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OXIDATION OF CARBON MONOXIDE OVER BARIUM CUPRATE CATALYSTS

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Catalytic activities of $BaCuO_2$, $Ba_2Cu_3O_5$ and CuO for CO oxidation were investigated. At 250 °C, $BaCuO_2$ was found to be about 7 times more active than CuO, while $Ba_2Cu_3O_5$ was found to be only slightly more active than CuO. This result also demonstrates that expensive rare earth elements such as La and Y are not necessary for a cuprate to have good activity for CO oxidation. After sintering at 940 °C in air, the conversion substantially decreased for CuO. At steady state, both barium cuprates exhibited higher activity than in the fresh state. Based on the absence of significant changes in the XRD spectra, the change in catalytic activity is attributed to changes at the surface and possibly slight reduction of Cu^{2+}. Reaction orders of CO were found to be 1.2 and 0.3, and reaction orders of O_2 were found to be 0 and 0.3 for $BaCuO_2$ and $Ba_2Cu_3O_5$, respectively.

1. Introduction

CO oxidation is one of the most important reactions in air pollution control processes [1,2]. An example is catalytic automotive exhaust fume abatement [3,4]. Current automotive catalytic converters contain mostly noble metal catalysts. However, the limited supply, high cost, and sintering tendency of noble metals have led to a continuing search for alternatives since the early seventies [3–9]. A number of base metal oxides, such as Co_3O_4, $LaCoO_3$, and CuO, among others, were found to have similar or even better specific activity for CO oxidation compared to the noble metal catalysts. However, some undesired effects, such as susceptibility to sulfur poisoning, low thermal resistance, and the loss of low temperature activity, have limited their application.

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The discovery of high temperature superconductors has stimulated intensive research on the catalytic behavior of different cuprates. Earlier results [10–17] suggest that some of these new oxide catalysts are promising candidates for minimizing the use of or for replacing noble metals in catalytic converters. The alkali and rare earth cuprates are usually synthesized above 900 ° C, and thus should not sinter extensively under typical catalytic converter conditions (< 800 ° C). The superconducting perovskite $YBa_2Cu_3O_7$ was found to be active in NO decomposition [10–12] and CO oxidation [13]. La_2CuO_4 and its strontium-doped derivatives were reported to have similar activity for CO oxidation as compared to $YBa_2Cu_3O_7$. In addition, these catalysts were also found to have good sulfur resistance [14]. The nonstoichiometric yttrium and lanthanum cuprates with perovskite-like structure are also active in the reaction of CO + NO to form CO_2 and N_2 [15,16]. We have recently shown that the nature of surface atoms play a more important role in determining the activity for CO oxidation than the electrical conductivity or having the perovskite structure. Thus, orthorhombic non-conducting Y_2BaCuO_5, which has been suggested to contain enhanced numbers of accessible Cu^+ ions, was found to be about two orders of magnitude more active than superconducting $YBa_2Cu_3O_7$ [17].

All these cuprates contain expensive rare earth elements. As very little is known about the active sites of these catalysts, it is not known if the presence of rare earth metal is essential for catalytic activity. $SrCuO_2$ was reported [14] to be less active for CO oxidation than some Sr-doped lanthanum cuprates, but more active than pure La_2CuO_4. In this communication, we report our investigation of the activity for CO oxidation of two barium cuprates which do not contain a rare earth metal: $Ba_2Cu_3O_5$ and $BaCuO_2$. The catalytic activities are also compared to that of CuO, which is known to be highly active for this reaction [8,9]. $Ba_2Cu_3O_5$ is an excellent starting material for preparing yttrium- [18–20] and thallium- [21–23] based superconductors. While $BaCuO_2$ is not appropriate for synthesizing $YBa_2Cu_3O_7$ [19,20], it is good for making thallium- [22–25] and bismuth- [26] based superconductors. The first catalytic study of these barium cuprates [27] showed that their activities for selective methanol oxidation differ significantly, with $Ba_2Cu_3O_5$ being more active than $YBa_2Cu_3O_7$.

