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STRUCTURE AND CATALYTIC PROPERTIES OF Cu-Ni BIMETALLIC CATALYSTS FOR HYDROGENATION

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Characterization of Cu-Ni catalysts, Cu-Ni hydrogenation, bimetallic catalysts

The dependence of catalytic activity and selectivity of Cu-Ni bimetallic catalysts for oil hydrogenation on Cu : Ni ratios have been investigated while they were reduced at low temperature (230 ° C). Two maxima occurred at Cu_2Ni_1 and Cu_1Ni_3 in the activity-Cu : Ni curve. Cu riched catalysts have higher selectivity than Ni riched ones, and may cause dehydrogenation and isomerization of linoleate at the beginning of the reaction. The structures of the catalysts reduced at different temperatures have been studied by means of XRD, XPS, EXAFS and FMR et al. The structure of the catalysts reduced at 230 ° C can be described as an aggregate of Cu particles inlaid with Ni atoms and unreduced NiO, and the easily reduced Cu always segregates on the surface, while homogeneous solid solution particles can be formed in the case 400 ° C being used as reduction temperature.

1. Introduction

Some kinds of Cu-Ni bimetallic catalysts such as mixed oxide, Raney and supported Cu-Ni have long been used for hydrogenation of olefines and vegetable oils [1]. The dependence of catalytic activity upon the ratio of Cu-Ni was also investigated by some scientists [2]. It was shown that for hydrogenation of the vegetable oils the catalysts with the ratio of Cu : Ni from 1 : 3 to 3 : 1 have high activity, and that of 1 : 3 has the highest activity when the catalysts are made from the metal carbonates and reduced in oils at around 230 ° C.

Most of the investigations of the Cu-Ni catalyst structure have used catalysts reduced at high temperatures, or in alloy films or particles. It was found that a two phase system, Ni-rich and Cu-rich, can be gradually formed at temperatures lower than 180 ° C after a substantial heat treatment. Under a moderate temperature an egg type structure would be present in which the Cu covers the Ni nuclei [3]. Only at high temperatures can a homogeneous solid solution of Cu-Ni alloy be produced. For supported catalysts it was observed that with XPS and Auger the metal was highly dispersed on the support surface and copper would segregate preferably to the surface in comparison with Ni [3,4].

TPR measurements have shown that Cu facilitates the reduction of the dispersed NiO at low temperature. This is the important effect of Cu in the bimetallic catalysts. Even it was thought that the catalytic action mainly depends upon Ni [5]. Another effect of the Cu in catalysts is to decrease the number of Ni adsorption sites and lower the interaction between the adsorbed molecules and the catalyst surface, for preventing hydrogenolysis [6].

However, few comparative studies about the structure and function of copper in the Cu-Ni bimetallic catalysts for hydrogenation of vegetable oils are found in the literature. Some new observations will be presented in this paper: a relationship of two humps instead of a volcano type between hydrogenation activity and the proportion of Cu : Ni, the catalytic dehydrogenation and isomerization of oil on a few of the catalysts, and the studies of the structure of Cu-Ni clusters in these catalysts with EXAFS, XRD, FMR and XPS methods.

2. Experimental

All catalysts were prepared by the deposit-precipitation method from a mixture of $Cu(NO_3)_2$ and $Ni(NO_3)_2$ with ammonia hydrocarbonate on the support SiO_2 (200 mesh, S.A. of 327 m^2/g) followed by drying at 80 °C for 8 hours and reduction at different temperatures. The catalysts, marked as Cu_0Ni_1, Cu_1Ni_6, Cu_1Ni_4, Cu_1Ni_3, Cu_1Ni_2, Cu_1Ni_1, Cu_2Ni_1, Cu_3Ni_1, Cu_4Ni_1, Cu_6Ni_1 and Cu_1Ni_0 (the subscriptions indicate the weight ratios of the Cu to Ni, the corresponding atomic ratios are 0 : 1, 0.15 : 1, 0.23 : 1, 0.31 : 1, 0.46 : 1, 0.92 : 1, 1.85 : 1, 2.77 : 1, 3.70 : 1, 5.54 : 1 and 1 : 0), have the same total weight of the metal around 31% of the support weight being used in this study.

