

## Promotional action of Cu in Rh-Cu/activated carbon catalyst for selective hydrogenation of *para*-chloronitrobenzene to *para*-chloroaniline

Ajit Das, Riya Mukherjee, Ramesh Mandal, Kamala M. Hansda and Nagendranath Mahata\*

Department of Chemistry, Sidho-Kanho-Birsha University, Purulia-723 104, West Bengal, India

E-mail: nmahata@hotmail.com

Manuscript received 27 July 2018, accepted 08 August 2018

Hydrogenation of *para*-chloronitrobenzene was studied over Cu promoted Rh catalyst supported on activated carbon in liquid phase under 1.5 MPa hydrogen pressure at 393 K. Methanol has been used as solvent. The bimetallic RhCu catalysts exhibited performance much superior to the monometallic Rh catalysts, particularly in terms of *para*-chloroaniline selectivity and catalyst stability. Physico-chemical techniques like N<sub>2</sub> adsorption, H<sub>2</sub> chemisorption, transmission electron microscopy (TEM) were applied to characterise the catalysts. Catalytic performance (activity and selectivity) was correlated to the surface structure. Cu islands on Rh surface activate N=O bonds of *para*-chloronitrobenzene, which thereby undergoes facile hydrogenation leading to exclusive formation of *para*-chloroaniline.

Keywords: RhCu catalyst, carbon support, hydrogenation, *para*-chloronitrobenzene, surface mechanism.

### Introduction

Substituted aromatic amines, particularly halogenated amines, are extensively used in the synthesis of value added industrial products such as herbicides, pesticides, pigments etc. And thus, catalytic hydrogenation of halogenated nitro aromatics to corresponding haloamines is of immense importance. However, catalytic hydrogenation of halogenated nitro aromatics generates a range of by-products; and hence, product selectivity is a crucial issue in such processes<sup>1-4</sup>. The yield of desired haloamine may be reduced significantly due to side reaction – hydrodehalogenation<sup>5</sup>. The accumulation of hydroxylamine and other intermediates during the process also impart serious problem. Accumulated hydroxylamine may result in condensation products<sup>1</sup>. Hence, accumulation of hydroxylamine is highly undesired. Several supported metal catalyst systems have been explored in the selective hydrogenation of halonitro compounds to corresponding haloamines<sup>2-6</sup>. Noble metal catalysts have been found to be highly active in the hydrogenation of halonitro aromatics<sup>2,6-9</sup>. However, cleavage of the carbon-halogen bond, during the process, at least to some extent becomes almost inevitable. Applications of promoters are reported to be beneficial in suppressing the dehalogenation side reaction; and thereby enhancing the selectivity of haloamines<sup>3,5,6</sup>. However, mechanism of the action of promoters is not clear

yet. Further studies are demanding to enlighten this area.

Supported RhCu may make an interesting catalytic system for hydrogenation of organic substrates. Rh is well known as catalyst for hydrogenation of reducible functionalities in organic substrates and Cu may be applied as effective promoter. Thus, supported Rh-Cu is expected to be an effective system in the hydrogenation of halonitroaromatics to corresponding haloamines. The act of Cu as promoter of Rh in the hydrogenation of *para*-chloronitrobenzene to *para*-chloroaniline over activated carbon supported Rh-Cu has been explored in the present study.

### Experimental

Rh and Rh-Cu were supported on two commercial activated carbons procured from Merck (AC-M) and SRL (AC-S) following impregnation method and thereby Rh/AC-M, Rh/AC-S, RhCu/AC-M and RhCu/AC-S catalysts were obtained. The bi-metallic catalysts were prepared by applying co-impregnation procedure. RhCl<sub>3</sub>.3H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>.2.5H<sub>2</sub>O were used as Rh and Cu precursors, respectively. Calculated amount of metal precursors in the impregnating solutions were maintained to obtain 1 wt% loading of each metal over the supports. Water was used as impregnating solvent. After impregnation, the catalysts were dried at 383 K for 12 h. The dried catalysts were treated at 473 K for 1 h under

nitrogen flow ( $50 \text{ cm}^3 \text{ min}^{-1}$ ) and finally reduced at 473 K for 2 h under hydrogen flow ( $50 \text{ cm}^3 \text{ min}^{-1}$ ).