2. Experimental

The barium cuprates $BaCuO_2$ and $Ba_2Cu_3O_5$ were prepared by mixing stoichiometric amounts of $Ba(NO_3)_2$ and CuO in a porcelain crucible and heating in air at 940 ° C for 5 hours. The products were confirmed by powder X-ray diffraction [19,23]. The $Ba(NO_3)_2.2H_2O$ used is 99.9% pure and was obtained from the Merck Co. The CuO used in A.C.S. reagent grade (99% pure) from Spectrum Chemical MFg. Co. One sample of copper oxide was used without preheating; the other was heated under the same conditions as the barium cuprates and marked as CuO(940). X-ray powder diffraction patterns were measured on a Rigaku CN4148H2 diffractometer with 12 kW rotating anode and computerized data system, including the JCPDS data base.

The experiments were done with equal contact times for the various catalysts, so equal volumes (0.44 cm^3) of catalysts were used for the studies. The samples were contained in a borosilicate reactor (flow-through type with a low dead volume and having a 10 mm diameter porous glass frit to support the catalyst). The catalysts were preheated in a flow of 40 L/h of He at 500 °C for 3 h and then cooled to room temperature. After evacuation, BET surface areas were measured in situ by N_2 adsorption at 77 K, using a Sundstrand model 314D001 electronic pressure transducer to measure the uptake of gas in a fixed volume.

For catalytic measurements, appropriate amounts (about 1%) of pure O_2 and CO were mixed with He carrier gas at a total pressure of 1 atm (1.0×10^5 Pa) and a space velocity of 1.04×10^5 h^{-1} (total flow rate is 46000 ± 500 mL/h). The rate of each gas flow was controlled by a Brooks Model 5850 mass flow controller. The reaction system is constructed of brass with bellows seal valves (overall leakage of the total system was $< 6 \times 10^{-7}$ atm.cm^3/s), has a base pressure of 1×10^{-7} Torr, and is free of grease, mercury, and elastomers. The activity versus pressure dependence was measured in the conventional manner by varying the O_2 partial pressure from 930 to 4400 Pa and keeping a constant CO pressure (915 Pa), and by varying the CO partial pressure from 540 to 4200 Pa and keeping a constant O_2 pressure (4360 Pa). Since the reaction is strongly exothermic, an increase in the rate of reaction can result in local heating of the catalyst and thus a sudden jump in conversion. This resulted in the kinetic measurements being restricted to a narrow range of temperatures: 150–170 °C for $BaCuO_2$ and 130–140 °C for $Ba_2Cu_3O_5$. To minimize the effects of concentration and temperature gradients in the catalyst bed, the data used for kinetic calculations were limited to a range of 1 to 12% conversion. The kinetic measurements were done while the temperature of the reactor was constant.

Products were analyzed by gas chromatography on 3 ft × 1/8 inch silica gel and 4.5 ft × 1/8 inch molecular sieve 5A columns at 90 °C, used in a series/bypass switching mode and controlled by a Carle Model 5520 6-way valve. Samples of the reactor effluent were injected into the GC by an automated gas sampling valve. Initially, the columns were connected in series until oxygen and carbon monoxide passed through the silica gel column and entered the 5A column. The valve was then actuated, providing a bypass around the molecular sieve column. After CO_2 was detected, the valve was returned to the series position and CO and O_2 were eluted through the molecular sieve 5A column. Peak areas were integrated using a Hewlett Packard model 3393A digital integrator with appropriate calibration factors for each gas.

3. Results and discussion

PHYSICAL MEASUREMENTS

The bulk densities of the catalysts were 3.07, 2.10, 1.18, and 1.22 g/cm^3 for $Ba_2Cu_3O_5$, $BaCuO_2$, CuO, and CuO(940), respectively. The specific surface areas were 0.50, 0.25, 2.40, and 0.29 m^2/g for $Ba_2Cu_3O_5$, $BaCuO_2$, CuO, and CuO(940) respectively.

REACTION ON BARIUM CUPRATES

In order to obtain comparable results, activity studies for the catalysts were carried out at the same reaction conditions. The space velocity and CO concentration used in this study correspond to severe conditions for CO oxidation (high space velocity and CO concentration) in a typical catalytic converter for an automobile [9]. Equal catalyst volumes were used instead of equal weight or surface areas, to avoid complications introduced by different contact times.

