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# Determination of Reducibility and Identification of Alloying in Copper-Nickel-on-Silica Catalysts by Temperature-Programmed Reduction

S. D. ROBERTSON,[1] B. D. MCNICOL,[2]
J. H. DE BAAS AND S. C. KLOET

*Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B. V.), Badhuisweg 3, Amsterdam-N., The Netherlands*

AND

J. W. JENKINS

*Shell Development Company, MTM Process R & D Laboratory, Deer Park, Houston, Texas 77536*

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As part of a study of bimetallic alloying on a support, the reduction characteristics of various copper-, nickel-, and copper–nickel-on-silica catalysts have been examined. The method used for this study, a temperature-programmed technique, involves a continuous and quantitative monitoring of the hydrogen uptake due to the reduction of a particular species on the catalyst surface.

Irrespective of whether the bimetallic catalysts (in nitrate form) are or are not precalcined, both copper and nickel exist in the zero-valent metal state and are engaged in alloying after a hydrogen treatment at 500°C. The precalcination history of the bimetallic catalysts and the relative metal loadings of such preparations have a marked influence on the manner in which the two metals are reduced. Some possible causes for these findings and the potentialities of the temperature-programmed reduction technique are discussed.

## INTRODUCTION

Bimetallic catalysts are a subject of considerable interest in catalysis research because the performance of the bimetal species differs markedly from that of their components. For example, the selectivity of silver in the oxidation of ethylene to ethylene oxide (*1*) (as opposed to carbon dioxide and water) and of cumene to cumene hydroperoxide (*2*) is increased remarkably by alloying with gold, yet the latter is itself inactive in these reactions. Similarly, alloying nickel with copper clearly modifies the activity of the former metal in the hydrogenation of ethylene (*3,4*), benzene (*5,6*) and butadiene (*7*). This alloy system has also demonstrated a remarkable selectivity in the isomerization, as opposed to hydrogenolysis, of *n*-hexane though copper itself is virtually inactive (*8*).

The majority of these studies have been made on unsupported bimetallic systems (films or powders), where the nature of alloying can be judged by physical methods of structural analysis such as X-ray diffraction. The constitution of supported copper–nickel systems has also been examined in this way (*9*) but only after catalyst preparation. Therefore, it

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[1] To whom any correspondence should be sent.

[2] Present address: Shell Research Ltd., Thornton Research Centre, P. O. Box 1, Chester CH1 3SH, England.

seemed of considerable interest to explore the chemistry of bimetallic species on a carrier in the course of catalyst reduction. It is to this end that we have tested the applicability of a temperature-programmed reduction (TPR) technique to the hydrogen treatment of copper-nickel-on-silica catalysts.

## EXPERIMENTAL METHODS

### *The Temperature-Programmed Reduction (TPR) Technique*

The TPR method is a variation of the temperature-programmed desorption (TPD) technique (*10*). A diagram of the (TPR) system is shown in Fig. 1. The reducing gas, a mixture of 6% v hydrogen in nitrogen, was purified over a $Pt/Al_2O_3$ catalyst and dried in a cold trap at −78°C. It was directed at a rate of 600 ml/hr and an overpressure of 0.5 atm first through the reference compartment of a thermal conductivity (TC) cell, then through the reactor containing the catalyst and finally, via a cold trap, through the other compartment of the TC detection cell. The amount of catalyst used depended upon the nature and the loading of the metals employed; for the low-loaded systems ($\leq 1\%$ w) about 0.35 g of catalyst was taken. The reactor was heated at a linear rate (usually at 4.5 to 10°C $min^{-1}$) from −80 to 700°C. The consumption of hydrogen due to the reduction of a specific species on the catalyst was monitored by the TC cell in conjunction with an amplification and integration system. The catalyst can be purged with nitrogen (or treated in air) as required.

This technique therefore permits a profile or "finger print" of catalyst reduction to be obtained. It is eminently suitable for studying low-loaded highly dispersed systems whose characteristics are beyond the limits of detectability by most other direct methods of structural analysis (e.g., X-ray diffraction).