Hydrogenation of refined soybean oil was carried out in a stirred reactor in a flow of H_2 at atmospheric pressure. The progress of hydrogenation was followed by sampling periodically and measuring the iodine value (IV) of filtered oil samples [7]. The iodine value is defined as the milligrams of I_2 absorbed by the C=C bonds in 100 g oil while in I-Br glacial acetic acid solution. In determining the aliphatic acid compositions, including trans-oleic acid, the products and intermediate samples were methylated and then analyzed by GLC under the conditions: OV-275 on Chromsorb P AW DMCS, 80–100 mesh, 6 m column; H_2 carrier of 12 ml/min and column temperature of 220 °C [8].

For catalysts, Cu_2Ni_1, Cu_1Ni_1 and Cu_1Ni_3, TPR curves were obtained with SP-2305 GC (Beijing Analysis Instrument Co.) equipped with a tube-type micro-reactor which was controlled by a temperature-program heater.

EXAFS studies [9] of the catalysts reduced at different temperatures were carried out on Rigaku D/MAX, 12 kVA, Mo anode rotating diffractometer. The X-ray beam from Mo target excited under the conditions: 20 kV and 120 mA were monochromatized with a LiF (220) crystal and passed through R.S (0.15 mm), Soller slit (1°) and DS(1°). I_0 and I were measured separately under the same operation conditions, while the collection time for I_0 was 10 seconds and that for I was 40 seconds. The scan step is 0.002°. For each sample selected for EXAFS measurement K-edge absorption spectra of Cu and Ni were recorded separately in transmission mode at room temperature and used for calculating the structural parameters of the environment of the Cu and Ni atoms.

The crystal structure of the catalysts were determined on the same diffractometer before EXAFS study.

The compositions on the catalyst surfaces reduced at 230 °C were determined with the ESCA LAB5 MK-II XPS instrument.

The Ferromagnetic Resonance Spectra (FMR) were measured at room temperature on the ER-200D spectrometer.

3. Results and discussion

3.1. CATALYTIC PROPERTIES OF CATALYSTS WITH DIFFERENT RATIOS OF Cu : Ni

It has been found that the catalytic properties of Cu-Ni catalysts greatly depend on the ratio of Cu : Ni. As shown in fig. 1, for the hydrogenation of the refined soybean oil, which was determined under controlled condition (160 °C, 1500 rpm, 0.28% catal.), two maxima occurred at Cu_2Ni_1 and Cu_1Ni_3 in the activity-Cu : Ni curve, instead of a single maxima as reported in the literature [2,4]. According to the data of the activity (table 1), which is expressed as average iodine value drop per minute, we can get the following sequence of hydrogenation of the catalysts,

$$Cu_1Ni_3 \gg Cu_2Ni_1 > Cu_1Ni_4 \sim Cu_4Ni_1 \sim Cu_3Ni_1 \sim Cu_1Ni_2$$
$$> Cu_1Ni_1 \gg Cu_6Ni_1 \gg Cu_1Ni_6 \gg Cu_1Ni_0 \gg Cu_0Ni_1.$$

The catalysts that have a very high or very low Cu : Ni ratio are almost inactive, which agrees with the early results [2]. However, the catalyst Cu_1Ni_1 is much less

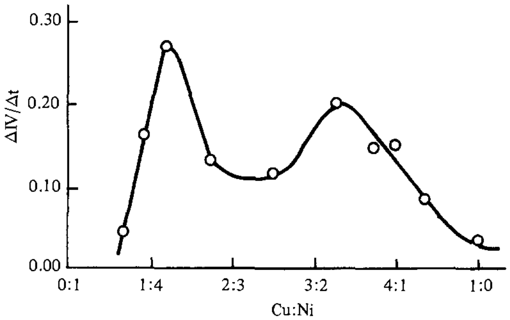

Fig. 1. Dependence of the catalytic activity on ratio of Cu : Ni.

