Catalysis Letters 26 (1994) 365–371

A study of the preactivation of a copper chromite catalyst [☆]

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Received 24 September 1993; accepted 27 March 1994

Copper chromite was studied for the reductive alkylation of aniline with acetone to N-isopropylaniline as a function of the catalyst prereduction conditions. In order to optimize prereduction conditions the catalyst was reduced in an atmosphere of hydrogen at different temperatures: 100, 150, 200, 250, 300, 350, 400 and 450°C and for different durations. The activity of reduced catalysts was determined. The X-ray diffractograms of all catalyst samples were taken. Partially reduced copper species were determined by chemical analysis. Prereduced catalyst having more Cu(I) species showed a greater activity than the fresh catalyst containing only Cu(II) ions and than that of the catalyst containing more Cu(0) ions. From these studies it was inferred that the active sites of the copper chromite catalyst used for reductive alkylation of amines are Cu(I) species.

Keywords: copper chromite; reductive alkylation; N-isopropylaniline; preactivation

1. Introduction

Copper chromite catalyst has been used for the hydrogenation of polyunsaturated compounds [1], allylic alcohol [2], fatty acids [3], edible oils [4], etc. Stroupe has reported that copper–chromium oxide catalysts used in low temperature hydrogenations showed partial or complete reduction to metallic copper and cuprous chromite [5]. Herman et al. [6] discussed that in the pretreated copper chromite catalyst used for methanol synthesis, Cu(I) is the active species which adsorbed carbon monoxide. This report was confirmed by XPS studies on copper–chromia catalyst used for methanol synthesis by Monnier et al. [7]. Fleisch and Mievelle's attempts to correlate CO conversion data (studies on the chemical state of Cu in $CuO/ZnO/Cr_2O_3$ catalyst during methanol synthesis) with relative amounts of Cu(I) and Cu(0) were not successful because the reaction of CuO to metallic copper was completed at the onset of measurable CO conversion at about 130°C [8].

[☆] This paper is dedicated to the 60th birthday of Professor C.N. Pillai, Department of Chemistry, Indian Institute of Technology, Madras, India.

Sheffer's XPS studies on a copper catalyst used in methanol synthesis suggested that Cu(I) are the active sites [9]. Miya et al. stated that the activity of copper chromite catalyst was enhanced, when a small amount of methanol was added to the water–gas reaction system under vacuum at the reaction temperature [10,11]. The report [11] suggests that a partially reduced form of the copper chromite is active for reduction of fatty esters to higher alcohols. Bechara et al. [12] reported that Cu(I) species are active sites for the hydrogenation of dienes on copper chromite. Copper chromite has proved to be an excellent catalyst for the reductive alkylation of amines [13]. A major disadvantage of this catalyst is rapid deactivation. From our earlier studies it was found that the catalyst requires prereduction to obtain maximum activity. The active site in the copper chromite catalyst used for reductive alkylation was not reported. From the activity studies of the catalyst prereduced for different temperatures and different durations in flowing hydrogen, information about the active species of the catalyst was speculated. The objective was to optimize the conditions for activation.

2. Experimental

Barium oxide promoted copper chromite Cu-1184 T (Harshaw) was used in these studies. The catalyst contains CuO (44 wt%), CrO (45 wt%), and BaO (9 wt%). The catalyst (10 g) was kept in a quartz tube, which was heated in a tubular furnace. The catalyst was heated in a current (40–45 ml/min) of air free of carbon dioxide and moisture (air was purified by passing through potassium hydroxide pellets to remove carbon dioxide followed by molecular sieves to remove traces of moisture) for 4 h at temperatures between 100 and 450°C. Afterwards, nitrogen was passed over the catalyst for 30 min followed by hydrogen (hydrogen was passed through pyragallol solution to remove oxygen and then it was passed over molecular sieves to remove moisture) for 1–8 h at the same temperature. After cooling in hydrogen, the catalyst was kept in a container which was flushed with hydrogen (transferred without contacting air). The activity of the prereduced samples was tested for the reductive alkylation of aniline with acetone. The reductive alkylation was carried out in a teflon lined autoclave of 500 ml capacity. Aniline (9.1 g, 0.1 mol), acetone (17.4 g, 0.3 mol) and catalyst (4% by weight of reactants) were charged to the reactor. The reactor was flushed with nitrogen followed by hydrogen and finally pressurized to 50 bar with hydrogen. The stirring was carried out with a magnetic stirrer and the reactor was heated at 140°C for 1 h. After 60 min the heating and stirring were stopped. The reactor was allowed to cool to room temperature and the pressure was slowly released. The catalyst was separated from the liquid phase by centrifugation. The analytical yield of products was determined by gas chromatography using a 10% carbowax column of 5 m length (using FID, the rate of flow of carrier gas nitrogen was 45 ml/min). Since N-isopropylaniline was the only product formed from aniline the product selectivity was 100%.

