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Anomalous Metal–Support Interactions in Cu/TiO_2 Catalysts

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Anomalous metal-support interactions have been discovered in titania-supported copper catalysts. Aldehyde hydrogenation studies and temperature-programmed reduction experiments show that reduction of Cu/TiO_2 catalysts at 500°C leads to catalyzed support reduction and depression of aldehyde hydrogenation activity compared to samples reduced at 300°C. Silica-supported analogs exhibit no similar disparity between samples reduced at 300 and 500°C. The disparity in catalytic activity of the Cu/TiO_2 materials when reduced at different temperatures is due to an electronic interaction between the copper and the reduced support. We believe that this is the first example of such an interaction involving a non-group VIII metal.

INTRODUCTION

Group VIII metals supported on reducible metal oxides have recently been the subject of a great deal of attention (*1–4*). This is particularly the result of the discovery by Tauster *et al.* (*5*) of a strong metal-support interaction (SMSI) in titania-supported noble metals following high temperature reduction. This interaction has since been found in many other group VIII metals supported on reducible transition metal oxides. The effect of this interaction is to radically alter the chemisorptive and catalytic properties from those normally associated with the supported metals. Specifically, CO and H_2 chemisorption following low temperature reduction at 200°C (LTR[200]) of these catalysts are found to be normal. However, following high temperature reduction at 500°C (HTR[500]), sorption of CO and H_2 is essentially absent. In spite of this loss of ability to chemisorb hydrogen and carbon monoxide, many SMSI catalysts show methanation activities superior to their normal counterparts (*4*).

The changes in chemisorption and catalytic activity are dramatic, but are only manifestations of a more fundamental change in the physical properties of the supported metal. The exact nature of this change is not well understood. As noted above, there is a fairly compelling correlation between the phenomenon and support reducibility (*1*). Arguments for metal and/or support sintering have not stood up to experimental test (*5, 6*). While alloy formation, e.g., Pt_3Ti, is thermodynamically favored under certain conditions (*7*), it is difficult to rectify with the return to the normal state on exposure to oxygen at ambient temperatures (*8, 9*). Most explanations claim a strong interaction between the support and metal which invokes changes in the supported metal. The interaction could be discrete, e.g., Pt-Ti bond formation, or collective, as in Schottky barrier formation between a metal, Pt, and a semiconductor, TiO_{2-x}.

We have undertaken an investigation of transition metals supported on various materials in order to probe the nature of this interaction. This article reports results on the titania-supported–copper system. Reactor data and temperature-programmed reduction studies suggest that there is an anomalous copper–support interaction invoked by high temperature reduction. Furthermore, reduction stoichiometries suggest that this is directly related to copper-catalyzed reduction of the titania support to a lower oxide. We believe this is the first example of SMSI in a non-group VIII metal.

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EXPERIMENTAL SECTION

Materials. The titania support used in this study was a P-25 grade obtained from Degussa Corporation. The silica support was Cab-O-Sil, HS-5 grade, from the Cabot Corporation. Both materials were prepared from the flame hydrolysis of the appropriate tetrachloride. The TiO_2 is predominately anatase (~80%), most of the remainder being rutile. It has a reported surface area of ~50 m^2/gm. The SiO_2 is amorphous with a surface area of 325 m^2/gm. Copper nitrate [$Cu(NO_3)_2 \cdot 3H_2O$] Analytic Reagent, was obtained from Mallinckrodt. Catalysts were prepared via impregnation of aqueous copper nitrate using ~0.5 ml/gm for titania and ~1 ml/gm for silica.

Appropriate amounts of copper nitrate were used to yield approximately 1 and 4% (w/w) of copper metal and the support. The samples were vacuum dried at 75°C overnight and sieved to 10–40 mesh for reactor studies. All samples were calcined in 10% O_2 (balance Ar or He; total flow 100 ml/min) at 450°C for 1 h. Two different reduction temperatures were used. Low temperature reduction (LTR) was carried out at 300°C. This was the minimum temperature at which complete reduction of the copper was insured. High temperature reduction (HTR) was performed at 500°C.