Table 1
IV drop rate of soybean oil on catalysts [a]

Cu : Ni	1 : 0	6 : 1	4 : 1	3 : 1	2 : 1	1 : 1	1 : 2	1 : 3	1 : 4	1 : 6
IV/t	0.025	0.078	0.145	0.143	0.196	0.107	0.130	0.270	0.160	0.042

[a] catal./oil, 0.278% (wt). H_2, 80 ml/min., 160 ° C, 1500 rpm.

active than Cu_1Ni_3 and Cu_2Ni_1. Although it was reported previously that Cu_1Ni_3 was the most active one, a detailed comparison of the catalytic activities between it and Cu_1Ni_1 was not found.

Another extraordinary difference in the catalytic properties of the catalysts with different ratios of Cu : Ni can be seen from the direction of IV change with the reaction time at the beginning period of the hydrogenation process. As a general rule the IV should monotonically decrease with the reaction time in the hydrogenation of vegetable oil, as it is for the catalysts in which Cu : Ni ratio is less or equal to 1 (fig. 2). On the other hand, the tendence of the IV increase is obvious from Cu_3Ni_1, Cu_4Ni_1 to Cu_6Ni_1. The analysis of the composition of some "hydrogenated" products with GLC demonstrated that the catalytic selectivity could be largely effected by addition of more copper in the bimetallic catalysts. From the representative data (table 2) of the various aliphatic acids in the hydrogenated samples, we can see that some amount of oleate (18 : 1, means a 18-C-atom chain with one C=C bond) was produced from linolenate (18 : 2) in the reaction. In the meantime the amount of linolenate (18 : 3) increased. Take Cu_4Ni_1 for example, when the IV increased from the original 120.4 to 122.2, the amount of linolenate increased from 6.0% to 16.5%. We conclude that the dehydrogenation of some linoleate really took place on the catalysts Cu_4Ni_1 at the beginning.

When the IV of the hydrogenated oils decreased to that lower than the original value of 120.4, the content of linolenate in the hydrogenated oils using Cu_4Ni_1 and Cu_6Ni_1 is higher than that using Cu_1Ni_4 and Cu_1Ni_6 respectively. However, the higher content of oleate means that Cu_4Ni_1 and Cu_6Ni_1 also have higher catalytic hydrogenation activity of linoleate than Cu_1Ni_4 and Cu_1Ni_6, and the

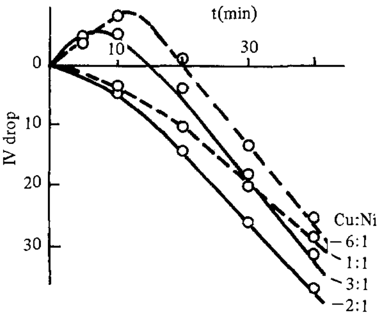

Fig. 2. IV-time comparisons 0.5% catal. 30 ml/min H_2, 500 rpm, 230 ° C.

Table 2
Contents of aliphatic acids in hydrogenated oils [a]

Cu:Ni:i	IV	16:0	18:0	c-18:1	t-18:1	18:2	18:3
4:1	122.2	11.8	3.7	40.7 [b]		27.3	16.5
6:1	104.8	13.1	3.4	46.8	6.6	34.2	6.5
1:6	104.8	12.4	3.8	40.4 [b]		38.5	4.9
4:1	98.1	11.8	3.6	45.2	10.9	22.7	5.8
1:4	98.1	11.9	4.1	49.3 [b]		31.5	3.4
oil [c]	120.4	12.1	3.4	34.5	0.0	48.0	6.0

[a] catal./oil, 0.5% (wt). H_2, 40 ml/min., 200 ° C, 500 rpm.
[b] trace trans-18:1.
[c] refined soybean oil.

content of trans-oleate in the formers is much higher than that in the latters, that is, Cu_4Ni_1 and Cu_6Ni_1 have stronger isomerization for linoleate.

