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DETERMINATION OF THE REACTIVITY OF CuO ON Al_2O_3 USING THERMAL ANALYSIS*

G. W. BAILEY AND J. T. WADE

Esso Research Laboratories, Exxon Company U.S.A., Baton Rouge, La. 70821 (U.S.A.)

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ABSTRACT

The reactivity, or availability, of the metal oxide component in various metal oxide–Al_2O_3 catalysts is an important parameter in assessing the performance of catalysts. For CuO on Al_2O_3 systems, reduction of the CuO with H_2 followed by back oxidation with air gives an indication or measure of the reactivity of the CuO. In order to determine how this reactivity varies with the nature of the support, method of preparation, etc., oxidation–reduction studies have been conducted on a series of experimental catalysts using a Mettler Thermoanalyzer. Thermogravimetric analysis with continuous recording of the weight changes of the catalysts during oxidation–reduction experiments has permitted determination of the "percent reactive CuO" in different catalysts at two different temperatures: 550 and 650°F. In addition to furnishing data and correlations regarding the CuO–Al_2O_3 catalysts, these experiments have demonstrated the potential of thermal analysis for such investigations in general.

INTRODUCTION

The reactivity, or availability, of the metal oxide component in various metal oxide–Al_2O_3 catalysts is an important parameter in assessing the performance of catalysts. For CuO on Al_2O_3 systems, reduction of the CuO with H_2 followed by back oxidation with air gives an indication or measure of the reactivity of the CuO. In order to determine how this reactivity varies with the nature of the support, method of preparation, etc., oxidation–reduction studies have been conducted on a series of the experimental catalysts using a Mettler Thermoanalyzer.

MATERIALS INVESTIGATED

The following samples were examined in this thermal analysis investigation. Sample 1: calcined Al_2O_3, 8.9% CuO added; Sample 2: calcined Al_2O_3, 10% CuO+

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+10% Cr_2O_3 added; Sample 3: spray dried Al_2O_3 (26% volatiles), 10% CuO added, calcined.

EXPERIMENTAL

These oxidation–reduction studies were conducted using a Mettler Thermoanalyzer. Because the principal objective of this investigation was to determine the oxidation–reduction behavior of the CuO, only the thermogravimetric analysis (TGA) features of the Thermoanalyzer were used in conducting these experiments. Thus, differential thermal analysis (DTA) measurements were not made. The TGA technique permitted determination of the change in weight of the sample as a function of oxidation and reduction.

By using only the TGA features of the apparatus it was possible to spread out a single layer of the catalyst particles on a specially constructed specimen crucible to assure good contacting with the reducing or oxidizing atmospheres. Thermogravimetric analysis experiments were conducted on each sample using two complete reduction and oxidation cycles at each of two different temperatures, 550 and 650°F. Dry H_2 was used for reduction and dry air for oxidation. The duration of each reduction and each oxidation was 15 minutes. A typical experimental run was conducted as follows. (1) Sample placed in Thermoanalyzer furnace at room temperature and system evacuated. (2) System back-filled with N_2 and heated up to 550°F. (3) H_2 admitted for 15 minutes, system then flushed with N_2 for 30 minutes. (4) Air admitted for 15 minutes, system then flushed with N_2 for 30 minutes. (5) The above reduction and oxidation cycles were repeated for the same times and at the same temperature, then (6) system heated up to 650°F in N_2, and the reduction–oxidation cycles repeated twice.

During these treatments the changes in weight of the sample—weight loss during reduction and weight gain during oxidation—were continuously recorded with both the regular and expanded TGA scales of the Thermoanalyzer. As stated above, each reduction or oxidation was completed during the first minute or so. From the TGA data it is possible to determine the "lined-out" weight changes occurring during the reversible reduction and oxidation cycles. A theoretical weight change calculation can be made using the percent CuO present, the percent O_2 in CuO and the sample weight as follows:

$$\text{Maximum theoretical loss} = (\%\ \text{CuO})\ (\%\ \text{O}_2\ \text{in CuO})\ (\text{sample weight}).$$

This calculation yields the maximum loss that could occur during reduction which would also equal the maximum weight gain during subsequent re-oxidation of the formed Cu metal. Combining the observed "lined-out" weight changes and the maximum theoretical weight change, it is then possible to define the percent reactive CuO as:

$$\%\ \text{Reactive CuO} = \frac{\text{“lined-out” weight change}}{\text{maximum theoretical weight change}} \times 100$$

The data obtained from the thermal analysis experiments and the weight change calculations for each sample are presented in Table 1–3. The "% reactive CuO" data are summarized as follows:

Sample No.	*Sample description*	*% Reactice CuO*	
		550°F	*650°F*
1	CuO deposited on calcined Al_2O_3	57.5	72.5
2	CuO + Cr_2O_3 deposited on calcined Al_2O_3	59.6	80.5
3	CuO deposited on spray dried Al_2O_3	50.6	58.2

DISCUSSION

The oxidation–reduction properties of the CuO in the various catalysts examined in this investigation indicate differences in reactivity of the CuO that can be related to the properties of the alumina support. Thus, the history, or treatment, of the support plays an important role in the behavior of the CuO. The variables involved in preparing the catalysts used in this study included: (1) the pretreatment of the alumina, i.e., precalcination at 1000°F vs. drying at 250°F and (2) the presence of Cr_2O_3. These thermal analysis experiments have permitted an evaluation of the behavior of these catalysts as a function of these variables.

