

Reductive alkylation of aromatic amines over copper chromite: Deactivation of catalyst†

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Reaction of aniline with acetone in the presence of hydrogen and copper chromite as catalyst at 140°C and 50 kg/cm² pressure has been studied with a view to understand the reasons for the rapid deactivation of the catalyst. Poisoning of the surface by the by-products of the reaction is the major cause of deactivation.

Copper chromite is the most successful catalyst used in the reductive alkylation of aromatic amines. One of the problems encountered in this process is the rapid deactivation of the catalyst. The present study was undertaken to have an insight into the mechanism of catalyst deactivation during the reductive alkylation of aniline by acetone to N-isopropylaniline.

Experimental

Procedure adopted for experiments 1-19

The catalyst used was Harshaw Cu-1184 containing BaO as promoter. In experiment No. 1, catalyst (9 g) without any pretreatment was taken along with aniline (37.74 g, 37 ml) and acetone (89.38 g, 113 ml) in a 500 ml teflon lined autoclave. The mixture was subjected to hydrogenation at 50 kg/cm² H₂ pressure and 140°C, for 60 min. The catalyst was removed by centrifugation and products were analysed by G C. The catalyst residue was rinsed with acetone and used for experiment No. 2. Experiment Nos 2 to 7 were done using the sample of recovered catalyst after each experiment as described above. These catalysts are designated as C₁ to C₇ respectively.

The catalyst after the 7th run was washed with acetone and acetic acid, dried and heated successively in streams of air and hydrogen at 250°C for 4 hr each. This catalyst, designated as C₈ was used for experiment No. 8.

Samples of the fresh catalyst were heated in a stream of hydrogen at 100°, 150°, 200°, 250°, 300°, 350° and 400°C for 4 hr in separate experiments. These hydrogen-treated catalysts labelled as C₉ to C₁₅ were used for the reactions in experiments 9-15.

The catalyst prerduced in hydrogen at 300°C for 4 hr, which had maximum activity, was repeatedly used for reductive alkylation as in experiments 1-7. These are listed as experiments 17-19.

Product analysis

The liquid product mixture obtained after removal of the catalyst by centrifugation was analysed by gas chromatography using a Carbowax 20 M column. N-Isopropylaniline could be recovered by distillation and identified by its PMR spectrum. The residue remaining after distillation was calcined and the ash was dissolved in nitric acid and analysed by atomic absorption spectroscopy. The results showed the presence of trace quantities of copper and chromium in the ratio of 6:1.

X-ray, XPS and thermogravimetry studies on catalyst

Catalysts C₁ (fresh), C₁₃ (hydrogen-pretreated) as well as the used catalyst before regeneration, were examined by XPS and by thermogravimetry. BET surface areas and pore volumes of these catalyst were also determined.

Results and Discussion

Nature of chemical reactions involved

The reductive alkylation of aniline involved initial formation of the schiff base followed by hydrogenation. Acetone itself got hydrogenated to isopropyl alcohol in a parallel reaction.

The pot residue after distillation and the material obtained by repeated extraction of the deactivated catalyst by hexane solvent, was found to contain higher boiling nitrogenous compounds which could not be identified. They were formed only in very minor quantities but seemed to play a major role in deactivating the catalyst (vide infra).

Deactivation of catalyst

The results of experiments 1 to 7 (Fig. 1) show that the activity for acetone hydrogenation rapidly

† Paper presented in the National Workshop on Spectroscopic Methods in Heterogeneous Catalysis held at Bombay during 20-22 December 1989.