According to the results mentioned above, both Ni and Cu play important roles in hydrogenation. The function of copper is not only to make the reduction of NiO in Cu-Ni bimetallic catalyst easier than when only NiO is present, but also to catalyze isomerization, dehydrogenation and hydrogenation of the oil molecules.

3.2. REDUCTION OF CATALYSTS

It is well known that reduction is an extremely important step for metal catalyst. The studies of Ni/SiO_2 catalysts show that not only the large amount of catalytically active metal, but also the suitable size of the metal particles for hydrogenation of vegetable oil molecules can be produced by means of the preferred reduction procedure [10]. Two important factors are reduction temperature and time. However, as the Cu-Ni catalysts used for oil hydrogenation were usually put into use in their precipitated state, they have to be reduced in situ at the beginning of the reaction in oils at low temperature around 230 ° C. Therefore the degree of reduction would limit the activity of the catalysts under these conditions. Unfortunately, TPR studies demonstrated that only partial reduction of the hydrocarbonate precipitates could take place in this way. Further reduction must be carried out at a much higher temperature above 400 ° C, and the complete reduction of NiO is more difficult for catalysts containing more Ni [11,12] (fig. 3).

It can be seen from the TPR results (fig. 3) that the higher the copper content in the bimetallic catalysts, the easier the reduction. XRD (fig. 4) of the catalysts reduced at 230 ° C in oil and at 400 ° C in an oven with flowing H_2 indicates that with the increase of the reduction temperature the diffraction peaks corresponding to Cu or Cu-Ni alloy get more intense and sharp. As shown in fig. 6, the

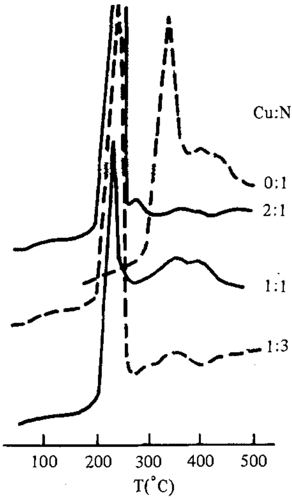

Fig. 3. TPR of catalysts with different ratio of Cu : Ni.

difference of the XRD patterns for catalysts with different Cu : Ni ratios is obvious. Comparing with Cu_2Ni_1 and Cu_1Ni_3, Cu_1Ni_1 has a relatively low degree of reduction and a very small particle size (~ 28 Å) which is not large enough for hydrogenation of vegetable oil molecules [1,6]. As expected, this catalyst would have low activity for this catalytic reaction in comparison with the two others. The most active catalyst Cu_1Ni_3 reduced at 230 ° C corresponds to a more or less suitable particle size (~ 68 Å) for oil molecule adsorption and a relatively high degree of reduction [13].

It can be seen that Cu_1Ni_1 can be greatly activated owing to the reduction at 400 ° C, which resulted in the increase of the particle size (~ 82 Å) and the degree of reduction [14]. Therefore the catalytic activity can increase remarkably to be comparable to that of Cu_1Ni_3 (0.23 to 0.26 IV drop per minute).

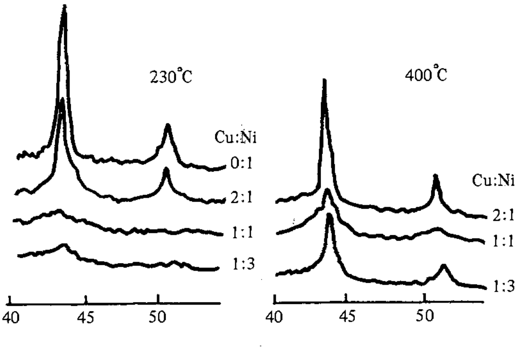

Fig. 4. XRD of catalysts reduced at different temperatures.

