Geometric and Electronic Effects in Silica Supported Bimetallic Nickel–Copper and Nickel–Iron Catalysts for Liquid-phase Hydrogenation of Acetophenone and Benzonitrile

P. S. Kumbhar, M. R. Kharkar, G. D. Yadav* and The Late R. A. Rajadhyaksha

Department of Chemical Technology, University of Bombay, Matunga, Bombay-400 019, India

Inclusion of Cu and of Fe in Ni/SiO_2 catalysts leads respectively to a decrease and an increase in activity for reduction of acetophenone and benzonitrile: the former is attributed to an ensemble-size effect and the latter to an electronic effect.

The activity and selectivity of various hydrocarbon conversions can be effectively controlled by using bimetallic catalysts.[1] The main aim of these investigations has been to influence the activity and selectivity of active metals such as nickel, cobalt, palladium and platinum (group VIII) by addition of a second metal such as copper (group IB), which is totally inactive or another metal from the same group (group VIII), such as iron. Carbon monoxide hydrogenation and ethane hydrogenolysis are the two most commonly studied systems using bimetallic catalysts. Recently, Goupil *et al.*[2] have successfully used bimetallic Pt–Fe/C catalysts for selective hydrogenation of cinnamaldehyde in the liquid phase. In this communication we report for the first time the effect of silica-supported bimetallic Ni–Cu and Ni–Fe catalysts on the liquid phase hydrogenation of model carbonyl and nitrile compounds, *viz.* acetophenone and benzonitrile, which have

Table 1 Crystallite sizes of silica supported Ni–Cu and Ni–Fe catalysts determined from X-ray diffraction

Catalyst composition	Crystallite size[a]/nm
Ni : Fe	
100 : 0	23.00
75 : 25	13.21
50 : 50	9.14
25 : 75	10.37
0 : 100	23.08
Ni : Cu	
75 : 25	15.90
50 : 50	20.95
25 : 75	25.43
0 : 100	28.50

[a] Determined by using Scherrer's equation after correcting the line width at half maxima for instrumental line broadening.

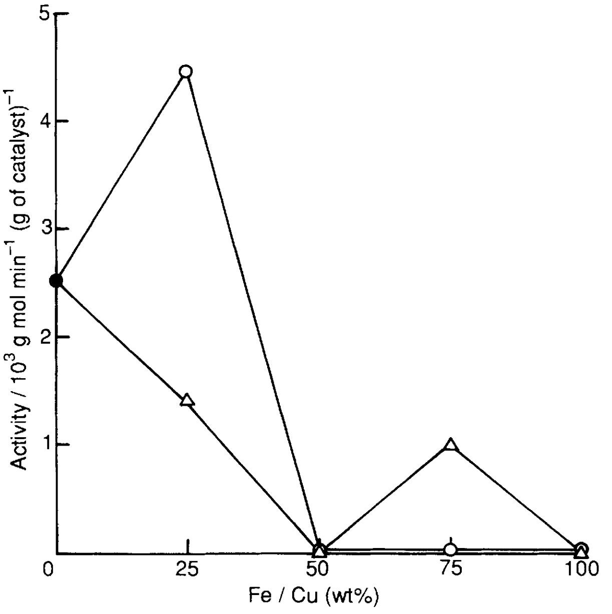

Fig. 1 Activity patterns for 20% Ni–Cu and 20% Ni–Fe on silica bimetallic catalysts for hydrogenation of acetophenone. *Reaction conditions*: *T* 135 °C; P_{H_2}, 850 psi (1 psi ≈ 6.89 × 10^3 Pa); speed of agitation, 1550 rpm; catalyst, 0.15 g; acetophenone, 15 g; methanol, 45 ml. ○ : Ni–Fe/SiO_2; △ : Ni–Cu/SiO_2; ● : Ni/SiO_2.

Table 2 Structural parameters of silica supported Ni–Fe catalysts determined from Ni and Fe K-edge EXAFS

Catalyst Composition Ni : Fe	Fe K-edge EXAFS[a]			Ni K-edge EXAFS[a]		
	N	*R*/Å	$\Delta\sigma^2$	*N*	*R*/Å	$\Delta\sigma^2$
100 : 0				12.0	2.50	0.0005
75 : 25	9.0	2.51	0.0001	12.0	2.50	0.0002
50 : 50	7.5	2.52	0.0006	11.0	2.52	0.0005
25 : 75	9.0	2.55	0.0002	9.5	2.51	0.0001
0 : 100	9.0	2.51	0.0001			

[a] *N* = coordination number; *R* = interatomic distance; $\Delta\sigma^2$ = disorder term of the nearest neighbours.

