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Characterization of a new mixed oxide catalyst derived from hydrogen storage alloy

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A mixed oxide catalyst was prepared from a binary hydrogen storage alloy, Mg_2Cu. Oxidation of Mg_2Cu alloy gave mixed oxides of MgO and CuO, which showed high activity and high selectivity for the synthesis of alcohols from methyl linoleate. On the other hand, a catalyst prepared by the coprecipitation method deactivated with time. The nature of the catalytically active site was discussed on the basis of characterization by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and infrared analysis (I.R.). The difference between these two catalysts could be attributed to differences in the co-ordination number of copper species at the surface.

1. Introduction

Hydrogen storage alloys have a number of potential applications in many fields of energy technology. Many research works have developed efficient materials for application as hydrogen storage containers. However, less attention has been paid to the chemical application of these alloys. Several studies have been reported using hydrogen storage alloys as catalysts [1–3]. In the hydrogenation of carbon monoxide, these intermetallic compounds are oxidized into metal particles, well dispersed in oxide phases during reaction. It is reported that this oxidation is responsible for the activity. These findings provide a new way of preparing supported catalysts by oxidizing such alloys [4, 5].

In previous papers [6–9], the catalytic activities of several hydrogen storage alloys were tested. The hydrogenolysis of methyl oleate to C_{18} alcohols was conducted by a pulse reaction system [6]. Among the tested alloys, Mg_2Cu showed hydrogenolysis activity under very mild reaction conditions, such as atmospheric pressure of hydrogen at 503 K, but the activity was unstable. Oxidation pretreatment of this alloy increased the stability, and the catalyst became durable for hydrogenolysis of methyl oleate and methyl linoleate in a continuous flow reactor [7–9]. The activity and selectivity of the oxidized catalyst for alcohols were better than either the original Mg_2Cu alloy or the conventional Cu–Cr–O catalyst (Adkins catalyst).

In this paper, the nature of the catalytically active site is discussed on the basis of characterization by XRD, SEM, transmission electron microscopy coupled with energy dispersive spectroscopy (TEM–EDX), XPS and i.r. The bulk and surface structures of the oxidized samples were compared with those of samples prepared by the coprecipitation method in order to explain the differences in catalytic activity.

2. Experimental procedure

2.1. Sample preparation

Two kinds of catalysts were prepared as follows.

AL-775: a binary hydrogen storage alloy, HY-302 (Mg_2Cu), was obtained from Ergenics, a division of MPD Technology Corporation [6–9]. The alloy was preoxidized overnight in a flow of air at 775 K and sieved into a 35–42 mesh.

PR-775: Another copper–magnesium oxide type catalyst, with the same composition to AL-775, was prepared according to the coprecipitation method. A mixed solution of corresponding nitrates with a ratio of magnesium to copper of 2:1, was hydrolysed with a sodium carbonate solution, with $pH = 9$ at 333 K. The mixed salts in the solution were precipitated as hydroxides. The precipitates were filtered, dried and calcined overnight at 775 K and sieved into a 35–42 mesh.

2.2. Measurement methods

The bulk and surface structures of AL-775 and PR-775 for various treatments were investigated. Fresh samples, samples with hydrogen pretreatment at 553 K for 2 h and samples used once in the hydrogenolysis were studied by the following methods. Before measurement, every sample was treated with helium at 473 K.

X-ray diffraction (Rigaku Geiger Flex Rad-IC) was used for the structural analysis, using a copper anode with a nickel filter. A scanning electron microscope (Hitachi S-570) and a transmission electron microscope fitted with an energy dispersive X-ray spectroscope (Jem 4000FX) were used for morphological observation. An X-ray photoelectron spectrometer (XPS) was used for surface analysis, using an Mg anode. For the XPS measurement, the sample powders were kept in a sealed tube after various treatments, and were mounted on a sample stage with

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double-sided adhesive tape in open air just before measurement. The sample was evacuated at room temperature to 10 Pa; then, it was transferred to an analysing chamber for measurement (1 Pa). An infrared spectrophotometer (Jas i.r.-G) was used to analyse the chemical characteristics of the surface. For i.r. measurement, the powder samples were pressed into tablets with potassium bromide powders.