BET surface area of the supports and the supported catalysts was determined from the analysis of  $\text{N}_2$  adsorption isotherms, measured at 77 K. Rh fractional dispersion ( $D$ ) was determined by chemisorption of  $\text{H}_2$  at 303 K, assuming chemisorption stoichiometry of  $\text{H}/\text{Rh} = 1$ . Prior to chemisorption measurements, the samples were reduced under  $\text{H}_2$  flow ( $40 \text{ cm}^3 \text{ min}^{-1}$ ) at 473 K for 2 h, and then the adsorbed hydrogen was removed by flowing He ( $40 \text{ cm}^3 \text{ min}^{-1}$ ) at 573 K for 2 h. Metal particle size in the catalysts was determined by TEM analysis, also. Over 100 individual metal particles were counted for each catalyst and the mean particle diameter was determined.

The catalytic hydrogenation of *para*-chloronitrobenzene (*p*-CNB) was carried out in a custom made stainless steel semi-batch 250 mL reactor at 393 K and 1.5 MPa of  $\text{H}_2$ , with continuous addition of hydrogen. In a typical experiment, calculated amount of catalyst (containing 0.002 mmol Rh) and 100 mL methanol were put into the reactor and purged 5 times with nitrogen, followed by 5 times with  $\text{H}_2$ . The temperature was then raised to 393 K,  $\text{H}_2$  pressure was adjusted to 0.5 MPa and the system was stirred for 2 h. Thus the catalyst was reactivated *in situ*. Meanwhile, 1.576 g (10 mmol) of *p*-CNB was dissolved in 100 mL methanol; nitrogen was bubbled through for 30 min to remove dissolved air, and kept under nitrogen. After reactivation of the catalyst, the temperature of the reactor was brought down to about 313 K, and the solvent was removed through the sampling port. The air-free substrate solution was then added into the reactor by means of a cannula, and the system was purged 5 times with  $\text{H}_2$  to remove the dissolved nitrogen. Finally, the temperature and  $\text{H}_2$  pressure were adjusted to 393 K and 1.5 MPa respectively, and the reaction was initiated by starting stirring. The progress of the reaction was followed by collecting aliquots of liquid samples periodically and analyzing chromatographically. Conversion of substrate and selectivity of products were calculated as follows:

Conversion of *p*-CNB (%) =  $[1 - \{\text{concentration of } p\text{-CNB} / (\text{concentration of all products} + \text{concentration of } p\text{-CNB})\}] \times 100\%$ . Selectivity of product, **P** (%) =  $(\text{concentration of } \mathbf{P} / \text{concentration of all products}) \times 100\%$ .

## Results and discussion

BET surface area of the supports and catalysts are presented in Table 1. The BET surface area of the supported catalysts is similar to the corresponding supports. It is clear from the results that loading of metals does not modify the BET surface area significantly. The results are quite expected because the extent of metal(s) loading is quite low.

**Table 1.** BET surface area of the supports and the supported catalysts

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )
AC-M	575
Rh/AC-M	575
RhCu/AC-M	565
AC-S	540
Rh/AC-S	545
RhCu/AC-S	535

$\text{H}_2$  chemisorption results are shown in Table 2. The fractional dispersion of Rh and the average metal particle size in the monometallic Rh catalysts was calculated from  $\text{H}_2$  chemisorption measurement. Metal particle size determined from TEM analysis are also presented in Table 2. The bimetallic catalysts exhibited extremely low hydrogen chemisorptions. This may be due to the coverage of most of the Rh surface by Cu, thereby strongly limiting hydrogen chemisorptions. Chou *et al.* investigated adsorption of  $\text{H}_2$  on  $\text{RhCu}/\text{Al}_2\text{O}_3$ . They reported that Cu atoms tend to occupy surface sites beyond a certain Cu loading ( $\text{mol}_{\text{Cu}}/\text{mol}_{(\text{Rh}+\text{Cu})} = 0.1$ ). Eventually, Cu islands are formed on the Rh surface and thereby  $\text{H}_2$  adsorption is strongly prevented<sup>10</sup>. TEM analysis clearly reveals good dispersion of metal particles in all the four catalysts. Small metal particles with similar average size were observed in the monometallic Rh as well as in the bimetallic RhCu catalysts (Table 2). Consequently, large interfacial contact area is expected to lead to good interaction between the