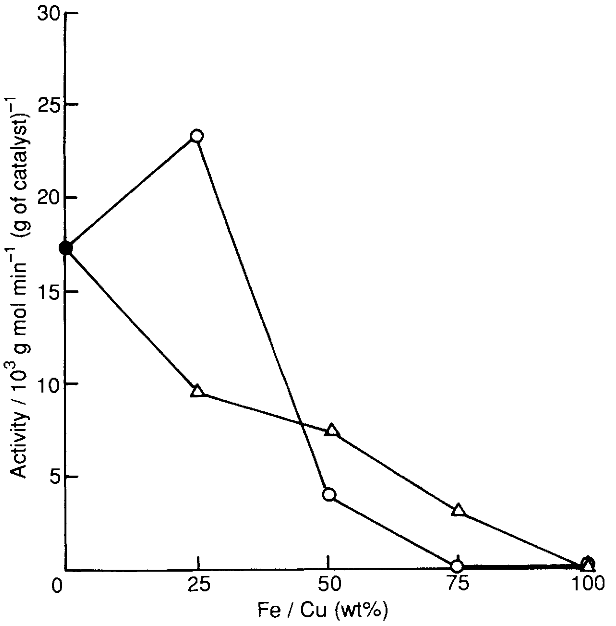

Fig. 2 Activity patterns for 20% Ni–Cu and 20% Ni–Fe on silica bimetallic catalysts for hydrogenation of benzonitrile. *Reaction conditions*: *T* 150 °C; P_{H_2}, 500 psi; speed of agitation, 1550 rpm; catalyst, 0.24 g; benzonitrile, 12.12 g; methanol, 40 ml. ○ : Ni–Fe/SiO_2; △ : Ni–Cu/SiO_2; ● : Ni/SiO_2.

commercial importance as well. The results are explained on the basis of geometric and electronic effects.

The silica (Aerosil 200, Degussa) supported Ni–Cu and Ni–Fe (100 : 0, 75 : 25, 50 : 50, 25 : 75, 0 : 100 by mass) catalysts were prepared by co-impregnation of their nitrates in an appropriate proportion by the incipient wetness technique. The total metal loading on the support was kept constant at 20% by mass. The nitrates were decomposed to their corresponding oxides by heating in a flow of air at 723 K for 4 h and were then reduced in a flow of H_2 at 723 K prior to their use. The X-ray diffraction (XRD) patterns of the reduced and passivated catalysts were recorded on a Rigaku diffractometer. The Mössbauer spectra were recorded in the cell *in situ* by using a ^{57}Co source. Ni and Fe K-edge extended X-ray absorption fine structure spectroscopy (EXAFS) of the Ni–Fe samples were also recorded in the cell *in situ* by using a Rigaku Mo-anode rotating diffractometer. The details of the characterization techniques and the data analysis procedure will be published elsewhere.[3] The hydrogenation reactions were carried out in a 100 ml Parr autoclave (30% solution of substrate in methanol) using the reduced catalysts, without exposure to air. The products were analysed by gas liquid chromatography (Perkin Elmer 8300) using a flame ionization detector (FID).

The XRD pattern of Ni–Cu(75 : 25)/SiO_2 showed a single phase face-centred cubic (FCC) alloy, whereas Ni–Cu (50 : 50 and 25 : 75)/SiO_2 showed formation of a biphasic alloy. The crystallite sizes determined by using Scherrer's equation are summarised in Table 1. The crystallite sizes of all the catalysts are fairly large. Ni–Fe (50 : 50) shows a minimum in the crystallite size. For Ni–Fe catalysts at all the compositions the Mössbauer spectra showed the presence of a Ni–Fe superparamagnetic alloy. Additionally, the 75 : 25 and 50 : 50 compositions showed a little ferromagnetic alloy component with a small amount of Fe^{2+}. The 25 : 75 composition showed non-alloyed iron and a little Fe^{2+}. Fe^{3+} was not observed in any compositions used in this study. The radial structure functions (RSF) of the Ni and Fe K-edge EXAFS of the Ni–Fe catalysts showed some interesting features. The RSF of Ni–Fe (75 : 25) is similar to that of pure Ni having FCC structure, whereas both Ni–Fe (50 : 50) and Ni–Fe (25 : 75) showed the presence of mixed phases [FCC + body-centred cubic (BCC)] Similar observations have been reported by Rao *et al.*[4] for Ni–Fe catalysts prepared by the precipitation technique. The summary of the structural parameters determined by fitting the EXAFS data is given in Table 2. The high values of coordination number, the same as those that are found in unsupported metals, indicate the presence of large crystallites supporting the earlier XRD data.