The surface areas of the samples were measured by the conventional Brunauer–Emmett–Teller (BET) method and were determined as 6.1×10^3 and $57.1 \times 10^3\ m^2\,kg^{-1}$ for AL-775 and PR-775, respectively.

2.3. Catalytic reaction procedure

The catalytic activities of the samples were examined in a continuous flow reactor. The details of the reaction apparatus was described in a previous paper [8]. The catalyst sample (1.0 g) was placed in a Pyrex glass reactor. Pretreatment of the catalyst was carried out in a flow of hydrogen at 553 K for 2 h.

Gas phase hydrogenolysis of methyl linoleate to alcohols was conducted at atmospheric pressure with $W/F = 5.2 \times 10^2\ kg\,s^{-1}\,m^{-3}$; H_2:methyl linoleate $= 148\ mol\,mol^{-1}$; $T = 513$ K. Since the reactant ester contained two unsaturated bonds, several products were expected during the reaction. These were linoleyl alcohol (with two double bonds), oleyl alcohol (with one double bond), stearyl alcohol (saturated) and paraffins.

The above products were analysed with a gas chromatograph equipped with a 6 m polyethyleneglycol (PEG-HT) column at 483 K. Methanol could not be analysed because the peak was masked by a larger solvent peak (acetone).

3. Results and discussion

3.1. Catalytic activity test

Activities of two catalysts (AL-775 and PR-775) were compared under the same reaction conditions ($T = 513$ K, $W/F = 5.2 \times 10^2\ kg\,s^{-1}\,m^{-3}$). Fig. 1 shows the changes in conversion with time. AL-775 showed steady state activity after 300 min. PR-775 showed high conversion at the initial stage. The conversion, however, decreased steeply to almost zero. The effluent contained copper salt of reactant acid. This suggests that a part of the copper component of PR-775 might react with the reactant ester. Active copper species might be deactivated by this reaction. the effluent for AL-775 did not contain copper salt and thus the steady state activity could be obtained.

3.2. Change in catalyst's structure

The changes in the bulk structures of two catalysts by hydrogen pretreatment and hydrogenolysis were studied by XRD analysis. Fig. 2a–c shows the XRD spectra of AL-775 with various treatments. Fresh AL-775 (Fig. 2a) consisted of a mixture of cooper oxide and magnesium oxide. After hydrogen pretreatment at 553 K for 2 h (Fig. 2b), the characteristic peaks of CuO disappeared and those of Cu metal appeared. After hydrogenolysis (Fig. 2c), AL-775 showed the same diffraction patterns as Fig. 2b. the characteristic peaks of MgO appeared continually with various treatments.

Fig. 3a–c shows the XRD spectra of PR-775 with various treatments. Each diffraction pattern of PR-775 was similar to that of AL-775. Therefore, no apparent differences could be found in the bulk structures between AL-775 and PR-775.

Crystallite size, estimated by the Scherrer method, is shown in Table I. PR-775 gave smaller particle size than AL-775 in the oxide state; but the crystallite sizes of reduced Cu for AL-775 and PR-775 are similar.

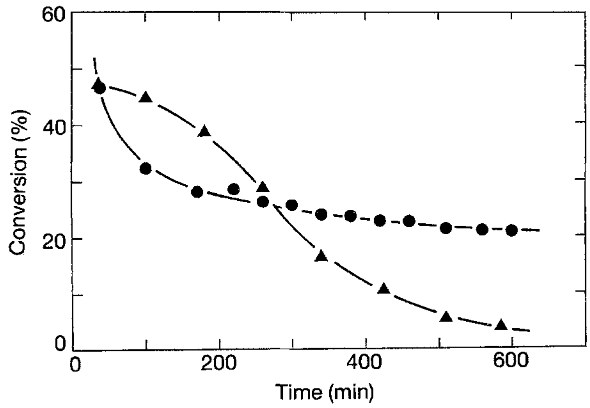


Figure 1 Activities of different catalysts at $T = 513$ K: (●) AL-775; (▲) PR-775.