Catalyst samples were analyzed for copper content via atomic absorbance. The experimentally determined copper content is noted parenthetically following the nominal weight loading: 1% (0.9%) Cu/TiO_2, 4% (3.8%) Cu/TiO_2, 1% (1.0%) Cu/SiO_2, and 4% (4.4%) Cu/SiO_2. The nominal weight loadings will be refered to for brevity, while calculations will use the experimentally determined loadings.

The 2-methylbutanal used in the reactor studies was obtained from BASF and distilled before use. The H_2, He, Ar, and O_2 were supplied by Acetylene Gas Company. The CO gas was from Air Products. The N_2 was supplied in-house. Hydrogen, helium, and nitrogen were purified over Na/Alumina. Gases used in the chemisorption studies were further purified by passing through a dry ice/acetone trap.

Temperature-programmed reduction and oxidation (TPROX) and chemisorption apparatus. A dynamic frontal sorption technique was used for both TPROX and selective chemisorption studies with H_2, O_2, and CO. The instrument was developed along the concept described by Robertson *et al.* (*10*). Hardware modifications and microcomputer control have improved the original design to the point where specific metal surface areas may be determined with a reliability equal to static-volumetric techniques (*11*). Specific details will be reported elsewhere. Nominal 4% O_2, H_2, or CO in an Ar carrier were used at a total flow rate of 95 ml/min (STP). This translates into a reactive gas (H_2, O_2, or CO) pressure of 45 torr. Typical sample size is 1 g. Temperature-

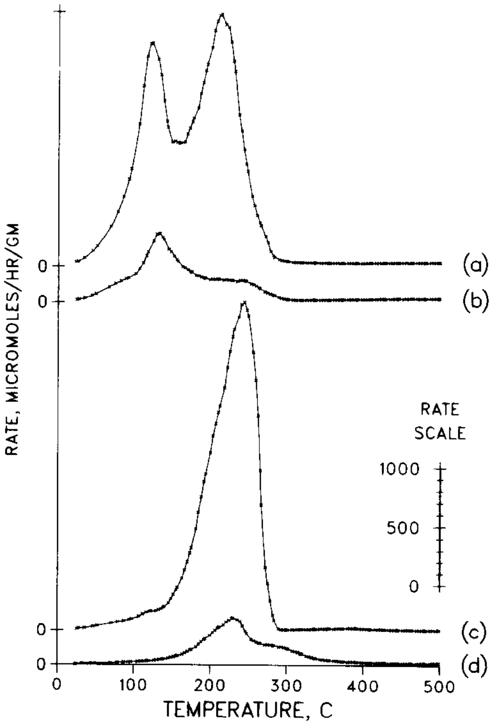
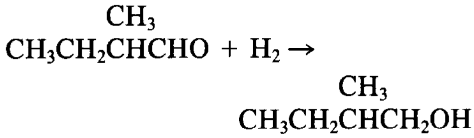


FIG. 1. Temperature-programmed reduction of supported copper catalysts following calcination at 450°C. (a) 4% Cu/TiO_2. (b) 1% Cu/TiO_2. (c) 4% Cu/SiO_2. (d) 1% Cu/SiO_2.

programmed runs were carried out with an initial frontal sorption at room temperature followed by temperature programming and a 1-h soak at the final temperature. An optional 1-h desorption at the final temperature could be invoked when deemed necessary (typically the case following hydrogen reduction). Chemisorption experiments were carried out at ambient temperature (23–27°C). These experiments were conducted on samples following temperature-programmed reduction (TPR). Sorption was measured by the disappearance of the reactive species from the argon carrier by thermal conductivity detector. Equilibrium was typically established in less than 200 s, but measurement was continued for a minimum of ~400 s. Desorption into the neat argon carrier was similarly measured. Reversible species were arbitrarily designated as those desorbing in less than 420 s.