In most of the experiments conducted it was observed that in the first cycles of reduction and oxidation at 550°F, the amount of CuO reduced and oxidized was

TABLE 1

OXIDATION–REDUCTION DATA ON SAMPLE 1

CuO deposited on calcined Al_2O_3.

	Weight change (mg)
Room temperature to 550°F	2.13
After H_2 reduction no. 1 at 550°F	0.93
After air oxidation no. 1 at 550°F	0.73
After H_2 reduction no. 2 at 550°F	0.66
After air oxidation no. 2 at 550°F	0.65
550°F to 650°F	0.16
After H_2 reduction no. 1 at 650°F	0.70
After air oxidation no. 1 at 650°F	0.83
After H_2 reduction no. 2 at 650°F	0.83
After air oxidation no. 2 at 650°F	0.82
Initial weight of sample	63.38 mg
Maximum theoretical weight change	1.13 mg
"Lined-out" weight change at 550°F	0.65 mg
% reactive CuO at 550°F	57.5%
"Lined-out" weight change at 650°F	0.83 mg
% reactive CuO at 650°F	72.5%

TABLE 2

OXIDATION-REDUCTION DATA ON SAMPLE 2

$CuO+Cr_2O_3$ deposited on calcined Al_2O_3.

	Weight change (mg)
Room temperature to 550°F	1.86
After H_2 reduction no. 1 at 550°F	1.64
After air oxidation no. 1 at 550°F	1.27
After H_2 reduction no. 2 at 550°F	0.98
After air oxidation no. 2 at 550°F	0.98
550°F to 650°F	0.28
After H_2 reduction no. 1 at 650°F	1.23
After air oxidation no. 1 at 650°F	1.30
After H_2 reduction no. 2 at 650°F	1.29
After air oxidation no. 2 at 650°F	1.32
Initial weight of sample	81.88 mg
Maximum theoretical weight change	1.64 mg
"Lined-out" weight change at 550°F	0.98 mg
% reactive CuO at 550°F	59.6%
"Lined-out" weight change at 650°F	1.32 mg
% reactive CuO at 650°F	80.5%

TABLE 3

OXIDATION-REDUCTION DATA ON SAMPLE 3

CuO deposited on spray dried Al_2O_3.

	Weight change (mg)
Room temperature to 550°F	2.54
After H_2 reduction no. 1 at 550°F	0.43
After air oxidation no. 1 at 550°F	0.58
After H_2 reduction no. 2 at 550°F	0.53
After air oxidation no. 2 at 550°F	0.53
550°F to 650°F	0.19
After H_2 reduction no. 1 at 650°F	0.51
After air oxidation no. 1 at 650°F	0.58
After H_2 reduction no. 2 at 650°F	0.62
After air oxidation no. 2 at 650°F	0.62
Initial weight of sample	52.44 mg
Maximum theoretical weight change	1.05 mg
"Lined-out" weight change at 550°F	0.53 mg
% reactive CuO at 550°F	50.6%
"Lined-out" weight change at 650°F	0.62 mg
% reactive CuO at 650°F	58.2%

generally higher than in the subsequent cycles. This phenomenon could be due to the higher original reactivity of the CuO which, because of agglomeration or crystal growth of the formed Cu and/or CuO during the initial cycle, becomes less reactive in the subsequent cycles. However, the reactivity of the CuO appears to line out by the second cycle as evidenced by the essentially duplicate weight changes for all samples (Tables 1–3) for the respective reduction vs. oxidation cycles. In addition, the amount of CuO reduced in the first cycle of reduction at 650°F was generally lower than that oxidized or reduced in subsequent cycles. This initial reduction level at 650°F was generally at about the same level as the "lined-out" oxidation–reduction levels observed for the corresponding 550°F cycles. This initial lower level of reactivity at the higher temperature suggests a delayed effect of the temperature increase.