The results of acetophenone and benzonitrile hydrogenation over Ni–Cu and Ni–Fe catalysts are shown in Figs. 1 and 2, respectively. The activities are compared on the basis of unit mass of the catalyst. The main feature of these plots is the improved activity of the Ni–Fe (75 : 25) catalyst as compared to Ni on silica. The reproducibility of the results was checked by repeating the runs at least three times on the same batch of the catalyst and for another three times for a different batch of the catalyst and was found to be within acceptable limits (±5% for the same batch of the catalyst and ±10% for different batches of the catalyst).

The decreased activity of Ni–Cu catalysts is in accordance with that reported for CO hydrogenation. This has been attributed to the geometric or ensemble effect,[5] wherein addition of an inactive metal (Cu) dilutes the critical ensemble size of Ni atoms essential for the hydrogenation reaction to take place. In the case of Ni–Fe the results are unique in that there is an improvement in activity (1.5 fold) for Ni–Fe (75 : 25). Earlier reports on Pt–Fe, Rh–Fe and Pd–Fe catalysts for CO hydrogenation have reported similar improvement in activity.[6,7] The improved activity of these catalysts has been attributed to the formation of either (*i*) M–Fe^{3+} sites in which CO bonds by the oxygen end to Fe^{3+} or (*ii*) M–Fe^0 alloyed sites, in which case there is a charge transfer from Fe to the metal. Such a charge transfer produces what is commonly called electronic or ligand effects. Particle size effect can be ruled out as the least active Ni–Fe (50 : 50) shows the lowest particle size (Table 1). Hence, the higher activity of Ni–Fe(75 : 25) can be attributed to the Ni–Fe^0 sites which has pure FCC phase. Furthermore, Chourasia and Chopra[8] have reported charge transfer from Fe to Ni for Ni–Fe (76 : 24) by using soft X-ray appearance potential spectroscopy. Hence, the improved activity for hydrogenation of acetophenone and benzonitrile on Ni–Fe(75 : 25) catalyst can be attributed to the electronic effect. The further drop in the activity for Ni–Fe 50 : 50 and 25 : 75 compositions is probably due to the decreased ensemble size and a large decrease in hydrogen chemisorption capacity; even though they have lower crystallite size as compared to the Ni–Fe (75 : 25) and Ni on silica.

In the case of acetophenone hydrogenation α-phenylethanol is obtained as the sole product up to a conversion of 70%, after which the hydrogenolysis of α-phenylethanol to ethylbenzene starts. The benzonitrile hydrogenation reaction proceeds according to the scheme described by Rylander[9] and the major final product is the primary amine with some secondary amine. For both the reactions, the product pattern remained unchanged by the addition of either Cu or Fe.

Thus, this work shows that the addition of Cu and Fe affect the catalytic activity of nickel in an opposite manner in the hydrogenation of acetophenone and benzonitrile. Addition of Cu to Ni produces a geometric effect, whereas addition of Fe to Ni produces an electronic effect. Further studies are in progress to test these catalysts for selective hydrogenation of α,β-unsaturated carbonyl and nitrile compounds.

We thank the DST, Government of India for providing financial support. P. S. K. and M. R. K. thank the UGC for providing financial assistance. The help of Professor C. N. R. Rao and his group (IISc Bangalore) for EXAFS and Mössbauer spectroscopy is duly acknowledged.

Received, 6th December 1991; Com. 1/06162C

References

1 V. Ponec, *Adv. Catal.*, 1984, **32**, 149.
2 D. Goupil, P. Fouillox and R. Maurel, *React. Kinet. Catal. Lett.*, 1987, **35**, 185.
3 P. S. Kumbhar, G. D. Yadav and R. A. Rajadhyaksha, unpublished work.
4 C. N. R. Rao, G. U. Kulkarni, K. R. Kannan and S. Chaturvedi, *J. Phys. Chem.*, submitted.
5 M. Araki and V. Ponec, *J. Catal.*, 1976, **44**, 439.
6 A. Fukuoka, T. Kimura, N. Kosugi, H. Kuroda, Y. Minai, Y. Sakai, T. Tominaga and M. Ichikawa, *J. Catal.*, 1990, **126**, 434.
7 L. Guczi, *Catal. Lett.*, 1990, **7**, 205.
8 A. R. Chourasia and D. R. Chopra, *Surf. Sci.*, 1988, **206**, 484.
9 P. N. Rylander, *Catalytic Hydrogenation in Organic Synthesis*, Academic Press, New York, 1979, p. 138.