Reactor system. The hydrogenation of an aldehyde, 2-methylbutanal (2Mebal), was used as a probe of the catalytic activity of the various Cu catalysts investigated in this study:

(a)



$$\mathrm{CH_3CH_2\overset{CH_3}{C}HCHO + H_2 \rightarrow CH_3CH_2\overset{CH_3}{C}HCH_2OH}$$

The catalyst reactivity experiments were carried out in an automated gas phase reactor system. The system is fully controlled by a dedicated Motorola 6809 microprocessor (Southwest Technical Products Corp. configuration) with full on-line temperature, process, and GC control plus GC peak integration and floppy disk data archiving. The fixed bed reactor was designed with a reactant preheat zone and conveniently held ~5 cm^3 of catalyst. A 5 mol% aldehyde feed stream was generated by feeding the appropriate amount of liquid into a H_2/He gas stream for subsequent vaporization and admission to the catalyst bed. The aldehyde feed rate was 2.3 mmol/gm catalyst-h; the H_2 feed was 7 times that of the 2Mebal. The total GHSV was 1000 cm^3 vapor (STP)/cm^3 catalyst-h. An air-actuated valve in the reactor exit stream was used for GC sampling at appropriate time intervals. In instances where only the aldehyde was desired as a reactant, the H_2 was simply removed from the reaction stream. In all cases, the system was run at atmospheric pressure.

The catalyst materials were all pretreated as described above. The aldehyde hydrogenation reaction was monitored from 150 to 300°C at 25°C intervals; conversion/selectivity stability was verified at all temperatures. A dual column GC arrangement was utilized: (i) 1.2 m bis(2-ethoxyethyl adipate) (BEEA) on Chromosorb PAW at 25°C was used for H_2 quantitation and (ii) a 50-m × 0.25-mm 20M polyethylene glycol glass capillary column at 120°C for the hydrocarbon analyses. Reaction products were also verified by GC/MS.

RESULTS AND DISCUSSION

Results of temperature-programmed reduction (TPR) experiments on titania- and silica-supported copper are shown in Fig. 1. The most obvious and significant difference is the lower reduction temperature of the titania-supported copper. Both the 1 and 4% Cu/TiO_2 show reduction peaks at ~130°C. There is a second reduction peak at ~220°C in the 4% Cu/TiO_2. In the 1% Cu/TiO_2 there is a shoulder at the same temperature. For 4% Cu/TiO_2 the integrated hydrogen consumption represented by the low and high temperature peaks is 330 and 395 μmol/g, respectively. The hydrogen consumption depicted by the low temperature peak and high temperature shoulder for 1% Cu/TiO_2 is 110 and 50 μmol/g, respectively. In the case of the silica-supported copper, the reduction peaks are found at 268 and 229°C for the 4 and 1% Cu/SiO_2 samples, respectively. The 1% Cu/SiO_2 also displays a shoulder at ~275°C.

A more subtle feature of the TPR experiments is the increasing hydrogen consumption of the titania-supported copper samples as the temperature increases to 500°C. This is more clearly evident by considering the data in Table 1. High temperature reduction at 500°C (HTR[500]) of the titania-supported copper yields hydrogen consumption significantly in excess of that required for complete reduction of Cu(II), while the silica-supported materials do not. Furthermore, there is a significant difference in hydrogen consumption between the HTR[500] and the LTR[300] (low temperature reduced at 300°C) Cu/TiO_2. There is not a corresponding discrepancy between the HTR[500] and LTR[300] silica-supported catalysts and there is not excess hydrogen consumption. This difference is also evident from the hydrogen uptake during the high temperature soaks. Finally, the titania-supported copper catalysts desorb a much larger amount of hydrogen following the soak.