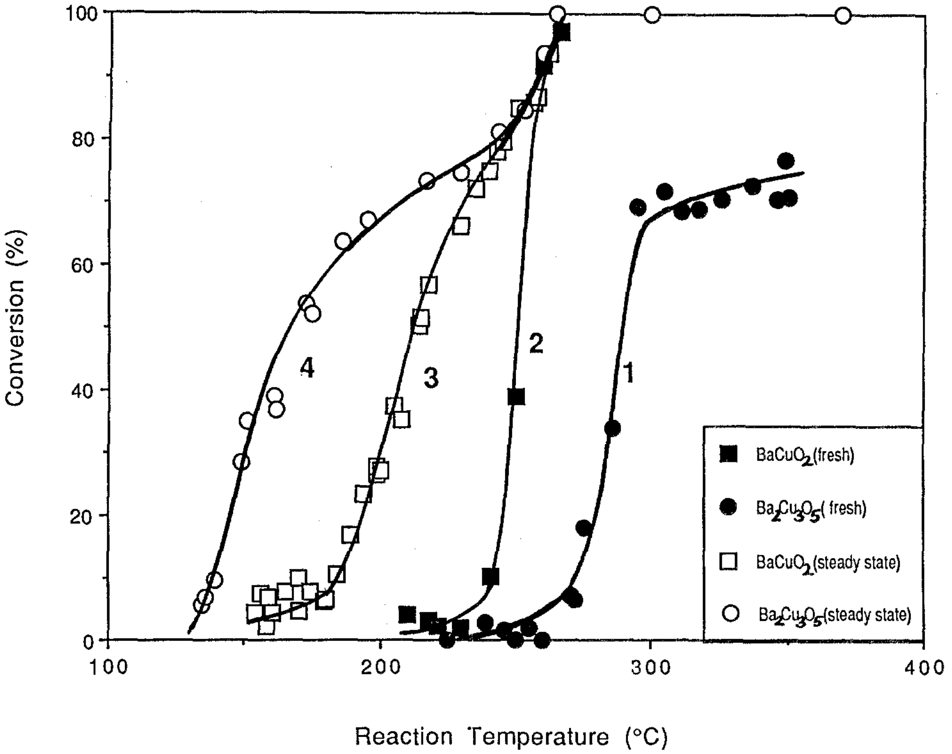

Fig. 1. CO conversion versus reaction temperature on fresh and steady state $Ba_2Cu_3O_5$ and $BaCuO_2$ catalysts; partial pressures of reactants: $P_{O_2} = 990$ Pa, $P_{CO} = 940$ Pa; carrier gas He; total pressure 1.0×10^5 Pa; SV $= 1.04 \times 10^5$ h^{-1}.

Temperature dependencies of the activity of barium cuprates are shown in fig. 1. About 1 to 2% CO conversion was observed near 220 °C and 240 °C on fresh $BaCuO_2$ and $Ba_2Cu_3O_5$, respectively (curves 2 and 1). The initial conversion remained below 5% over a relatively wide temperature range (~ 20 °C) on both fresh catalysts. This was followed by a sharp increase in activity at around 250 °C and 270 °C for $BaCuO_2$ and $Ba_2Cu_3O_5$, respectively. After achieving 100% conversion, the $BaCuO_2$ showed enhanced activity during the cooling cycle, curve 3. The increased activity was stable throughout several heating and cooling cycles (also shown on curve 3), even after more than 100 hours at different reaction conditions. As the catalysts were prepared in air at a much higher temperature, the presence of CO seems to be responsible for the increase in activity, in spite of the presence of excess oxygen. A similar result was observed for Y_2BaCuO_5 for which it is believed that reduction of some of the surface Cu^{2+} to Cu^+ may be responsible for the enhanced activity [17]. The same phenomenon may be operational here.

The $Ba_2Cu_3O_5$ catalyst exhibits similar behavior (curves 1 and 4). However, a conversion limit of about 80% was observed with the fresh catalyst. A similar leveling off in activity was observed for Y_2BaCuO_5, and this phenomenon is not well understood [17]. Also, the enhanced and stable activity (curve 4) did not appear immediately after curve 1, which contains points for both a heating and cooling cycle. Rather, this was observed after making kinetic measurements near 230 °C for approximately 10 h with different partial pressures of CO (the O_2/CO ratio was always larger than 1). Another noteworthy difference is that the activity of fresh $Ba_2Cu_3O_5$ is lower than the activity of fresh $BaCuO_2$, but the steady state activity of $Ba_2Cu_3O_5$ is in general higher (curves 3 and 4).