### *Catalyst Preparation*

Davison 70 silica, after purification with 4 *M* hydrochloric acid, washing with water, drying and calcining (500°C, 3 hr), had a BET surface area of 380 $m^2/g$. In some cases Davison 950 silica (surface area 700 $m^2/g$) was used. The carrier, in

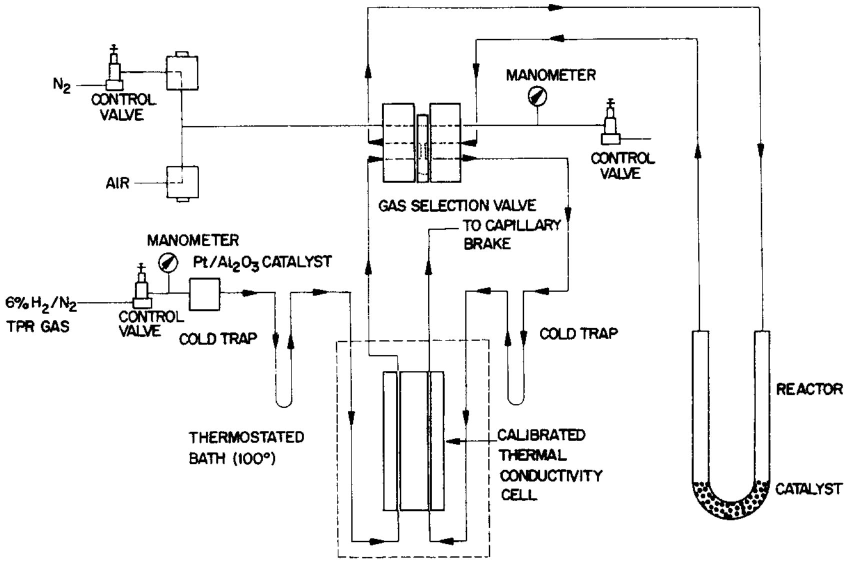

FIG. 1. Diagram of temperature-programmed reduction (TPR) system.

particle form (0.42–0.18 mm), was impregnated *in vacuo* to incipient wetness with a copper and/or nickel nitrate solution (Analar reagents) to give the desired metal loadings (quoted as wt%). The catalyst was dried *in vacuo* at 100°C for 2 hr prior to the TPR studies. Unsupported copper and nickel oxides obtained from calcination of their nitrates were also studied.

## RESULTS

The reducibilities of supported and unsupported nickel oxide are given in Fig. 2. When supported on the high-surface-area silica (0.25% Ni loading) the nickel oxide is more difficult to reduce (the temperature for maximum hydrogen uptake is about 410°C) despite its being more finely divided. We conclude, therefore, that there must be a nickel oxide/support interaction which, though hindering the reduction, does not, however, suppress it. Thus the observed hydrogen uptake is 1.01 ml/g cat compared to 0.90 ml/g cat. required for complete conversion of nickel oxide to zero-valent nickel, the difference of which is within the limits of accuracy of our technique (±10%). In contrast to this, however, copper oxide, when supported on the silica carrier, is more easily reduced, as demonstrated for 0.75% Cu loaded catalyst in Fig. 3. The support in this case appears to function purely as a dispersing agent, enhancing the reactivity of this oxide towards reduction. The measured hydrogen consumption (2.58 ml $H_2$/g cat) corresponds approximately to that required for complete copper reduction (2.83 ml $H_2$/g cat).

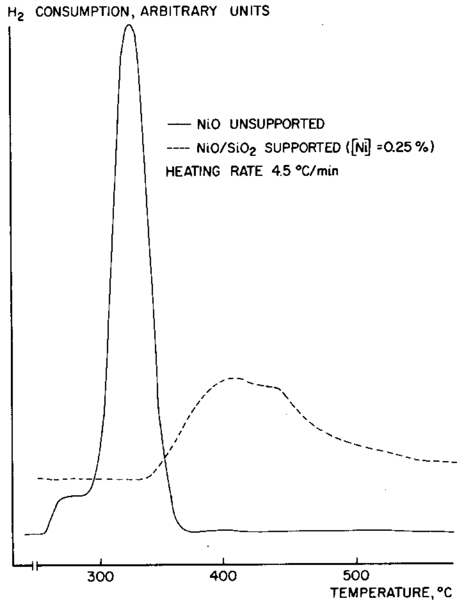

FIG. 2. Temperature-programmed reduction of unsupported and silica-supported nickel oxide.

