanism of the superior performance of the Cu/Al₂O₃ catalyst system needs further clarification, this work presents a highly efficient approach for improving the direct synthesis of H₂O₂ from the CO/O₂/H₂O system under heterogeneous conditions.

Experimental

The alumina-supported copper catalyst was prepared by an impregnation-wet reduction method previously established by our group.^{11,12} Alumina (40–60 mesh, from Shanghai Super Chemical Material Co., Ltd, 203 m² g⁻¹) was first impregnated in a 0.1 M CuCl₂ aqueous solution overnight. Then the excessive solution was removed. After being calcined at 383 K for 12 h, this was followed by reduction with a 2 M KBH₄ aqueous solution containing 0.2 M NaOH [$n(\text{BH}_4^-):n(\text{Cu}^{2+}) = 3$]. After reduction, the catalysts were thoroughly washed by oxygen-free distilled water and absolute ethanol successively. The as-prepared catalyst is denoted as Cu/Al₂O₃, where the loading of Cu is 5 wt %. For comparison purposes, the catalysts loaded with other types of metal ions (*i.e.*, Ni, Co, Fe, Ru, Au and Pd) were prepared by following the same procedure.

Catalytic activity measurements were carried out using a 150 ml stainless steel autoclave fitted with a Teflon liner. The reaction conditions were: 1.0 g of catalyst, 50 ml of distilled water containing H₂SO₄ (the concentration of the acid is *ca.* 0.01 M), CO and O₂ total pressure of 4 MPa, reaction temperature of 273 K or 293 K and a stirring rate of 1000 rpm. After the reaction was allowed to proceed for 3 h, the aqueous samples taken out were analyzed by colorimetry after complexation with a TiOSO₄/H₂SO₄ reagent.¹⁷

**Fig. 2** TEM image of as-prepared Cu/Al₂O₃ catalyst obtained by the chemical reduction method.

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