It is evident that the titania support significantly enhances the reducibility of the calcined, supported copper. The reduction peak is fully 100°C lower than for the silica-supported copper. The bicuspid reduction profile found for the 4% Cu/TiO_2 is at first confusing. It is tempting to ascribe this to stepwise reduction of the copper, i.e., $Cu^{2+} \rightarrow Cu^{1+}$ then $Cu^{1+} \rightarrow Cu^0$. However, the integrated hydrogen consumptions do not support this conclusion. The percentage of total hydrogen consumed in the low temperature peak : high temperature peak is 44% : 53% for 4% Cu/TiO_2 and 62% : 29% for 1% Cu/TiO_2. Another possibility is that there are two copper species to be reduced. We speculate that one is in intimate contact with the titania support and experiences enhanced reduction at low temperature. The other is not in close contact and reduces at the same temperature as the silica-supported copper. At lower weight loadings the dispersion is likely better and a larger fraction of the total copper is in contact with the support and exhibits enhanced reduction. Indeed, in the 1% Cu/TiO_2 the peak at 230°C (observed in the TPR of the 4% Cu/TiO_2) has been diminished to a small shoulder.

TABLE 1

Hydrogen Consumed during TPR/Soak/Desorption

Sample		μmol/g catalyst				
		Total[a]		Excess[b]	Soak[c]	Desorp.[d]
4% Cu/TiO_2	HTR	748.0	[1.25]	150.0	11.8	−7.5
4% Cu/TiO_2	LTR	718.4	[1.19]	115.1	8.8	−9.4
1% Cu/TiO_2	HTR	175.5	[1.24]	33.9	11.0	−8.4
1% Cu/TiO_2	LTR	149.3	[1.05]	7.6	7.8	−9.1
4% Cu/SiO_2	HTR	634.8	[0.93]	0	2.5	−2.8
4% Cu/SiO_2	LTR	626.8	[0.90]	0	6.5	−2.3
1% Cu/SiO_2	HTR	139.6	[0.83]	0	4.6	−2.7
1% Cu/SiO_2	LTR	135.9	[0.83]	0	3.6	−1.7
TiO_2	HTR	24.6	—	24.6	16.3	−4.2
TiO_2	LTR	3.6	—	3.6	1.6	−0.8

[a] The quantities in brackets represent the molar ratio of molecular hydrogen consumed to total copper.

[b] Hydrogen consumed in excess of that required for complete reduction of Cu(II) to Cu(0).

[c] Portion of total hydrogen consumed during 1 h soak at final temperature.

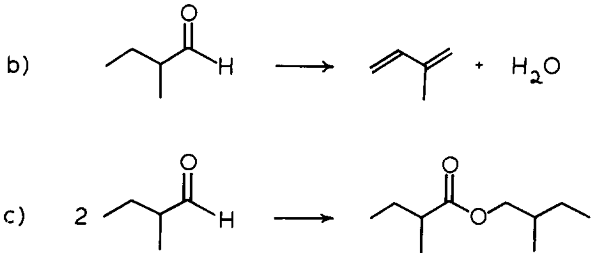
[d] Quantity of hydrogen desorbed from sample into argon sweep in 1 h at final temperature. See text for details.

The observed hydrogen consumption stoichiometries indicate that in each of the materials studied here the calcined precursor is essentially reduced to zero valent copper by 300°C, hence the choice of the LTR temperature. The silica-supported copper catalysts are 83–93% reduced, consistent with other reports in the literature (*12*). The titania-supported copper materials exhibit hydrogen sorption in excess of that required for complete reduction of Cu(II). In fact the excess is seen from Table 1 to be consumed largely at temperatures above 300°C. We believe that this corresponds to reduction of the titania support. This accounts for the difference in hydrogen consumed during the high temperature soaks between the titania- and silica-based catalysts. Comparison of the neat titania reduction and the Cu/TiO_2 reduction further suggests that the copper is catalyzing the support reduction and yields a deeper reduction of the support than in the case of the titania alone.

Chemisorption experiments were conducted using hydrogen and carbon monoxide. None of the reduced catalysts studied sorbed hydrogen at room temperature.