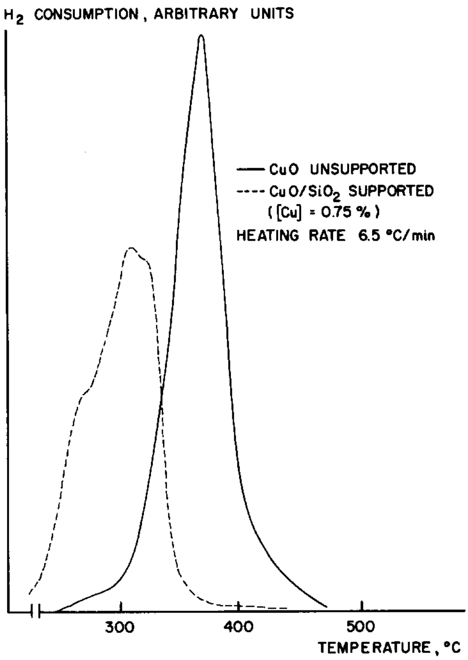

FIG. 3. Temperature-programmed reduction of unsupported and silica-supported copper oxide.

A 0.75% copper–0.25% nickel catalyst was calcined at 500°C for 1 hr after a "flash" (about 20°C/min) air pretreatment to this temperature. The sample was subsequently maintained in a stream of nitrogen at 400°C for 0.5 hr prior to cooling in this gas to −75°C for temperature-programmed reduction. The peak at −50°C in the reduction profile (Fig. 4, solid line) is due to the desorption of nitrogen from the carrier; the resultant de-

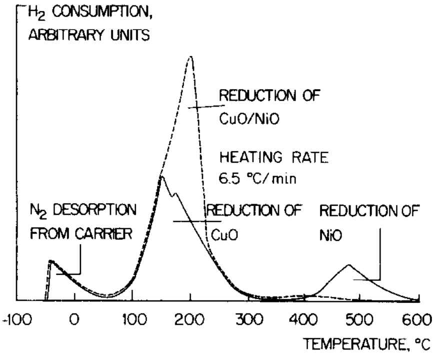

FIG. 4. Temperature-programmed reduction of 0.75% copper–0.25% nickel-on-silica catalyst. (—) 1st TPR after calcination (500°C, 1 hr); (---) 2nd TPR after reduction (500°C, 16 hr) +calcination (400°C, 0.5 hr).

crease in hydrogen concentration is recorded as an apparent hydrogen uptake. The remainder of the profile comprises two well-defined peaks. The first of these is generated at temperatures between 100 and 250°C. The consumption of hydrogen here corresponded to that required for the reduction of *all the copper* from the divalent to the zero-valent state (see Table 1). The second peak (between 400 and 500°C) arises similarly from the subsequent reduction of *all the nickel* from the divalent to the zero-valent state (see Table 1). This finding of complete nickel reducibility in such a calcined bimetallic catalyst was confirmed by our previous observation for the monometallic 0.25% Ni reference standard. This two-stage reduction, observed for the bimetallic catalyst, was essentially independent of the heating rate used in the precalcination treatment (about 2 or 20°C/min to 500°C). Further reduction of this copper–nickel catalyst at 500°C for 16 hr and recalcination at 400°C for 0.5 hr afforded a second reducibility profile (broken line in Fig. 4). This profile exhibited only one well-defined peak at about 200°C. The quantity of hydrogen consumed here corresponded to complete reduction of *all the copper and nickel* of the catalyst (see Table 1). Such a "simultaneous reduction" of these metals, together with the absence of a reduction peak at higher temperatures, suggests that alloying had occurred either during the reduction or on the subsequent (16 hr) treatment under hydrogen at 500°C.

However, a catalyst with a copper–nickel ratio of 1:3 (viz, 0.25% Cu–0.75% Ni on $SiO_2$) after precalcination and the nitrogen treatment described previously, gave a TPR profile showing that the two metals were for the greater part concomitantly reduced at about 280°C (Fig. 5, solid line). Subsequent reduction of this catalyst (500°C, 16 hr) produced, after a mild calcination (0.5 hr at 400°C in air), essentially the same TPR profile (Fig. 5, broken line) and we conclude, therefore, that metallic alloying (although incomplete) had occurred during the initial programmed reduction of the oxide precursors.