**Table 2.** Rh dispersion and average metal particle size of the catalysts

Catalyst	Fractional Rh dispersion ( $D$ ) [from $\text{H}_2$ chemisorption]	Metal particle size $d$ (nm)	
		$\text{H}_2$ chemisorption	TEM
Rh/AC-M	0.18	6.8	4.5
RhCu/AC-M	–	–	4.7
Rh/AC-S	0.17	6.9	4.8
RhCu/AC-S	–	–	4.9

**Table 3.** Catalytic performance in the hydrogenation of *para*-chloronitrobenzene

Catalyst	Run #	Specific activity ( $\text{mol}_{p\text{-CNB}}$ $\text{mol}_{\text{Rh}}^{-1} \text{min}^{-1}$ ) at conversion (%) <sup>a</sup>			$t_{100}^b$ (min)	Selectivity (%)		
		20	50	80		<i>p</i> -CAN	AN	Others
Rh/AC-M	1	64.2	62.2	59.8	100	84	14	2
	2	60.1	55.3	50.4	135	83	16	1
	3	55.0	45.0	37.2	180	80	18	2
Rh/AC-S	1	64.0	61.9	59.1	105	83	15	2
	2	60.4	55.0	49.7	145	81	17	2
	3	54.2	45.4	36.3	190	80	19	1
RhCu/AC-M	1	38.5	37.3	36.1	135	98	1	1
	2	38.5	38.5	36.3	135	98	2	–
	3	38.5	38.4	36.1	135	98	2	–
RhCu/AC-S	1	38.2	37.1	36.0	140	98	1	1
	2	38.2	37.6	36.1	140	98	2	–
	3	38.3	37.8	36.0	140	98	2	–

<sup>a</sup>Calculated from slope of the reaction profiles, <sup>b</sup>time required for complete conversion. Reaction conditions: Amount of catalyst – containing 0.002 mmol Rh, 100 mL methanol (solvent), 10 mmol *p*-CNB, 393 K, 1.5 MPa  $\text{H}_2$ , 1400 rpm.

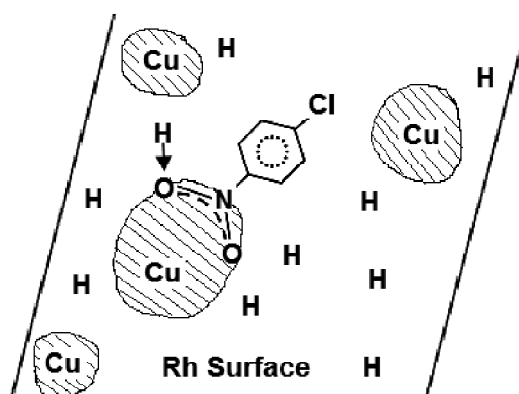
metal particle and the support in the catalysts.

Table 3 shows the performances of the catalysts in the hydrogenation of *para*-chloronitrobenzene (*p*-CNB). The monometallic catalyst showed excellent rate at the initial stages of the reactions. However, significant amount of activity is lost at the later stages, and in the second or subsequent reaction runs. On the contrary, the bimetallic catalyst maintained almost constant activities throughout a reaction run and also in multiple runs. Consequently, the activities of the bimetallic catalysts in the second or subsequent runs become superior to that of the monometallic catalysts (Table 3:  $t_{100}$  – time required for complete conversion). In terms of stability, the bimetallic catalysts were found to be excellent and they can be used in multiple reaction runs without significant loss of activity.

The relatively lower activity of the bimetallic catalysts in the first run/initial stage can be explained as follows.  $\text{H}_2$  chemisorption results indicate that Rh surface is partially covered by Cu in the bimetallic catalysts<sup>11–13</sup>. Consequently, lower amount of surface Rh sites leads to lower catalytic activity. However, Cu induces good stability to the catalyst. The bimetallic catalyst exhibited almost constant activity in multiple runs (Table 3).

Table 3 also lists the selectivity of *para*-chloroaniline (*p*-CAN) and aniline (AN). The other product(s) observed was/were not identified, as their concentration was very low and

insignificant. Particularly, the other product(s) are practically absent over the bimetallic catalysts. It is clear from Table 3 that the bimetallic catalysts, RhCu/AC-M and RhCu/AC-S, hydrogenate *p*-CNB almost exclusively to *p*-CAN (98%). On the contrary, the monometallic catalysts, Rh/AC-M and Rh/AC-S, showed much lower selectivity of *p*-CAN (80–84%). Significant amount of AN (14–19%) is formed as a result of hydrodechlorination over the monometallic catalysts. In the bimetallic catalyst, it seems that partial coverage of Rh surface by Cu (Cu islands on Rh surface) becomes beneficial in activating N=O bond<sup>14</sup>. Thereby, *p*-CNB undergoes hydrogenation selectively to *p*-CAN. A scheme is shown in Fig. 1.