X-RAY POWDER DIFFRACTOGRAMS OF FRESH AND STEADY STATE BARIUM CUPRATE CATALYSTS

In order to gain a better understanding of possible structural modifications, XRD measurements were carried out for both the fresh and steady state catalysts. As shown in fig. 2, the X-ray powder patterns of fresh $BaCuO_2$ and fresh $Ba_2Cu_3O_5$ are very similar (curves C and D). The cubic structure of $BaCuO_2$, containing 360 atoms/unit cell, has been identified by single crystal X-ray diffraction [28].

There is speculation that $Ba_2Cu_3O_5$ could actually be a mixture of $2BaCuO_2 + CuO$. However, there are many experimental findings which indicate that it is a true compound. (1) A tetragonal structure of $Ba_2Cu_3O_5$, constructed of perovskite type units, was deduced from powder X-ray data [29] (no data for a single crystal are available). (2) A new, unidentified phase with a stoichiometry close to $Ba_3Cu_5O_8$ has been reported [30], and it is possible that this phase is $Ba_2Cu_3O_5$. (3) There are differences in the ESR signals [20] and melting points [31] of $BaCuO_2$ and $Ba_2Cu_3O_5$. (4) The two substances have different electrical interac-

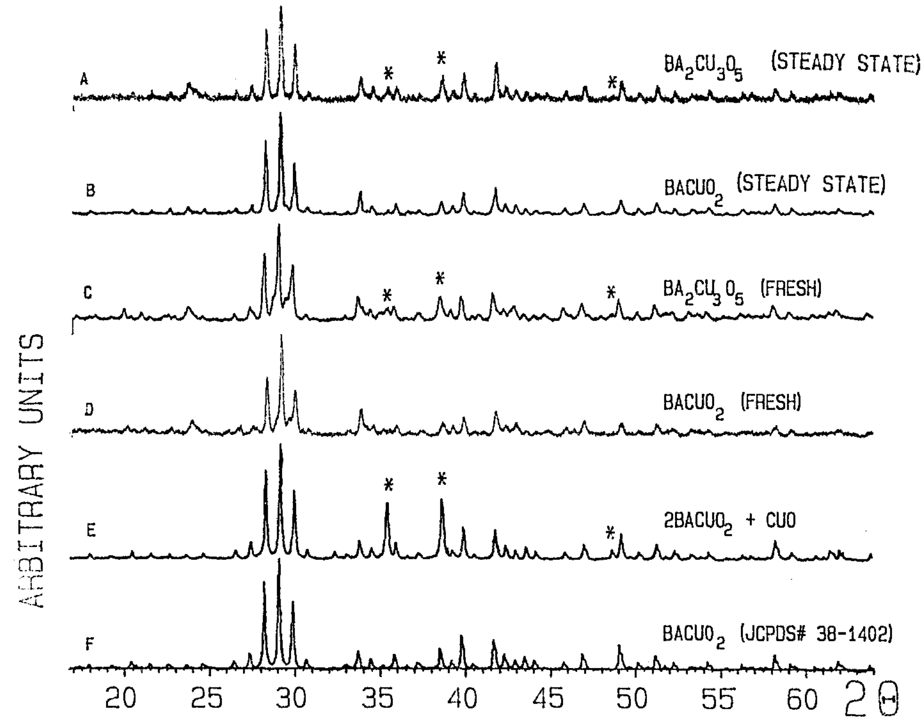

Fig. 2. X-ray powder diffraction patterns of the fresh and steady state barium cuprates; pattern F is from the JCPDS data file; pattern E is a superposition of the JCPDS data file patterns for $2BaCuO_2 + CuO$; CuO peaks are marked by an asterisk *.