3.3. STRUCTURE OF CATALYSTS

EXAFS study of Cu_1Ni_1 indicates that the bimetallic Cu-Ni catalyst applied for the hydrogenation of edible oils actually consists of copper-nickel clusters with a minor part of nickel and unreduced nickel oxide. The small average coordination numbers in the nearest neighbour shell in the reduced state correspond to the relatively small particle size of metals dispersed on the support [6]. Here, we must indicate that XRD can only give an average size of the relatively large particles which seems very large for EXAFS, and on the other hand, EXAFS gives the total average result, including all minim clusters or particles which are unmeasurable for XRD.

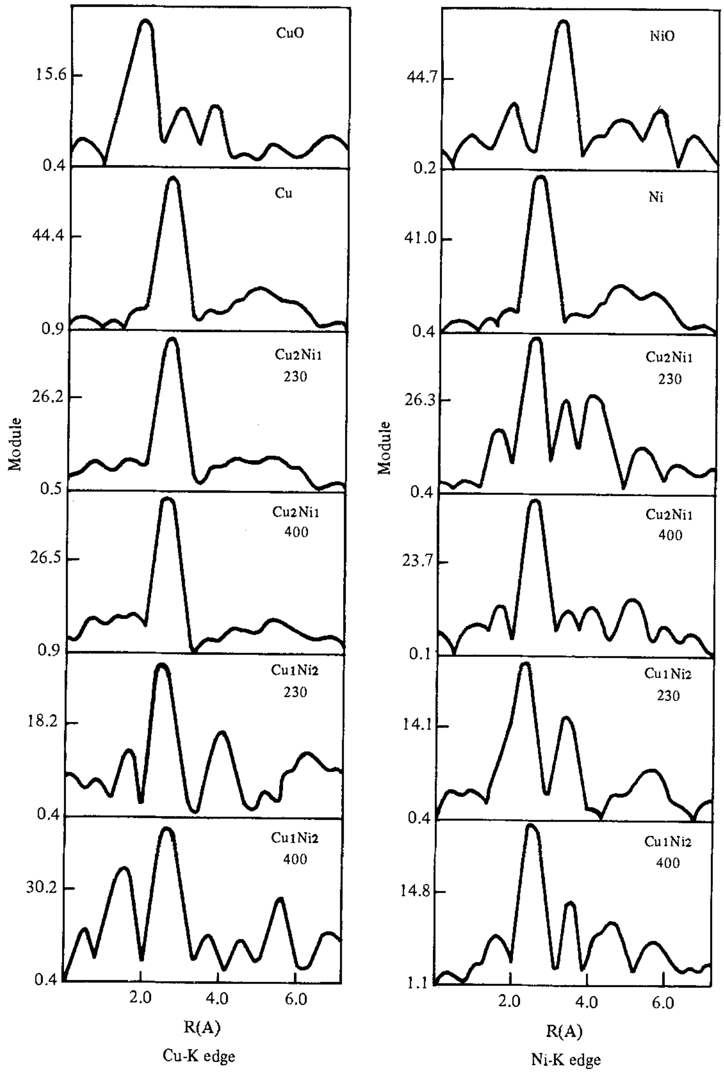

Fig. 5. RSFs of Cu-K edge and Ni-K edge.

The Radial Structure Functions (RSF) of Cu absorber obtained from EXAFS of Cu K-edge is independent of the ratios of Cu : Ni and reduction temperature. In any case a strong coordination peak at the distance around 2.56 Å can be clearly observed, which can be attributed to metallic atom coordination including copper and nickel surrounding Cu atoms (fig. 5). This corresponds to the completely reduced state of copper in these bimetallic catalysts.

A somewhat complicate RSF of copper (fig. 5) for Cu_1Ni_3 may come from the bad signal/noise because of the small amount of copper in the catalysts.