Similarly, CO adsorption could be ascribed to the titania support in the case of Cu/TiO_2; both HTR and LTR 1% Cu/TiO_2 sorbed 35 μmol/g CO, both HTR and LTR 4% Cu/TiO_2 sorbed 32 μmol/g CO, and neat titania sorbed 37 μmol/g CO at P_{CO} = 48 Torr. The Cu/SiO_2 samples sorbed small quantities of CO; 1% Cu/SiO_2 LTR and HTR sorbed 5 and 2 μmol/g, respectively, while 4% Cu/SiO_2 LTR and HTR sorbed 10 and 5 μmol/g, respectively. We believe this is due to small amounts (<2%) of Cu(I) in reduced Cu/SiO_2. This is consistent with our picture of essentially complete reduction of the supported copper.

The reaction of 2Mebal and hydrogen over the copper catalysts studied produced three major products within the temperature regime of interest: (a) 2-methyl-1-butanol (2Mebol), (b) 2-methyl-1,3-butadiene (isoprene), and (c) 2′-methylbutyl-2-methylbutanoate (ester). The latter two products are synthesized via the following reactions:



The dehydration to isoprene is mainly due to the titania support; isoprene does not appear below 250°C and dominates the product stream at 300°C. The ester is formed via the Tischenko reaction (*13, 14*). Minor reaction products included ethers and acetals which are generated by aldehyde and/or alcohol condensations.

The specific reaction of interest was the hydrogenation of 2Mebal to 2Mebol (Reaction (a)). There have been several reports (*8, 15–17*), which indicate that titania-supported group VIII metal catalysts display attenuated hydrogenation reactivity upon high temperature reduction. Our results (Figs. 2 and 3 and Table 2) show that the titania-supported copper is also sensitive to the reduction temperature. For comparison, data for the silica-supported copper are presented (Figs. 4 and 5 and Table 2). Clearly, the reactivities of the titania-based catalysts are considerably different than the silica-based catalysts. The 4% Cu/SiO_2 catalyst produced 2Mebol almost exclusively at low temperatures.

Furthermore, the largest ester and isoprene yields were 2.7% (300°C) and 11.7% (300°C), respectively. Coke formation was a significant reaction path at high temperatures. In contrast, the titania-based catalysts produced very little alcohol below 200°C; the reacted aldehyde was converted to either ester or unidentified by-products. Initially, the reproducibility of the low temperature reactivity data was poor for the Cu/TiO_2 catalysts. However, the results stabilized within several reaction cycles. The titania support has clearly had an unusual effect on the ability of the copper to hydrogenate the aldehyde. The neat titania support produced a negligible yield of the alcohol under the conditions of interest.

The most striking feature of the reactor data is the difference in activity between the LTR and HTR Cu/TiO_2 catalysts (Figs. 2 and 3). Between 200 and 250°C, the alcohol yields over the LTR catalysts were generally 2 to 4 times as great as the HTR yields. This result is consistent with observations made in other hydrogenation/hydrogenolysis studies involving strong metal–support interactions (*8, 15–17*). As seen in Figs. 4 and 5 and Table 2, the Cu/SiO_2 reactivities are unaffected by the re-