The copper-rich catalysts which were, however, calcined externally by heating to 500°C (3°C/min to 500°C; 1 hr at 500°C),

TABLE 1
METAL REDUCIBILITIES OF 0.75% COPPER–0.25% NICKEL-ON-SILICA CATALYSTS

| Treatment | TPR | Hydrogen consumption (ml/g cat) | | |
|---|---|---|---|---|
| | | Observed | | Expected[a] |
| Calcined (500°C, 1 hr) | 1st | Cu | 2.9 | 2.83 |
| Then, reduced (500°C, 16 hr) + calcined (400°C, ½ hr) | 2nd | Cu/Ni | 3.6 | 3.85 |
| Dried only | 1st | Cu/Ni | 10.4 | 3.85 |
| Then, reduced (500°C, 16 hr) + calcined (400°C, ½ hr) | 2nd | Cu/Ni | 3.7 | 3.85 |

[a] Based on $Cu^{2+} \rightarrow Cu^0$ and/or $Ni^{2+} \rightarrow Ni^0$ reduction.

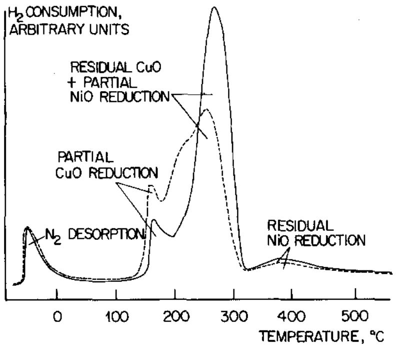

FIG. 5. Temperature-programmed reduction of 0.25% copper–0.75% nickel-on-silica catalyst. (—) 1st TPR after calcination (500°C, 1 hr); (---) 2nd TPR after reduction (500°C, 16 hr) + calcination (400°C, ½ hr); heating rate 6.5°C/min.

then air cooled to room temperature (rather than subsequently nitrogen-treated as described previously) prior to transfer to the reactor, demonstrated reproducibly the absence of the high-temperature nickel oxide peak in the resulting TPR profile (Fig. 6). That such copper enrichment in this type of catalyst facilitates nickel reduction is clearly shown in Fig. 7. Here a more uniform reduction of the components occurs at high relative copper loadings in a total loading of 10%. Moreover, each of the profiles in Figs. 6 and 7 correspond to a hydrogen consumption sufficient to reduce all the copper and nickel to the zerovalent state.

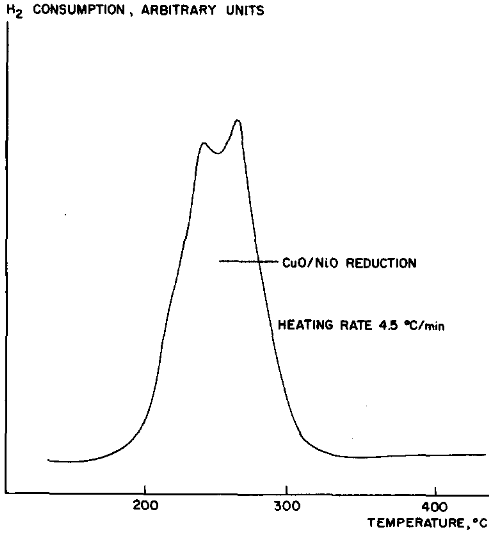

FIG. 6. Temperature-programmed reduction of 0.75% copper–0.25% nickel-on-silica catalyst after external calcination at 500°C (1 hr).