The RSFs of Ni absorber in these catalysts show definite dependence upon the reduction temperature and Cu : Ni ratio. All the RSFs of the catalysts reduced at 400 °C have a clearly strong coordination peak at the distance around 2.49 Å (fig. 5), despite the different ratios of the Cu : Ni. This kind of metal-metal coordination is characterized as a more highly reduced state of Ni in these situations. On the contrary, a Ni-O coordination at a short atomic distance and a Ni-Ni at a further distance overlapping on the nearest metal coordination peak can be recognized from Cu_2Ni_1 to Cu_1Ni_3 reduced at 230 °C (fig. 5).

The estimate of the coordination number about the absorber Cu and Ni proves that for Cu_2Ni_1 reduced at 400 °C the proportions of coordinated Cu to Ni surrounding both Cu and Ni can reach the maximum of 2 : 1 as a homogeneous solid solution, as to the high reduction temperature and less content of Ni in it. For the catalyst reduced at 230 °C the proportion of 3.0/1.5 coordinated Cu to Ni about Cu is near to 2 : 1, but that about Ni, 2.9/1.1, is rather far from it. The decrease of the coordinated number about Ni may be caused by some Ni in the unreduced NiO.

The difficulty in completely reducing NiO at low temperature and high content of Ni in these catalysts as mentioned in the previous paragraphs is supported by the EXAFS results.

XRD patterns of the catalysts reduced at 230 °C with different Cu : Ni ratios are shown in fig. 6, from which a plot of the *d*-spacings of the strongest lines against the percentage of the Ni in catalysts is given in fig. 7, together with that for the catalysts reduced at 400 °C. It is very interesting that the particle size changes with the Ni content, but the *d*-spacing will keep the same value of metallic copper of around 2.09 Å. This means that only the same crystal structure as that in Cu metal, in which Cu is predominantly present and constructs its own arrangement, can form and Ni atoms just take some places of Cu atoms without change of the atomic distance at low temperature.

From fig. 4 and fig. 7, it can be seen that the *d*-spacing for catalysts reduced at 400 °C is getting shorter with the increase of the content of Ni with small atomic radius in catalysts, as to a homogeneous solid solution consisting of copper and nickel at high temperature.

The change of the coordination distance causing the change of the *d*-spacing can be observed from EXAFS study (fig. 5). The results obtained from XRD and EXAFS are in agreement with each other.

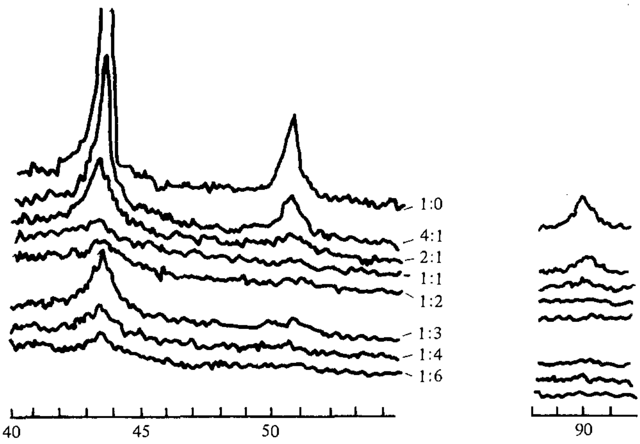

Fig. 6. XRD patterns of the catalyst with different Cu : Ni ratios (230 ° C reduced).

The state of Ni presented in the catalysts reduced at 230 ° C and 400 ° C were studied by means of FMR. The intensities of the signals due to the metal state of Ni are shown in fig. 8 and table 3, from which we can deduce that, (a) NiO was not much reduced at 230 ° C in Cu_1Ni_1 according to a very weak signal comparable to that of nickel oxide; (b) much more metal nickel can be obtained with reduction at 400 ° C in Cu_1Ni_1 and Cu_1Ni_3 from comparison with those at 230 ° C; (c) a homogeneous solid solution in Cu_2Ni_1 was produced with reduction at 400 ° C so as to the FMR signal of Ni could be much weakened. According to the theory of magnetic moment for Cu-Ni alloy (u_{Ni}) will become zero when the Ni content reaches to 40% or less. It is the case for Cu_2Ni_1 reduced at 400 ° C; (d) The remarkably large line width and g values for Cu_1Ni_3 reduced at 400 ° C mean the strong interaction between the metal nickel atoms which can be present a lot under these conditions.