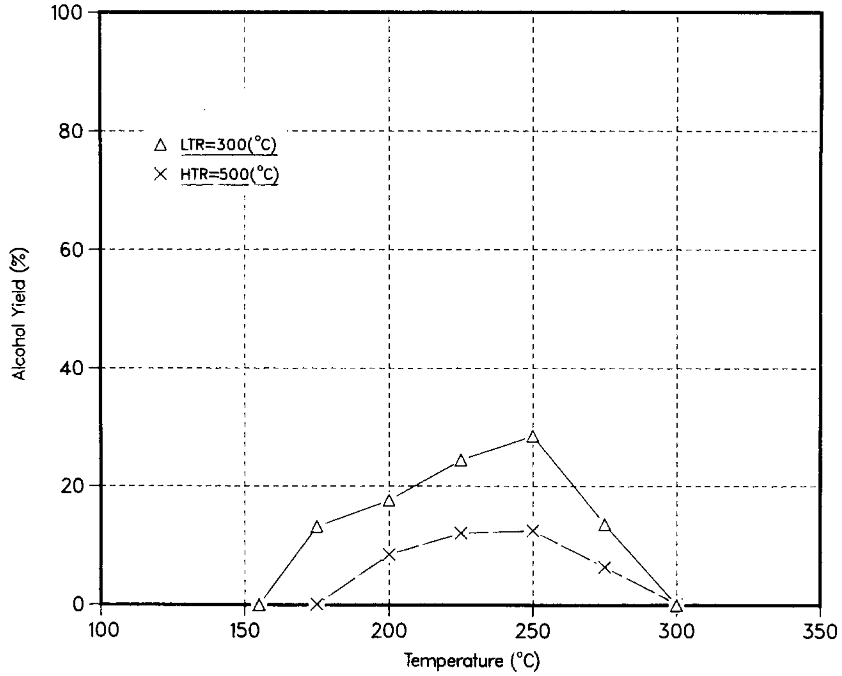


FIG. 2. 2-Methyl-1-butanol yield from hydrogenation of 2-methylbutanal over 1% Cu/TiO_2.

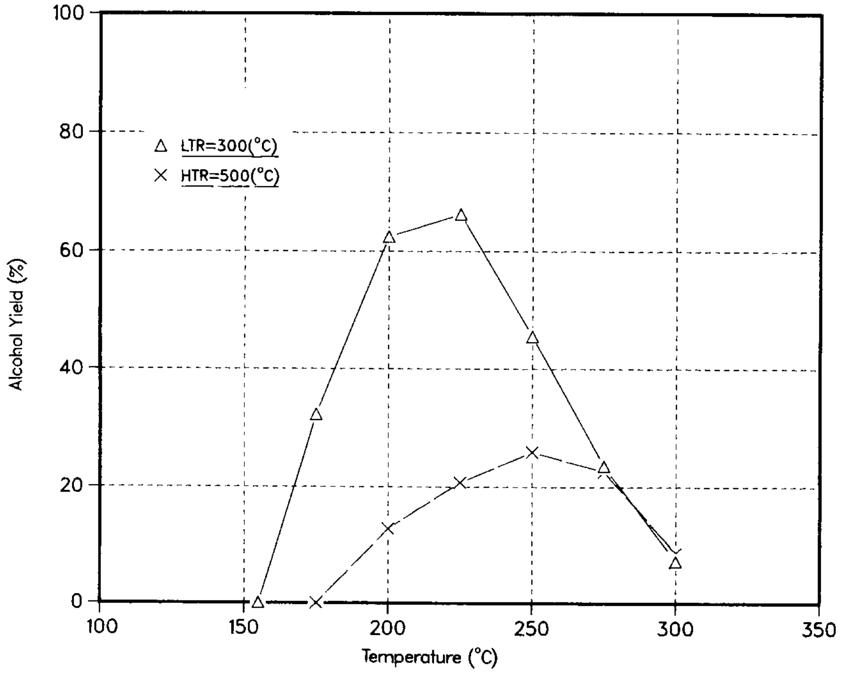


FIG. 3. 2-Methyl-1-butanol yield from hydrogenation of 2-methylbutanal over 4% Cu/TiO_2.