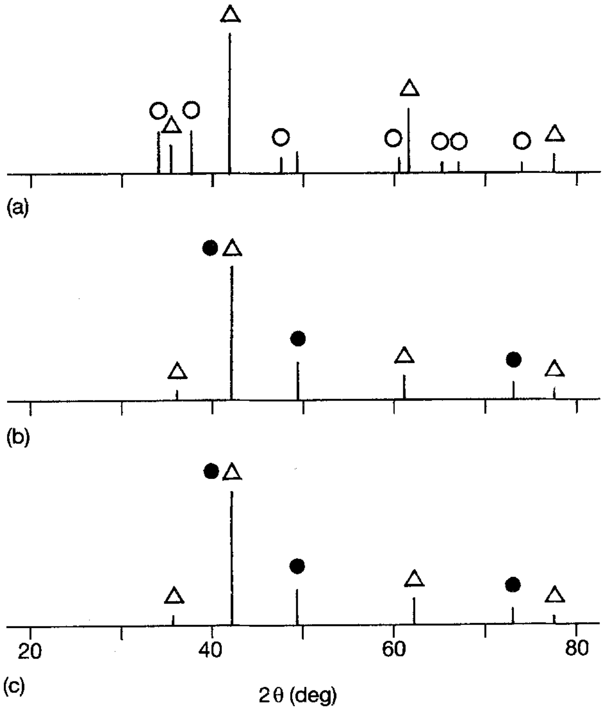


Figure 2 X-ray diffraction spectra for AL-775: (a) fresh, (b) after hydrogen pretreatment at 553 K for 2 h, (c) after hydrogenolysis, (△) MgO; (○) CuO; (●) Cu.

3.3. Morphological observation

Observation of catalyst morphology was carried out by SEM, TEM, and TEM–EDX. Fig. 4 shows the SEM results of the catalysts surfaces after various treatments.

Mg_2Cu alloy (Fig. 4a) shows a smooth surface. AL-775 (Fig. 4b) has many whiskers of 2–3 μm length. The whiskers were identified as copper oxide by TEM–EDX. It was considered that oxidation pretreatment resulted in formation of the whiskers. After hydrogen pretreatment (Fig. 4c), the whiskers disappeared and the surface became very rough. After hydrogenolysis (Fig. 4d), the state of the surface is similar to that of Fig. 4c.

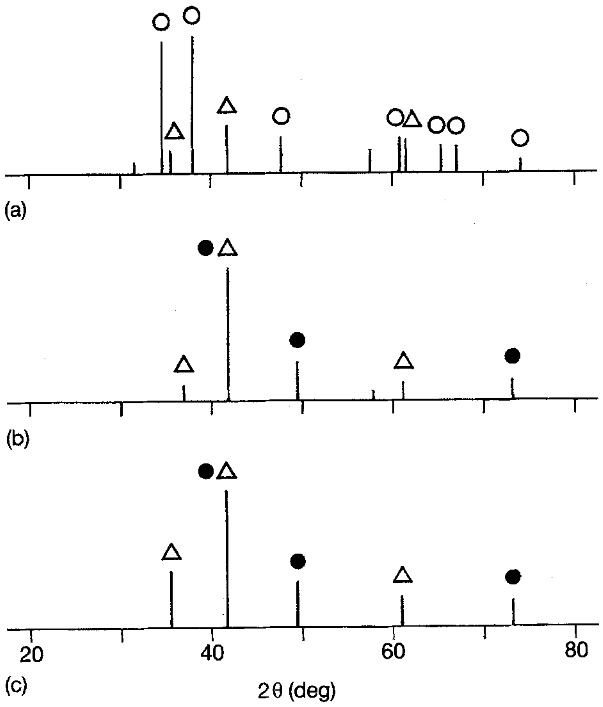


Figure 3 X-ray diffraction spectra for PR-775: (a) fresh, (b) after hydrogen pretreatment at 553 K for 2 h, (c) after hydrogenolysis. (△) MgO; (○) CuO; (●) Cu.

PR-775 has coarse surfaces, as shown in Fig. 4e. Whiskers did not grow on the surfaces by following calcination treatment. Thus, differences in the copper species in the oxide state were found between AL-775 and PR-775. For PR-775, no apparent differences at the surfaces could be found following various treatments.