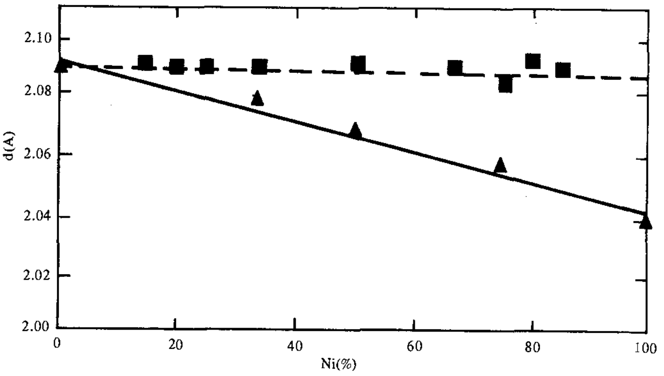

Fig. 7. Plot of d-spacing against percentage of Ni in the catalysts. ■ 230 ° C reduced; ▲ 400 ° C reduced.

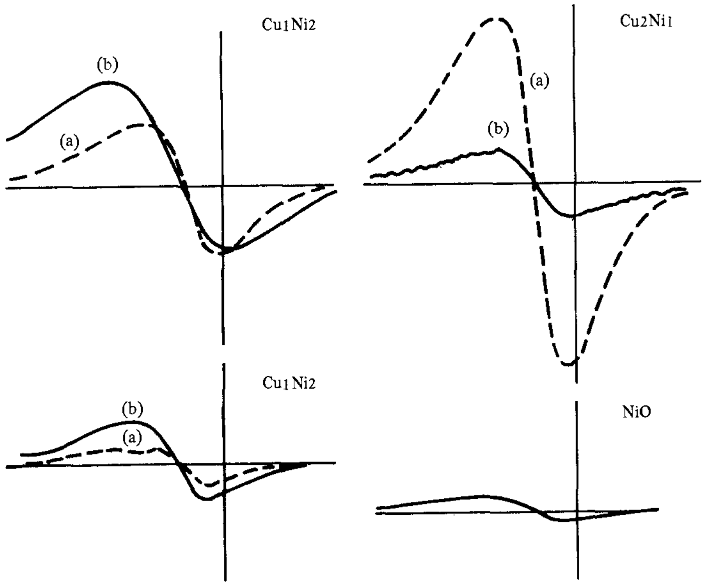

Fig. 8. FMR spectra of different catalysts. (a) 230 ° C; (b) 400 ° C.

Figure 9 shows XPS of Cu_3Ni_1 and Cu_1Ni_3 catalysts reduced in oil at 230 ° C. We can see that the surface copper mainly consists of Cu^0, while the surface nickel mainly consists of Ni^{2+}. There is no obvious Ni^0 peak in the spectra. Table 4 shows both bulk and surface Cu : Ni atom ratios of some catalysts. The bulk