3. Results and discussion

From our earlier studies [13] it was observed that fresh copper chromite catalyst (not prereduced) required an induction period to gain maximum activity. However, no induction period was observed if the catalyst was reduced in hydrogen before use. The reaction mechanism of the reductive alkylation of aniline is straightforward. Aniline condenses with acetone to give the imine, which gets reduced in the presence of copper chromite and hydrogen. Though N-isopropylaniline can in principle react further with acetone to form tertiary amine, this was not observed in any of the reactions studied. Acetone was reduced to isopropyl alcohol in a parallel reaction. When the reaction was carried out without catalyst at 140°C and 50 bar hydrogen pressure, the formation of secondary amine was not observed; only the imine was formed, showing that the catalyst is necessary for the reduction of imine to secondary amine. In order to design an effective catalyst it was necessary to optimize the prereduction conditions.

4. Optimization of prereduction conditions

4.1. EFFECT OF TEMPERATURE

Different batches of catalyst were prereduced at 100, 150, 200, 250, 300, 350, 400 and 450°C, for 4 h in a stream of hydrogen (50–60 ml/min). The results of activity for reductive alkylation are presented in table 1. In a separate study of reductive alkylation of aniline with acetone, the fresh catalyst used for reaction times of 15, 30, 45 and 60 min showed aniline conversions of 9.7, 16.3, 31.5, 51.8 mol%, respectively. This suggested that the fresh catalyst gained activity upon

Table 1

Effect of temperature of catalyst prereduction on its activity for reductive alkylation of aniline [a]

Prereduction temperature	Yield of N-isopropylaniline (mol%)	Weight of Cu(I) per gram of catalyst
100	52.0	0.0249
150	59.1	0.0303
200	62.4	0.0358
250	68.2	0.0371
300	76.3	0.0406
350	65.9	0.0386
400	57.0	0.0322
450	48.2	0.0231

[a] Reaction conditions: time = 60 min, temperature = 140°C, pressure = 50 bar; aniline : acetone = 1 : 3 (mol), catalyst = 4% by weight of reactants; mol% yield is based on aniline. The catalyst was prereduced for 4 h with hydrogen, rate of flow of hydrogen for prereduction = 50–60 ml/min.

prolonged usage. This is due to in situ activation involving the reduction of Cu(II) to Cu(I). The activity of the catalyst prereduced at 100°C was the same as that of the fresh catalyst. The yield of N-isopropylaniline increased with increasing prereduction temperature as compared to the not pretreated catalyst and a maximum was found for the catalyst prereduced at 300°C. Higher prereduction temperatures decrease the activity of the catalyst (table 1). This was due to the formation of more copper metal at the higher temperatures used for prereduction. The XRD analyses of these samples will be discussed in the following part.

4.2. EFFECT OF THE REDUCTION TIME

The catalyst was heated in a current of air (40–45 ml/min) at 300°C for 4 h. Nitrogen was passed over the catalyst for 30 min, then hydrogen was passed over the catalyst at the rate of 50–60 ml/min for 1 h at 300°C. Six more batches of catalyst were prereduced following the same procedure but with increasing time of reduction of 2, 3, 4, 5, 6 and 7 h. Measurement of catalyst activity (table 2) showed that 4 h reduction time was optimum to achieve maximum activity. The lower activity of the catalyst reduced for longer times (6 or 7 h) was due to the formation of more copper metal. The fresh catalyst (not prereduced) showed an activity of 52% (table 3) due to in situ reduction of Cu(II) to Cu(I). The catalyst prereduced at 300°C for 4 h in hydrogen showed the maximum activity (76.8). This prereduced catalyst contained relatively more Cu(I) ions than the other samples (from XRD and chemical analysis of the sample). The catalyst reduced at 450°C contained more of Cu(0) than the other samples and showed the lowest activity (48%). If Cu(II) species are the active sites in the catalyst, the fresh catalyst should have shown the maximum activity. If Cu(0) are the active species, the sample containing the most Cu(0) should have shown higher activity. Since the sample containing

Table 2
Effect of catalyst reduction time on activity for reductive alkylation of aniline [a]

Reduction time (h)	Yield of N-isopropylaniline (mol %)	Weight of Cu(I) per gram of catalyst
1	53.6	0.0124
2	56.9	0.0287
3	70.5	0.0343
4	76.8	0.0417
5	74.4	0.0302
6	73.8	0.0288
7	69.8	0.0241
fresh catalyst	52.0	0.0016

[a] Reaction conditions: time = 60 min, temperature = 140°C, pressure = 50 bar; aniline : acetone = 1 : 3 (mol), catalyst = 4% by weight of reactants; mol% yield is based on aniline. Rate of flow of hydrogen for preactivation = 50–60 ml/min, the catalyst was prereduced at 300°C.

Table 3
Comparison of activity of catalyst

Catalyst[a]	Time (min)	Temp. (°C)	Pressure (bar)	Mol% yield of N-isopropylaniline
1	60	140	50	52.0
2	60	140	50	76.8
3	60	140	50	48.2

[a] 1: fresh catalyst (nor prereduced); 2: catalyst prereduced at 300°C for 4 h in hydrogen; 3: catalyst prereduced at 450°C for 4 h in hydrogen. Catalyst = 4% by weight of reactants, aniline : acetone = 1 : 3 (mol).

only Cu(II) and the sample containing the most Cu(0) showed less activity than the sample containing the maximum Cu(I) species, it is suggested that the active site in the catalyst is Cu(I).