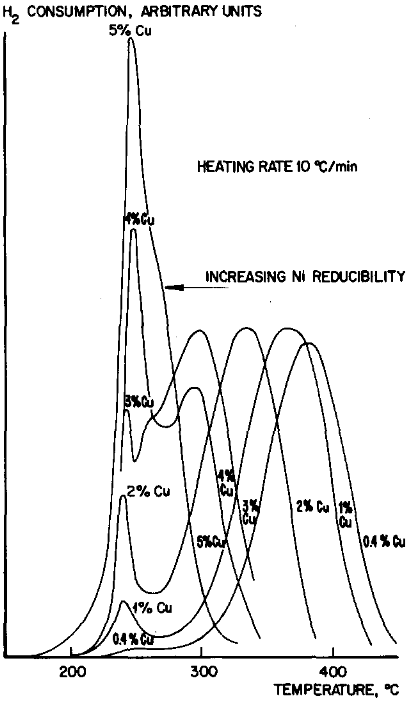

FIG. 7. Temperature-programmed reduction of copper–nickel-on-silica catalyst (total metal loading 10%) after external calcination at 500°C.

To examine the effect of omitting the precalcination step on the reduction properties of the bimetallic Cu-rich catalyst, a TPR study was made of the copper–nickel (nitrate) preparation after drying only (100°C). The reducibility profile, obtained as described previously, is given by the solid line in Fig. 8. Apart from the peak due to desorption of nitrogen from the carrier (at −50°C) there was essentially *only one* large reduction peak (but with small shoulders at 100, 150 and 290°C). This latter peak corresponded (see Table 1) to a hydrogen uptake about three times that required for the simple reduction of all the copper and nickel present as oxides in the catalyst and indicates that partial reduction

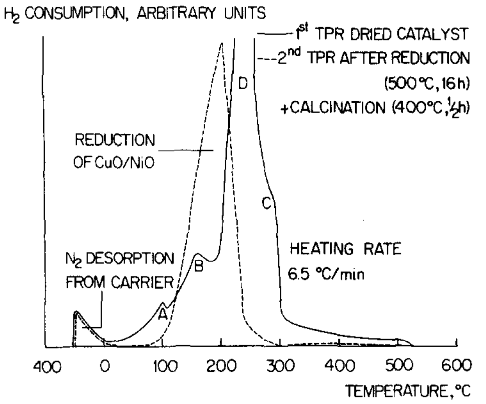

FIG. 8. Temperature-programmed reduction of 0.75% copper–0.25% nickel-on-silica catalyst.

of the nitrate ion also occurs. That such an enhanced hydrogen uptake is due to the direct interaction of the reduction gas with the dried nitrates was demonstrated by a TPR of the bimetallic catalyst after decomposition of the nitrates by pretreatment in *nitrogen only* up to 500°C and maintained for 0.5 hr at 500°C. Here no excess hydrogen consumption took place as the two major peaks corresponded to an essentially complete and stepwise reduction of the copper (at about 200°C) and nickel (at about 500°C) of the catalyst.

This enhanced hydrogen uptake in the TPR of the dried copper–nickel catalyst renders an assessment of the extent of metal reducibility very difficult, although the absence of a reduction peak at higher temperatures suggests that both metals are indeed completely reduced. To clarify this point, the catalyst was maintained for 16 hr under reduction conditions at 500°C and then recalcined (400°C, 0.5 hr) before measuring the second reducibility profile, given by the broken line in Fig. 8. This profile closely resembles that given by the broken line in Fig. 4, in that essentially only one reduction peak is observed, the hydrogen uptake corresponding to that required for the complete reduction of *all the copper and nickel* in the catalyst. Since they are now concomitantly reducible these two elements would appear to be in intimate contact with each other.

## DISCUSSION

The first TPR profiles in Figs. 4, 6 and 8 clearly illustrate the dependence of the mode of copper and nickel reduction on catalyst pretreatment. The high-temperature reduction peak (between 400 and 500°C) in the TPR of the catalyst after calcination (Fig. 4) demonstrates that *in situ* calcination (and nitrogen cooling) of the nitrates operates against a complete interaction of copper and nickel in this copper-rich type of catalyst. Such a diminished bimetallic interaction could be due to the low miscibility of NiO in CuO (about 5% m max) and that of CuO in NiO (about 35% m max) (*11*). Owing to this poor mutual solubility copper and nickel will be present largely as separate compounds on the carrier prior to hydrogen treatment.