tions with the superconductor $YBa_2Cu_3O_7$ [18–20]. (5) By reacting Y_2O_3 with $Ba_2Cu_3O_5$ in a wide range of starting compositions (from 1 : 1 to 1 : 500 mole ratio), the perovskite-type superconductor $YBa_2Cu_3O_7$ was formed exclusively [18,19]. Therefore, the $Ba_2Cu_3O_5$ structure can be considered a precursor to Y-Ba-Cu-O superconductors. However, when $BaCuO_2$ was reacted with different stoichiometric ratios of Y_2O_3, the nonconducting green phase Y_2BaCuO_5 was the major product [19,20]. (6) If $Ba_2Cu_3O_5$ were a stoichiometric mixture of $2BaCuO_2 + CuO$, large characteristic peaks of CuO should appear in the X-ray diffraction pattern if the CuO is at least partly crystalline. However, this is not observed [19]. To illustrate this, the diffractograms of $BaCuO_2$ (pattern F) and a simulated spectrum of $2BaCuO_2 + CuO$ (pattern E) are shown in fig. 2. The relative intensities of CuO peaks (marked with an asterisk) to $BaCuO_2$ peaks in pattern E are identical with those of an XRD pattern of a genuine mixture of $2BaCuO_2 +$ CuO [19]. Comparing patterns A and C to E, it is clear that at most only a small amount of CuO can be present in the $Ba_2Cu_3O_5$ catalyst, far less than would be expected if it were a mixture of $2BaCuO_2$ and CuO. (7) A careful comparison of the X-ray powder pattern of the two fresh cuprates (patterns C and D) also reveals subtle differences corresponding to their crystal structures [29]. The

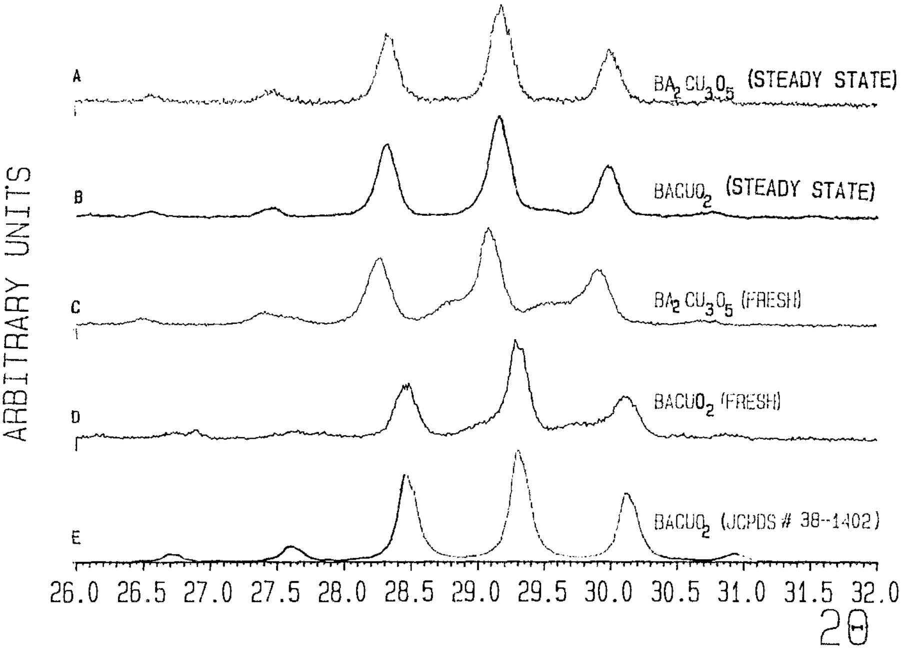

Fig. 3. Characteristic differences and changes in the 26.0-32.0 2θ region of X-ray powder diffraction patterns of the fresh and steady state $BaCuO_2$ and $Ba_2Cu_3O_5$ catalysts; pattern E is from the JCPDS data file.

typical shift to lower values of 2θ in the largest reflections (peaks between 2θ = 28 and 30.5 °) of $Ba_2Cu_3O_5$ with respect to $BaCuO_2$ is readily observable in fig. 3 (patterns C and D). (8) In contrast to the case with $BaCuO_2$, a reversible phase transformation was observed by TGA, DTA, and XRD when the preparation temperature of $Ba_2Cu_3O_5$ was varied between 750 ° C and 950 ° C [29,32].