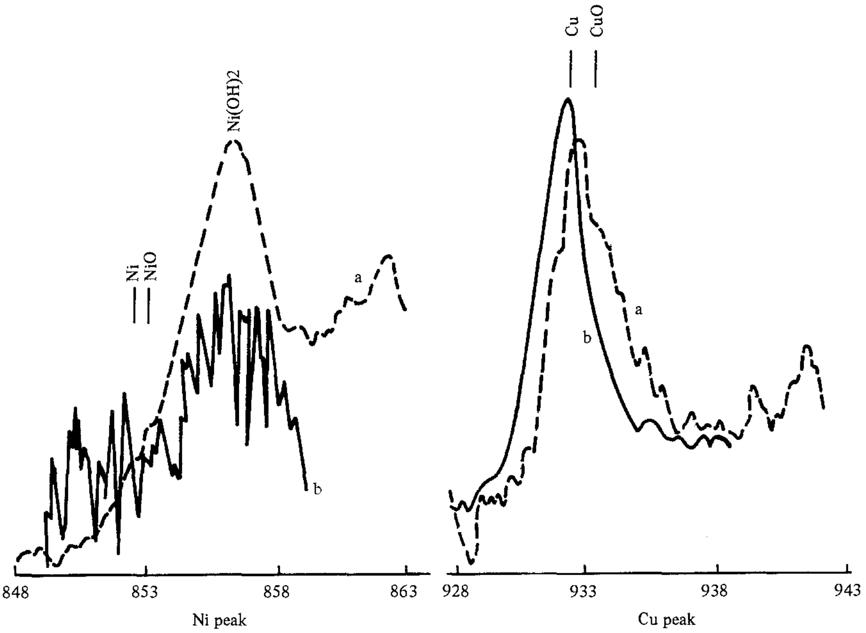

Fig. 9. XPS of some catalysts (a) Cu_1Ni_3; (b) Cu_3Ni_1.

Table 3
Ferromagnetic resonance results

Red. T(°C)	230 °C			400 °C			
Cu : Ni	2 : 1	1 : 1	1 : 3	2 : 1	1 : 1	1 : 3	NiO
g	2.25	2.24	2.25	2.26	2.27	2.31	2.22
(gauss)	600	625	650	575	625	975	700

Table 4
Surface and bulk Cu : Ni atomic ratios of some catalysts

Cu : Ni (weight)	Cu : Ni (bulk atom)	Cu : Ni (Surface atom)	
		Wagner	Scofield
6 : 1	1 : 0.15	[a]	[a]
3 : 1	1 : 0.31	1 : 0.15	1 : 0.13
1 : 1	1 : 0.92	1 : 0.88	1 : 0.76
1 : 3	1 : 2.80	–	1 : 2.22

[a] The signal of surface Ni is too weak to be detected.

ratios are calculated from weight ratios, and the surface ratios are from XPS. We find that the easily reduced Cu always segregates on the surfaces of the catalysts comparing with Ni, despite the low reaction temperature.

4. Conclusion

1. The dependence of the catalytic activity of Cu-Ni catalysts for hydrogenation of vegetable oils on the proportion of Cu to Ni has a characteristic of two maxima occurring at Cu_1Ni_3 and Cu_2Ni_1, and a minimum at Cu_1Ni_1 while they are reduced at low temperature at around 230 ° C.

2. The more the content of the copper in catalysts, the higher the selectivity for hydrogenation of linoleate. Dehydrogenation and isomerization of linoleate would greatly take place at the beginning of the reaction process on Cu_3Ni_1, Cu_4Ni_1 and Cu_6Ni_1.

3. Reduction is a very important procedure for the bimetallic catalysts. The low catalytic activity for Cu_1Ni_1 reduced at 230 ° C could be attributed to the incompleteness of the reduction. The treatment with H_2 at 400 ° C would greatly activate it so as to change the dependence of catalytic activity upon the Cu : Ni proportion.

4. EXAFS, XRD XPS and FMR studies show that the structure of the catalysts reduced at 230 ° C can be described as an aggregate of Cu particles inlaid with Ni atoms and unreduced NiO which may play its own role of catalytic action and binding intermediate between bimetallic cluster and support. In the

meantime Cu segregates on the surface of the catalysts. The degree of reduction of the catalyst also depends upon the Cu : Ni proportion of catalysts.

5. EXAFS, XRD and FMR studies provide the powerful support for the point of view that homogeneous solid solution particles consisting of Cu and Ni can be formed in the catalysts reduced at 400 ° C despite the difference of the Cu : Ni proportion. However the particle size is dependent upon the Cu : Ni ratios.

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