TABLE 2

Conversion of 2-Methylybutanal over Supported Copper Catalysts

Reaction temp. (°C)	Reduction conditions	4% Cu/TiO_2 (%)	1% Cu/TiO_2 (%)	4% Cu/SiO_2 (%)	1% Cu/SiO_2 (%)
157	LTR	22.4	16.7	95.3	35.5
	HTR	7.7	10.4	96.9	28.3
175	LTR	42.8	26.2	94.5	59.5
	HTR	17.3	18.5	90.4	48.3
200	LTR	76.9	35.4	90.6	86.1
	HTR	25.6	27.2	88.8	81.3
225	LTR	82.7	51.2	80.1	80.5
	HTR	36.1	33.2	80.1	79.9
250	LTR	73.1	67.5	67.1	65.5
	HTR	52.9	40.1	66.3	65.2
275	LTR	70.3	74.6	54.3	50.6
	HTR	62.8	52.1	52.4	49.2
300	LTR	80.2	95.9	45.7	40.5
	HTR	71.3	67.0	41.0	38.0

duction conditions. The lower 2Mebol yields over the HTR Cu/TiO_2 catalysts were due to both smaller aldehyde conversions and decreased alcohol selectivities. In general, both ester and isoprene selectivities were equal for the LTR and HTR catalysts such that the alcohol selectivity losses resulted in other by-product formation or more extensive catalyst coking.

We noted previously that the reduction stoichiometries of HTR and LTR Cu/SiO_2 were nearly identical. The catalytic perfor-

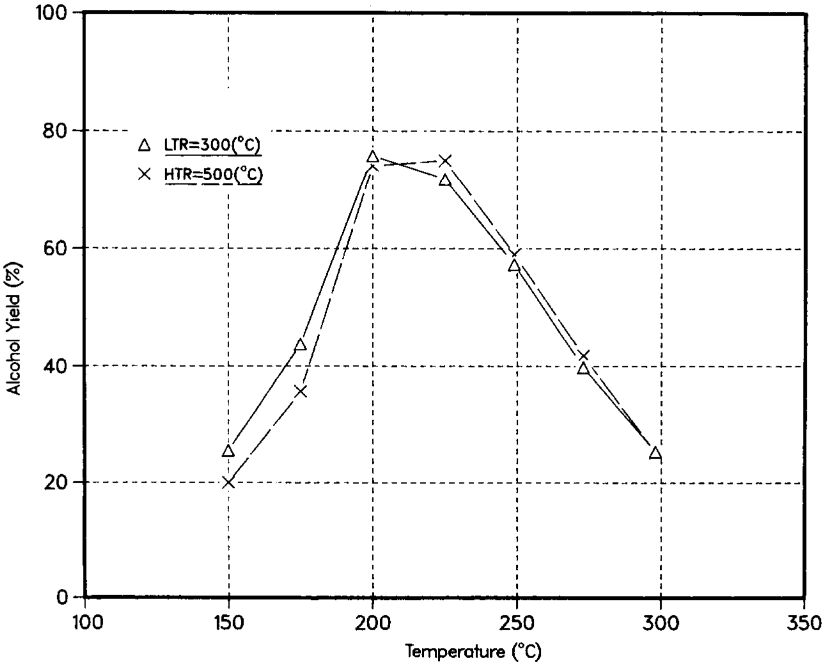


FIG. 4. 2-Methyl-1-butanol yield from hydrogenation of 2-methylbutanal over 1% Cu/SiO_2.