Despite the above considerations, special attention was given to the possible effect of CuO on catalytic activity, since this oxide was reported [8,9] as one of the most active catalysts for CO oxidation. A comparison of the X-ray powder patterns of the fresh and steady state catalysts in fig. 2 (pattern D versus B, and pattern C versus A) indicates that the bulk structure of the cuprates is nearly (but not totally, *vide infra*) unchanged after reaction. Therefore, he enhanced activity observed cannot be the result of a significant amount of bulk CuO or other compounds formed by decomposition. In addition, neither metallic Cu (whose most intensive peak would be at 2θ = 43.3) nor other copper oxides (e.g., Cu_2O, Cu_4O_3, etc.) could be detected. Thus, the increase in activity can probably be attributed to changes on the surface.

There are some fine alterations in the X-ray diffractograms. A small difference between the fresh and steady state catalyst can be seen near 2θ = 28.8 and 29.7 ° (fig. 3). The fresh catalysts show satellite lines which can be attributed to a small amount of a $Ba_2Cu_3O_{5+d}$ phase, which is usually prepared at lower temperatures

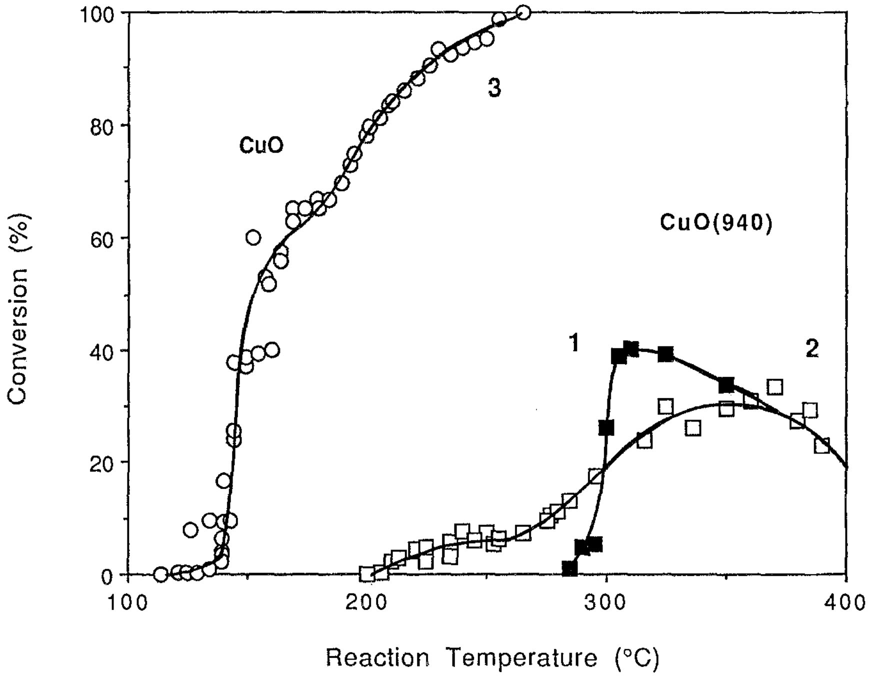

Fig. 4. CO conversion versus reaction temperature on CuO catalysts with and without preheating at 940 ° C; reaction conditions are the same as on fig. 1; curve 1: fresh CuO(940), curve 2: steady state CuO(940), curve 3: activity of fresh and steady state CuO.

and probably contains nonstoichiometric excess oxygen atoms ($0.1 < d < 1$) [29,32]. Their disappearance after reaction may be due to some reduction or slight change in lattice constants. Fig. 3 also shows the characteristic small difference in 2θ of 0.2° between the peaks of fresh $BaCuO_2$ and fresh $Ba_2Cu_3O_5$ (patterns D and C). After reaction, the reflections of $BaCuO_2$ shift 0.2° to lower values of 2θ, so the spectrum is now almost identical (and possibly identical within experimental error) to that of $Ba_2Cu_3O_5$ (patterns B and A). Various slight movements of the lattice could cause this change, but we are unable to pinpoint the reason.