4.3. CHEMICAL ANALYSIS FOR CUPROUS IONS IN COPPER CHROMITE CATALYSTS

Pure copper chromite contains Cu(II) and Cr(III) ions in the ratio of 1 : 2. The commercial catalyst (Harshaw Cu-1184 T) contained 44% CuO, 45% CrO and 9% BaO (copper content 35% and chromium content 31%). Thus the practical catalyst is not a pure material and contains in addition to the spinel $CuCr_2O_4$, cupric oxide, barium chromate and probably other phases. The need for an activation by reduction in hydrogen suggests that some of the metal ions on the surface have to be reduced to a lower oxidation state for catalytic activity. Results of the present study as well as literature reports [12] suggest that surface cuprous ions rather than copper metal or chromium ions are the active centers. The cuprous content of the catalyst was estimated by chemical analysis (tables 1 and 2). The results are indicative of the degree of reduction of copper in the catalyst.

4.4. X-RAY DIFFRACTION ANALYSIS (XRD)

In the present study XRD gave useful information about the nature of the catalyst. The solid phases in the catalyst samples were identified by X-ray powder diffraction technique using Cu K_α radiation. X-ray diffractograms were obtained for the powdered samples with a Philips diffractometer (Philips Generator Holland model PW 1130) provided with on line recorder and a dot matrix printer (Teletype, USA).

The XRD pattern of the fresh catalyst was in general agreement with that reported for copper chromite [5]. Upon preactivation, namely reduction in hydrogen new peaks appeared, notably at 2θ values 50.7, 43.27, 42.33 and 36.5 (fig. 1). The first two values (50.7 and 43.27) were taken as due to copper metal and peaks at 42.33 and 36.5 due to cuprous chromite. As the temperature of preactivation

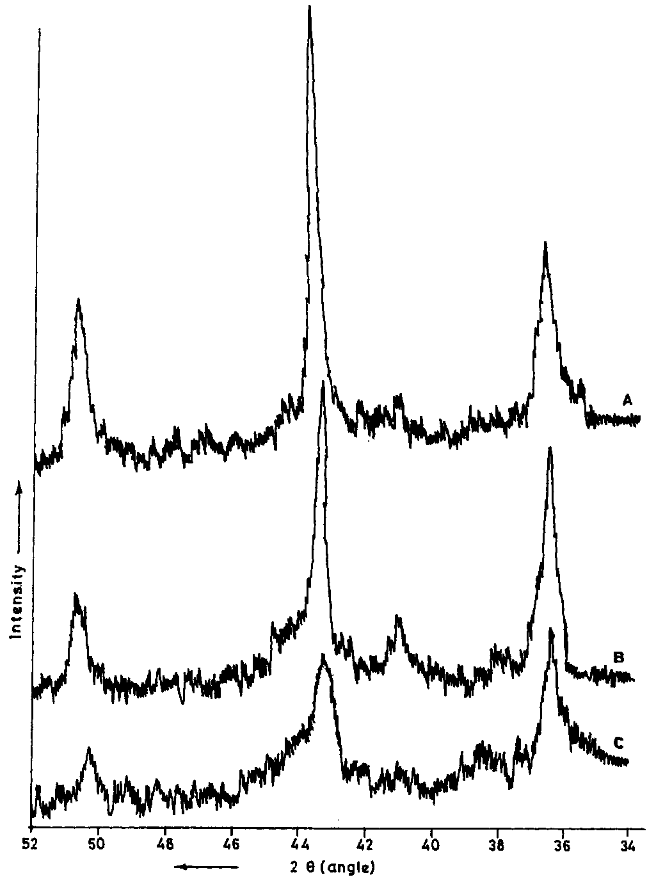

Fig. 1. XRD of copper chromite prereduced at 450°C (A), 300°C (B) and 150°C (C).

increased from 100 to 450°C the intensity of the peak at 36.5 (cuprous chromite) increased to reach a maximum at 300°C (preactivation temperature) and then decreased. The intensity of the peak at $2\theta = 43.27$ (copper metal) steadily increased.

The variations in the cuprous chromite peak are parallel to the change in activity of the catalyst with prereduction temperature (table 1). On the other hand increase in the copper metal content does not result in a parallel increase in activity. The catalyst reduced at 300°C for different periods of time also showed a similar trend (table 2). These results are taken to support the conclusion that cuprous ions are the active sites.

From the XRD studies the following conclusion can be drawn. The active catalyst obtained by reducing fresh "copper chromite" has peaks identified as copper metal and cuprous chromite which were not present in the fresh catalyst. The activity of the catalyst reduced under different conditions was closely parallel to the intensity of the cuprous chromite peaks and not that of the copper metal peaks. These studies support the view that Cu(I) are the active sites and not Cu(0).

5. Summary

The active site in copper chromite catalyst used for reductive alkylation of amines is copper(I). The optimum temperature for prereduction of catalyst to gain maximum activity is 300°C for 4 h.

Acknowledgement

The author thanks Professor C.N. Pillai of IIT, Madras for valuable discussions.

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