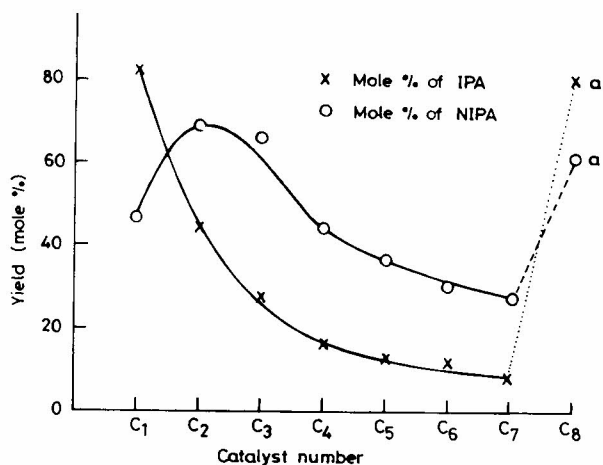


Fig. 1—Deactivation of fresh catalyst on usage [The catalyst number in the X-axis refers to the repeated usage of the catalyst in batch reactions without regeneration, except C_8 which is the regenerated catalyst, (X) mole % yield of isopropyl alcohol (IPA) based on acetone taken, (O) mole % yield of N-isopropylaniline (NIPA) based on aniline taken, (Xa) and (Oa) are results on re-generated catalyst].

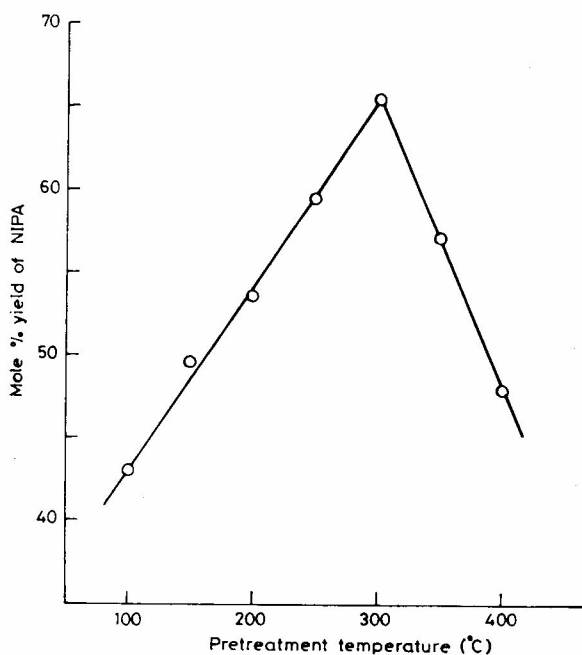


Fig. 2—Effect of pretreatment temperature of catalyst on the conversion of aniline into N-isopropylaniline.

decreases with catalyst usage, whereas the activity for reductive alkylation (N-isopropylaniline formation) initially increases with usage and reaches a maximum with the 2nd cycle of usage. Thereafter this activity also decreases. The deactivation seems to be due to the contamination of the catalyst surface by the minor high boiling products formed

Table 1—BET surface areas and pore volumes of catalysts

No.	Catalyst	Surface area (m^2g^{-1})	Pore volume (cm^3/G)
1	Harshaw Fresh	84	0.179
2	Pre-treated with H_2 at 300°C	81	0.244
3	Harshaw used	64	0.144
4	Regenerated	80	0.257

Table 2—XPS data of various catalysts

Sample	Obs. binding energy for $\text{Cu } 2\text{P}_{3/2}$ (eV)	Inference
Fresh catalyst	934.24	Copper is in Cu^{2+} state
Catalyst pretreated with H_2 at 300°C	933.40	Copper is in Cu^+ state
Deactivated catalyst	932.25	Copper is in Cu^0 state

from aniline. Hydrogenation of acetone seems to be much more sensitive to this poisoning, than the activity for the hydrogenation of the schiff base. (The schiff base itself could be the poisoning agent).

The initial increase in the rate of N-isopropylaniline formation suggests that the catalyst requires pre-activation in hydrogenation in order to acquire full activity. Part of the low activity for N-isopropylaniline formation with the fresh catalyst (Experiment 1) may be due to the consumption of acetone in the competing isopropyl alcohol formation, for which the initial activity is very high.