REACTION ON COPPER OXIDES

To check the possible effect of the presence of any CuO on the activity of $Ba_2Cu_3O_5$, oxidation experiments were carried out on pure CuO using the same experimental conditions as for the barium cuprates. Since the barium cuprates were prepared at 940 ° C, a sample of CuO was also calcined at this temperature, designated as CuO(940). Interestingly, the catalytic behavior of the CuO(940) was found to be very different from that of the untreated sample, as shown in fig. 4. The activity of fresh CuO(940), curve 1, was much lower than that for the untreated CuO, curve 3. Much, but not all, of the difference can be attributed to the 8-fold lower surface area of this catalyst. The first measurable conversion for

CuO(940) was obtained at 290 ° C. The conversion jumped to 40% within a 20 ° C temperature range, and the activity then decreased slightly. The steady state behavior of CuO(940) during several heating and cooling cycles is shown on curve 2. A small conversion (< 1%) was observed near 210 ° C, but the conversion never exceeded 40%, even with reaction temperatures up to 400 ° C. In contrast, on the untreated fresh CuO about 1% conversion was measured at 120 ° C on the untreated fresh CuO, and 100% conversion was achieved at 260 ° C (curve 3). The steady state activity was the same as for the fresh catalyst, and curve 3 contains points for several heating and cooling cycles. Temperature programmed reduction experiments [34] show that CuO(940) starts to reduce at a much higher temperature than CuO. Therefore, the much lower activity observed for CuO(940) below 200 ° C may be due to the difficulty in reducing the surface.

Assuming the widely accepted Mars-van Krevelen mechanism [33], the conversion limit on CuO(940) for reaction temperatures above about 300 ° C can be attributed to a slow diffusion controlled reduction or reoxidation of the catalyst surface through a chemisorbed layer of oxygen and CO molecules. Temperature programmed reduction experiments [34] suggest that a partial bulk reduction takes place in this temperature range, which can also cause a diffusion controlled process. However, the possibility of a reversible change in the surface at high temperatures must also be considered [17]. The chemisorption of CO on these materials has not been extensively investigated. The adsorption of CO on 8% CuO supported on activated carbon was small at 20 ° C, being 3×10^{-7} mol CO

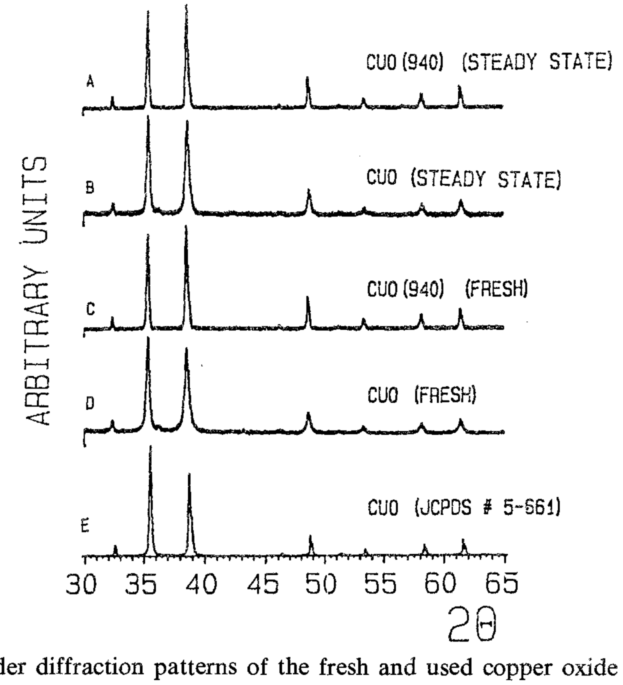

Fig. 5. X-ray powder diffraction patterns of the fresh and used copper oxide catalysts; CuO(940) was preheated at 940 ° C in air; pattern E is from the JCPDS data file.

per g catalyst [35]. The amount of adsorption of CO on $L_{2-x}Sr_xCuO_4$ was also found to be low [36].

The X-ray powder diffraction patterns of the fresh and used CuO catalysts (fig. 5) suggest that the difference between the activities is not due to bulk structural changes. Neither traces of metallic Cu nor of other copper oxides were detected by XRD in any of the samples. However, TGA experiments in pure oxygen showed [34] that the untreated CuO continuously loses weight between room temperature and 950 ° C (total loss was 0.85%), while CuO(940) adsorbed about 0.006 O atom/CuO formula unit between 750 and 950 ° C. About 85% of the weight loss for CuO occurs below 450 ° C and we believe that this is probably just the desorption of water from this relatively high surface area sample. The oxygen uptake by CuO(940) is probably due to slight nonstoichiometry of this sample caused by oxygen loss during its pretreatment at 940 ° C (CuO is a p type semiconductor). The results for copper oxides show that, as with many other catalytic reactions on metal oxides, the preparation temperature can strongly affect the catalytic activity.