3.4. Surface characterization by XPS

Analysis of catalysts' surfaces were carried out by XPS. Spectra of AL-775 and PR-775 were obtained in

TABLE I The crystallite size estimated by the Scherrer method

	State	Crystallite size (nm) CuO	Cu	MgO
AL-775	Fresh	20.6	–	22.1
	Hydrogen Pretreated	–	20.7	15.5
	Hydrogenolysis	–	20.0	17.5
	Reoxidation	20.4	–	21.6
PR-775	Fresh	18.8	–	14.7
	Hydrogen Pretreated	–	20.3	12.9
	Hydrogenolysis	–	24.2	13.4
	Reoxidation	17.6	–	13.4

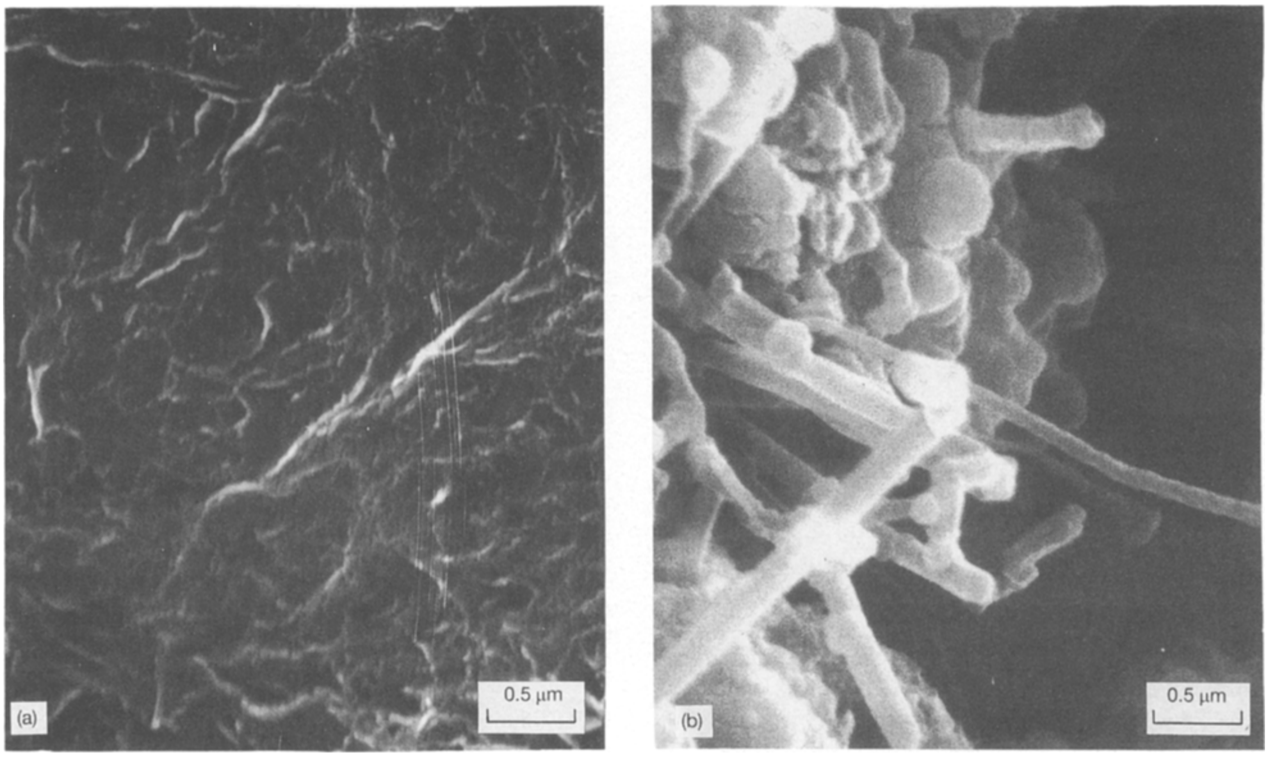
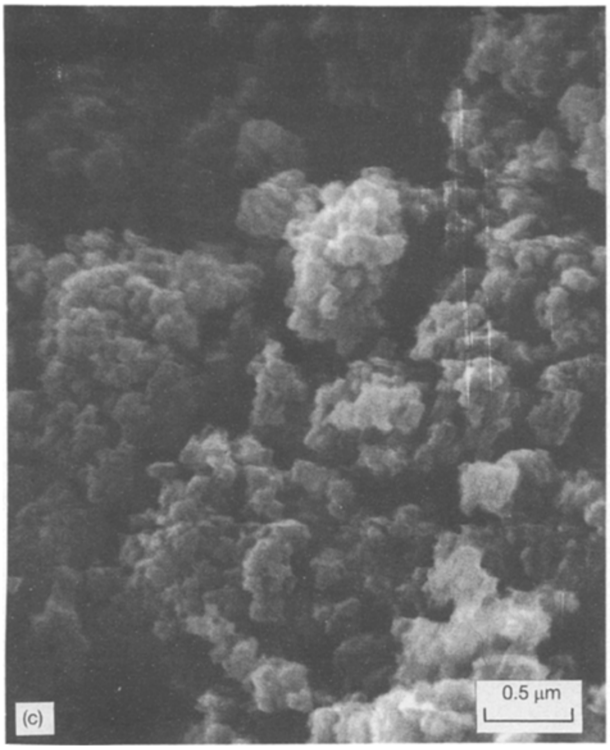
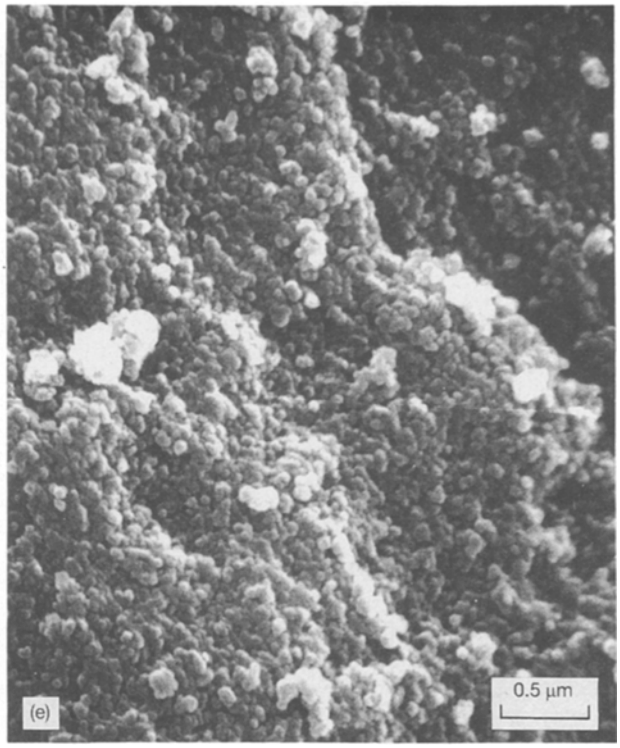