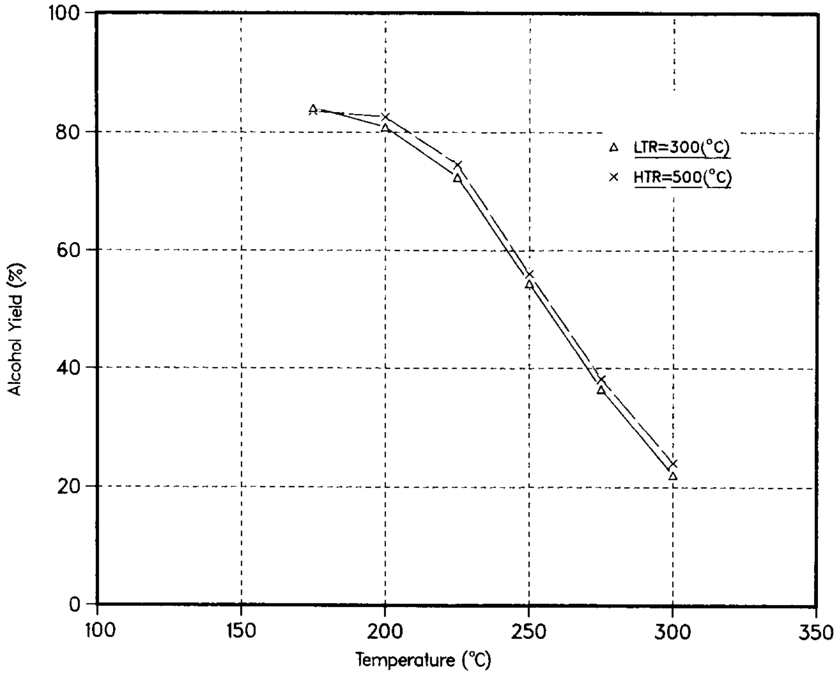


FIG. 5. 2-Methyl-1-butanol yield from hydrogenation of 2-methylbutanal over 4% Cu/SiO_2.

mance of these pairs of samples were also similar, as Figs. 4 and 5 show. The LTR and HTR Cu/TiO_2 catalysts show very different reduction stoichiometries and this is manifest in the reactivity differences. We believe that this is due to the greater support reduction during the HTR[500] than the LTR[300]. A correlation can be made between the greater hydrogen consumption (greater support reduction) and the decreased aldehyde hydrogenation activity observed for the titania-supported catalysts. As noted above, similar observations have been made for titania-supported group VIII metal catalysts. The magnitude of the yield decrease is not as pronounced as some examples in the literature (*8, 15–17*), however, we are not screening catalysts in a differential conversion mode so our high conversions may mask activity differences. In addition, the TPR experiments indicate that some support reduction occured during the LTR and may have led to some suppression of activity.

The activity loss may be due to simple sintering of the copper. While this was not the case for the silica-supported copper, nor for many other titania-supported metals (*6*), the following experiment was performed in an attempt to address this. Following Meriaudeau *et al.* (*8*), the HTR 4% Cu/TiO_2 (which produced a 26.0% 2Mebol yield at 250°C) was air exposed at ambient temperature for 72 h. After rereduction at 300°C, the alcohol yield at 250°C was 45.4%, indicating a return of the LTR activity. We do not believe that this treatment would reverse the effects of sintering, encapsulation or alloying, but it can reoxidize the support and break the metal-reduced support interaction. Transmission electron microscopy studies performed in this laboratory indicated that there is insufficient contrast between the Cu and the support to allow determination of metal particle size. We are currently planning to further address the sintering issue via N_2O decomposition to determine specific copper surface area (*18*); we are concerned, however, about the possibility of simultaneous reoxidation of the support yielding misleading results.

The mechanism by which catalytic and chemisorptive properties change when a catalyst enters the SMSI state has not been satisfactorily resolved. We concur with the model of electron transfer from the reduced support to the supported metal which is driven by differences in their Fermi levels (or chemical potentials) (*8, 19, 20*). Perhaps the Schottky barrier generated plays a role in changing the physical properties of the supported metal, though the electrons transferred to the metal should localize at the metal/support interface for electrostatic reasons. There may be more subtle effects from the electric field this charge separation generates. We are currently addressing these speculations via further experimentation.

CONCLUSIONS

We have investigated titania-supported copper and silica-supported copper catalysts. The titania-based materials are unusual in several respects. The Cu/TiO_2 catalysts are much more easily reduced following calcination than are the silica-supported counterparts. Furthermore, the copper catalyzes the reduction of the titania support above 300°C. The reduction temperature was found to critically affect the ability of the titania-supported catalysts to hydrogenate 2-methylbutanal, while it did not significantly affect the silica-based catalysts. We conclude that these are manifestations of an anomalous metal–support interaction invoked by the reducing pretreatment. We believe that this is the first example of SMSI in a non-group VIII metal.

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