COMPARISON OF THE ACTIVITY AND KINETIC RESULTS OF BARIUM CUPRATES AND COPPER OXIDES

Figs. 1 and 4 show that $Ba_2Cu_3O_5$ can be as effective for catalytic CO oxidation as the highly active CuO. The barium cuprates have the advantage that,

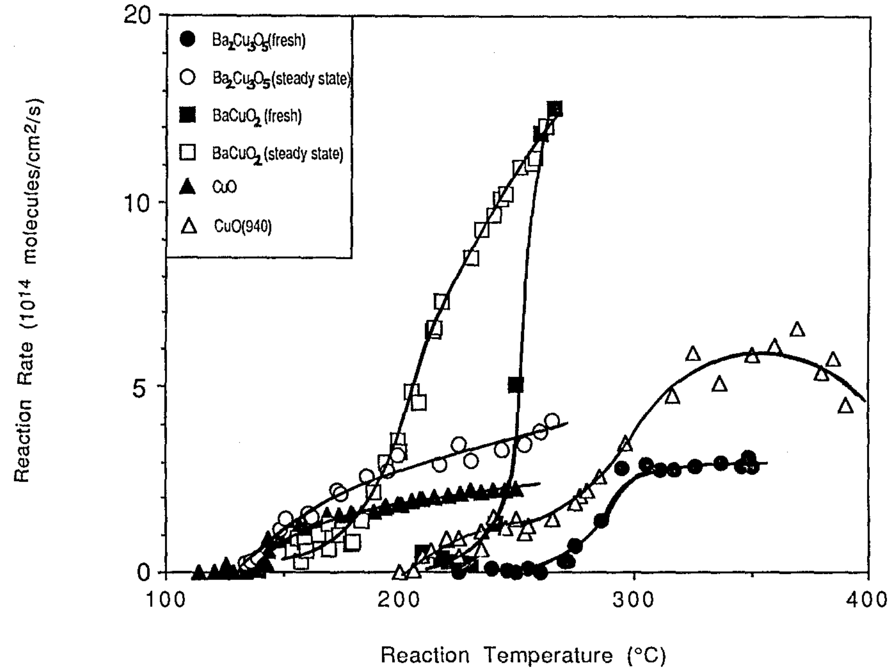

Fig. 6. Comparison of the reaction rates on the different CuO and Ba-Cu-O catalysts based on surface area; reaction conditions are the same as in fig. 1.

Table 1
Kinetic results for CO oxidation over steady state barium cuprate catalysts

Catalyst	Order in O_2	Order in CO	E_a (kJ/mol)	Rate at 250 °C (mL CO/m^2/min)
$BaCuO_2$	0 ± 0.1	1.2 ± 0.1	63 ± 5	30.8
$Ba_2Cu_3O_5$	0.3 ± 0.1	0.3 ± 0.1	165 ± 10	9.7

in contrast to CuO, high temperature treatments (at least up to 940 °C) will probably not cause any loss of activity.

The reaction rates per unit surface area are compared in fig. 6. At 250 °C, $BaCuO_2$ is 7 times more active than CuO, and its activity (table 1) is almost as high as that of a Pt wire (100 mL CO/m^2/min at 300 °C) [8,9]. This result also indicates for the first time that rare earth elements are not indispensable constituents for fabricating active cuprate catalysts for CO oxidation. Fig. 6 also demonstrates that the relative activity of the two types of CuO catalysts strongly depends on the temperature of reaction. It is not clear why $BaCuO_2$ is more active than CuO. However, according to the model for oxidation proposed by Noller and Vinek [37], it is expected that an increase in basicity of the catalyst should improve the activity. It is expected that the presence of Ba^{2+} should accomplish this.

The results of kinetic measurements carried out on steady state barium cuprate catalysts are summarized in table 1. It is known that CO oxidation has an activation energy of about 90 kJ/mol on the most active CuO catalysts in the temperature range of 150–250 °C and that the reaction orders are 0 and 0.7 for O_2 and CO, respectively [1,8,9]. At lower reaction temperatures the activation energy is higher, because reoxidation of the surface is hindered by the slow desorption of CO [1,8,9].

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