Figure 4 Photograph of catalyst surfaces by SEM: (a) Mg_2Cu alloy, (b) AL-775 fresh, (c) AL-775 after hydrogen pretreatment at 553 K for 2 h, (d) AL-775 after hydrogenolysis, (e) PR-775 fresh.





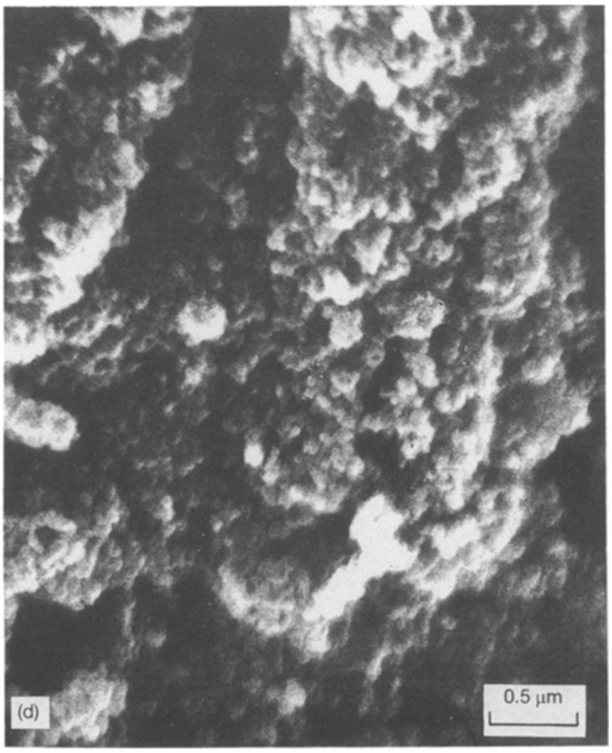


Figure 4 Continued.