Preactivation of the catalyst

The results of activating the catalyst by heating in a stream of hydrogen at various temperatures for 4 hr are given in Fig. 2. It can be seen that the catalyst activated at 100°C (C_9) is identical in activity to the fresh catalyst. Activation at higher temperatures ($150\text{--}300^\circ\text{C}$), i.e. using catalysts C_9 to C_{13} progressively increases the catalytic activity as measured by N-isopropylaniline yield. Activation $>300^\circ\text{C}$ causes a decrease in catalytic activity (catalysts C_{14} and C_{15}). Thus the catalyst pre-reduced at 300°C (C_{13}), as expected, did not show any induction period in the reductive alkylation (see experiments 16-19) (see also Fig. 3).

Nature of active sites and mode of deactivation

Literature reports¹ suggest that coordinately unsaturated sites of cuprous ions on the catalyst sur-

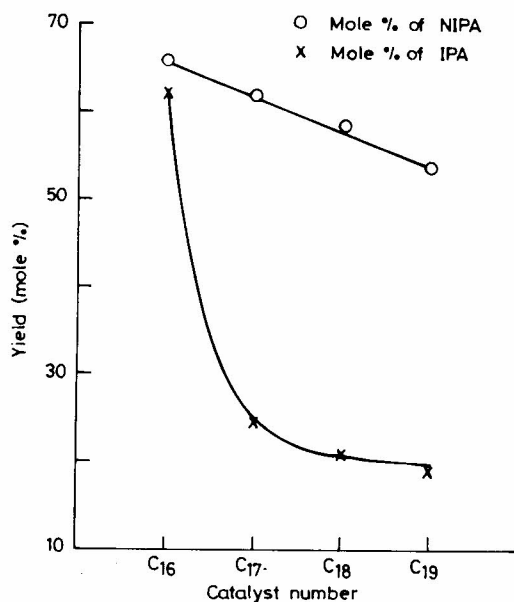


Fig. 3—Deactivation of catalyst hydrogen-treated at 300°C [(X) mole % yield of isopropyl alcohol (IPA) based on acetone taken, (O) mole % yield of N-isopropylaniline based on aniline taken.

face are the active sites for hydrogenation. XPS studies (Table 1) showed the absence of Cu^+ ions in the fresh catalyst and their presence in the hydrogen-treated catalyst. The used (deactivated) catalyst also did not show the presence of Cu^+ ions, but contained Cu^0 , suggesting that over-reduction to metallic copper may be one of the cause of deactivation.

Another reason for deactivation is the strong absorption of basic substances on the coordinately unsaturated Cu^+ sites. The role of such strong adsorption in catalyst poisoning has been pointed out by earlier workers¹. The observation that the hydrogen-copper and chromium in the ratio of 6:1. The total loss of metal in the course of an experiment was

enation of acetone is more sensitive to poisoning than the reductive alkylation reaction is understandable since the less basic acetone cannot compete successfully with the schiff base for the active sites.

Some of the metal ions are leached out as soluble complexes which along with tarry matter could be obtained as a black mass when the volatile reaction products were removed by distillation. No well defined compound could be isolated from this. Calcination of this residue in air and analysis by atomic absorption spectroscopy showed the presence of 1.5%. However, the loss of metal by this process seems to have no bearing on the loss of activity. This conclusion is drawn from the observation that the regenerated catalyst C₈ which has already suffered some loss of metal is as active as the preactivated catalyst C₁₃ (Fig. 1).

The used catalyst retained a lot of organic matter which could not be removed by washing with solvents. Thermogravimetric analysis of a catalyst which was used for 7 runs without regeneration and dried at 100°C, showed 6.8% mass loss at 180-230°C and 10.2% mass loss at 420-450°C, whereas the fresh catalyst showed no mass loss. This can only be due to the presence of organic matter on the surface either as resinous deposit or as surface complex. The surface areas and pore volumes of the fresh and used catalysts are given in Table 2. The reduction in surface area and pore volume of the used catalysts is likely to be due to the above reason.

Acknowledgement

The authors thank Harshaw/Filtrol, U.S.A. for a gift of copper chromite.

References

- Habaut R, Bonnelle J P, *J molec Catalysis*, 55 (1989) 170-183.