The more facile reduction of copper oxide, observed in the TPR of this calcined bimetallic catalyst (Fig. 4, solid line) may be attributed to the molar free energy of reduction being lower for this oxide (−24.04 kcal/mole at 25°C) than for the corresponding nickel compound (−2.94 kcal/mole at 25°C). Thus the incomplete miscibility and the different reducibilities of the two metal oxides appear to act against intimate contact, simultaneous reduction and homogeneous alloying of the two metals on hydrogen treatment of such calcined preparations.

At relative Cu:Ni loadings of 1:3, CuO and NiO have an increased mutual miscibility, which could explain the more concomitant manner of such silica-supported copper–nickel reduction after air calcination and subsequent nitrogen treatment.

When, however, catalysts with higher relative copper loadings were air cooled after calcination, a subsequent TPR showed reproducibly a greater uniformity of reduction in the two components (Figs. 6 and 7). The difference may be attributed to hydration of the copper and nickel oxides during the air cooling step, a suggestion which would seem to be supported by the following observation. Such a copper-rich bimetallic catalyst, after heating (and cooling) only in nitrogen, generated two discrete reduction peaks and we surmise, therefore, that it is the subsequent treatment and cooling procedure used that determines the manner of reduction of these (immiscible) oxides.

We suggest that the more uniform bimetallic reduction in these air-cooled copper-rich catalysts could be due to hydration creating an induction period in the reduction of copper oxide, an induction period being absent when completely dry CuO is treated with hydrogen (*12*). The reduction temperature of this oxide is therefore higher (ca. 230°C) in the TPR profiles of Figs. 6 and 7 than that (ca. 180°C) of the anhydrous (nitrogen-cooled) catalyst (Fig. 4). Such a hydrated environment, however, appears to facilitate the reduction of the nickel component of these higher-copper-containing catalysts, giving the more uniform bimetallic reduction observed.

The situation with respect to the reduction of the noncalcined bimetallic catalysts is more complicated since the amount of hydrogen consumed in reducing the nitrates is, of course, markedly in excess of that required to generate the free metals from their oxides. The stepwise nature of this reduction is evidenced by the discrete shoulders at A, B and C in the first reducibility profile of Fig. 8 (solid line). Shoulders B and C were present as two major peaks in the TPR of a dried 0.25% nickel-on-silica standard, where a similar excess hydrogen consumption was found. We can conclude, therefore, that the major peak, D, in Fig. 8 corresponds to the reduction of all the copper of the catalyst. The lack of a reduction peak at higher temperatures (400–500°C) suggests that direct reduction of the dried copper and nickel nitrates (i.e., omission of a precalcination step) gives rise to a more concomitant creation of the metals, implying the formation of alloys. Indeed the manner of copper and nickel nitrate decomposition is extremely sensitive to heating rates (*13,14*) and ambient conditions (*15*). This is also illustrated by the observation that addition of a small amount of hydrogen to the ambient nitrogen atmosphere suppresses the creation of discrete copper and nickel oxides.

It seems that when the metals are already in intimate contact with each other, a calcination treatment at 400°C for 0.5 hr does not produce separately reducible metal compounds. In fact, the Group Ib metal, when in this "mixed state," appears to facilitate the reduction of its Group VIII partner and indeed such copper promotion of nickel reduction has been reported elsewhere (*16*). We can conclude, however, that in all the copper–nickel-on-silica catalysts studied, both metals exist entirely in the zero-valent state and are engaged in alloying on or after reduction at 500°C.

The temperature-programmed reduction technique has enabled a quantitative estimate of metal reducibility of (copper-) nickel-on-silica catalysts to be made while the catalyst itself is actually being reduced. We affirm, moreover, that complete metal reduction occurs under the conditions of catalyst treatment described and that alloying can also be identified by this method. The manner of such supported metal reduction, however, is critically dependent upon the history of the catalyst preparation and treatment. This method, consequently, complements other chemical (*17,18*), magnetic (*19–21*) and static reducibility (*22*) studies on this subject and is potentially a technique whereby the reducibility of supported catalysts in general can be "fingerprinted." Temperature-programmed reduction has also yielded information on the relative reducibilities of the bimetallic species on the carrier and thus on their chemical nature. Such a quantification of metal–metal and perhaps metal–support interaction is a subject of increasing importance in heterogeneous catalysis.

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