**Fig. 1.** Surface reaction between *para*-chloronitrobenzene and hydrogen over activated carbon supported RhCu catalyst.

It may be worth to compare the results of present study with that of some studies reported in the literature, at least qualitatively. Even though direct quantitative comparison of studies is not possible as reaction conditions are different in different studies. And thus, comparison of substrate conversion does not make much of sense. However, comparison of product selectivity is obviously meaningful, at least to some extent. Mahata and co-workers have reported 91% selectivity of *para*-chloroaniline in the hydrogenation of *para*-chloronitrobenzene over Pt/C catalyst<sup>8</sup>. On the other hand, Zielinski and co-workers have reported 86% *ortho*-chloroaniline selectivity in the hydrogenation of *ortho*-chloronitrobenzene over Pt/MgF<sub>2</sub> catalyst<sup>7</sup>. However, it may be mentioned that application of promoter (Cu) to Pt augmented selectivity of chloroaniline significantly<sup>8</sup>.

### Conclusions

RhCu/activated carbon catalysts exhibited high activity, stability and excellent selectivity in the hydrogenation of *para*-chloronitrobenzene to *para*-chloroaniline.

Rh surface becomes partially covered by Cu as a result of interaction between Rh and Cu in the bimetallic RhCu/activated carbon catalysts.

Cu islands on Rh surface beneficially activates N=O bonds in *para*-chloronitrobenzene. Consequently, *para*-chloronitrobenzene undergoes hydrogenation selectively to *para*-chloroaniline.

### Acknowledgements

Ajit Das gratefully thanks Council of Scientific and Indus-

trial Research (CSIR), New Delhi for a Junior Research Fellowship.

### References

1. M. Studer, S. Neto and H.-U. Blaser, *Top. Catal.*, 2000, **13**, 205.
2. V. Kratky, M. Kralik, M. Mearova, M. Stolcova, L. Zalibera and M. Hronec, *Appl. Catal. A: General*, 2002, **235**, 225.
3. Y.-C. Liu, C.-Y. Huang and Y.-W. Chen, *Ind. Eng. Chem. Res.*, 2006, **45**, 62.
4. F. Cárdenas-Lizana, S. Gómez-Quero and M. A. Keane, *Appl. Catal. A: General*, 2008, **334**, 199.
5. B. Chen, U. Dingerdissen, J. G. E. Krauter, H. G. J. Lansink Rotgerink, K. Möbus, D. J. Ostgard, P. Panster, T. H. Riermeier, S. Seebald, T. Tacke and H. Trauthwein, *Appl. Catal. A: General*, 2005, **280**, 17.
6. B. Coq and F. Figueras, *Coord. Chem. Rev.*, 1998, **178-180**, 1753.
7. M. Zielinski, M. Pietrowski, A. Kiderys, M. Kot and E. Alwin, *J. Fluorine Chem.*, 2017, **195**, 18.
8. N. Mahata, O. S. G. P. Soares, I. Rodríguez-Ramos, M. F. R. Pereira, J. J. M. Órfão and J. L. Figueiredo, *Appl. Catal. A: General*, 2013, **464-465**, 28.
9. X. Xu, X. Li, H. Gu, Z. Huang and X. Yan, *Appl. Catal. A: General*, 2012, **429-430**, 17.
10. S. Chou, C. Yeh and T. Chang, *J. Phys. Chem. B*, 1997, **101**, 5828.
11. S. González, C. Sousa and F. Illas, *Intl. J. Modern Phys. B*, 2010, **24**, 5128.
12. F. Gauthard, F. Epron and J. Barbier, *J. Catal.*, 2003, **220**, 182.
13. O. S. G. P. Soares, J. J. M. Órfão, J. Ruiz-Martínez, J. Silvestre-Albero, A. Sepúlveda-Escribano and M. F. R. Pereira, *Chem. Eng. J.*, 2010, **165**, 78.
14. S. Galvagno, A. Donato, G. Neri, R. Pietropaolo and Z. Poltarzewski, *J. Mol. Catal.*, 1987, **42**, 379.