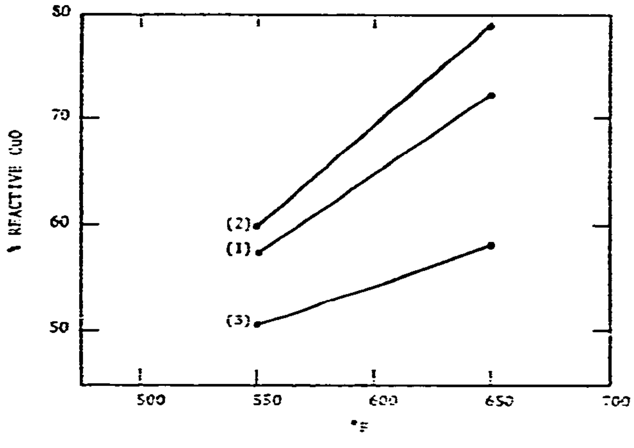

Fig. 1. CuO reactivity as a function of temperature. (1) CuO deposited on calcined Al_2O_3. (2) $CuO + Cr_2O_3$ deposited on calcined Al_2O_3. (3) CuO deposited on spray dried Al_2O_3 before calcining.

Examination of the data plotted in Fig. 1 reveals the dependence of the reactivity of the CuO on certain of the variables involved in preparation of the catalysts. Thus, the lowest reactivity levels (at both temperatures studied) are observed with the CuO on non-calcined alumina. For the calcined aluminas, the presence of Cr_2O_3 makes a significant improvement in the reactivity of CuO. This is somewhat at odds with what might have been expected to result from the presence of Cr_2O_3. In some catalysts Cr_2O_3 is added to inhibit reduction of CuO. However, these data show that such inhibition must be a function of preparation history rather than simply the presence of Cr_2O_3.

The effect of increased temperature on reactivity of the CuO is clearly indicated on all of the catalysts examined. The effect is more pronounced on the precalcined aluminas, as evidenced by the steeper slopes of the reactivity–temperature curves (Fig. 1, curves 1 and 2) for these aluminas. The slopes of the reactivity–temperature curves for the catalysts made with the precalcined aluminas are about equal but are different from the slope of the corresponding curve for the alumina calcined after Cu^{2+} addition (Fig. 1, curve 3). The differences in slope observed for the two different types of alumina indicate that the reactivity of CuO deposited on alumina that has been calcined prior to the Cu^{2+} addition is more dependent on temperature than the reactivity of CuO on non-calcined alumina. This suggests that CuO placed on non-calcined alumina is more associated in some way with the alumina than is the case for the calcined alumina. Thus, the non-calcined alumina may be more reactive toward the deposited Cu^{2+}, forming surface bonds, a spinel-type compound or other CuO–Al_2O_3 species. This would result in impaired reactivity of the Cu^{2+}.

As suggested above, these differences in behavior between CuO on calcined and non-calcined Al_2O_3 may be related to a spinel formation phenomena. It is well known that in the NiO–Al_2O_3 system, $NiAl_2O_4$ is difficult to reduce. In studies conducted on NiO–Al_2O_3 system, it has been reported that reduction at 360°C results in 95% reduction of bulk NiO and only 33% reduction of Ni in $NiAl_2O_4$[1]. For NiO co-precipitated with Al_2O_3 some spinel formation occurs during calcination along with some solid solution of $NiAl_2O_3$ and Al_2O_3 and some free Al_2O_3. It would not be surprising if such spinel formation also occurred by depositing Ni^{2+} on Al_2O_3 prior to calcining and then calcining. Though these observations were made on the NiO–Al_2O_3 system, it is quite possible that similar phenomena occur with the CuO–Al_2O_3 system. Thus, Cu^{2+} deposited on non-calcined Al_2O_3 might form some of the spinel type product during subsequent calcination in much the same manner as the $NiAl_2O_4$ is formed. This could account for the differences observed in reactivity of the CuO.

CONCLUSIONS

Conclusions from these studies are as follows. (1) The reactivity of the CuO is dependent on the condition of the alumina support during addition of the Cu^{2+} (Fig. 1). (2) Addition of Cu^{2+} to alumina before calcination resulted in lower CuO reactivity than when the Cu^{2+} was added to precalcined alumina. (3) For catalysts prepared with precalcined alumina, the presence of Cr_2O_3 makes a significant improvement in the reactivity of the CuO. (4) Reaction temperature has a pronounced effect on the CuO reactivity—reactivity increases with temperature. The increase in reactivity is greater for the CuO deposited on precalcined alumina than that deposited on the non-calcined alumina. (5) The smaller effect of temperature on reactivity of the CuO in catalysts prepared with non-calcined alumina suggests a greater degree of association of the CuO with the support. This association may result from increased reactivity of the non-calcined alumina toward the deposited Cu^{2+}, forming surface bonds, a spinel type compound or other CuO–Al_2O_3 species.

In addition to furnishing these data and correlations regarding the CuO–Al_2O_3 catalysts, these experiments have demonstrated the potential of the Thermoanalyzer for conducting such gas treating studies. Thus, adsorption experiments, regeneration studies and numerous other catalyst treating and/or evaluations can be conducted equally as well as these oxidation–reduction experiments. Because of the precision of the results and the sensitivity of the method to catalyst preparation history (which presumably influences catalyst performance), this technique could be valuable for designing catalysts, specifying catalyst performance tests and monitoring catalyst manufacture.

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