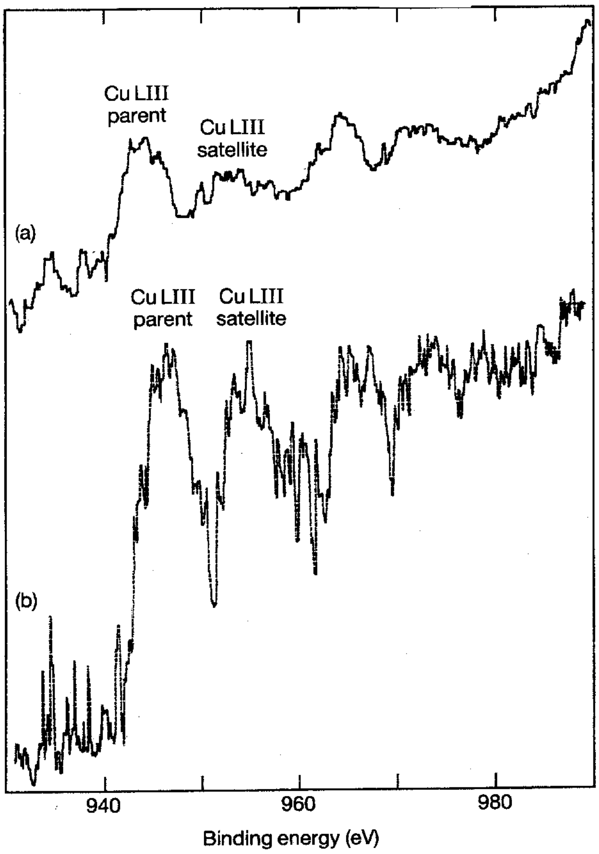


Figure 5 X-ray photoelectron spectra of AL-775 and PR-775: (a) AL-775 fresh, (b) PR-775 fresh.

the fresh state. Fig. 5 shows the spectra from 930 to 990 eV. Each spectrum has four peaks originating from the Cu L III band ($2P_{3/2}$) and Cu L II band ($2P_{1/2}$). Binding energies and the rations of the peak intensity of the Cu L III parent peak and satellite peak are shown in Table II. A chemical shift of binding energy appeared to be due to differences in the chemical bonding state. Since the Cu L III binding energy of AL-775 was smaller than that of PR-775, it was found that AL-775 was in a more reductive state than PR-775.

The ratios of the peak intensities of the parent peak (Cu L III 944, 946 eV) to that of the satellite peak (Cu L III 953, 955 eV) were compared in Table II. It was reported that the above ratios of CuO and $Cu(OH)_2$ were 0.53 and 0.70, respectively [9]. In order to estimate the nature of the distorted copper oxide

TABLE II The binding energies and the ratio of the peak intensity for the Cu L III($2P_{3/2}$) band

Catalyst	Binding energy (eV)		Ratio of the peak intensity
	parent	satellite	
AL-775	944	953	0.40
PR-775	946	955	0.78

structure, a correlation between the satellite intensity of the Cu level and the symmetry of the Cu^{2+} ion is required [10]. Further, it was reported that a highly distorted octahedral symmetry [such as $Cu(OH)_2$] showed generally strong and well resolved satellite peaks. In addition, Cu^{2+} ions in CuO showed a distorted square–planar symmetry [11]. Thus, those ratios shown in Table II presumed that a distorted CuO square–planar symmetry was present at the surface of AL-775, and that distorted octahedral symmetry was present at the surface of PR-775. It is estimated that the co-ordination numbers of copper species at the surface were different for AL-775 and PR-775.

3.5. Surface analysis by i.r.

Analyses of the catalysts' surfaces were carried out by i.r. Infrared spectra of AL-775 with various treatments are shown in Fig. 6. AL-775 (Fig. 6a) shows a small peak of isolated OH group, at 3700 cm^{-1}, on the surface. This isolated OH group increased after hydrogen pretreatment (Fig. 6b). After hydrogenolysis (Fig. 6c), the peak decreased. Characteristic peaks of CH_2 at 2930, 2840 and 1460 cm^{-1} appeared. These peaks suggest that hydrocarbon chains were formed on the catalyst during reaction. The difference in the spectrum between Fig. 6b and c is shown in Fig. 6d. It was found, Fig. 6d, that the isolated OH group peak decreased a little during the reaction.

Infrared spectra of PR-775 with various treatments are shown in Fig. 7. PR-775 (Fig. 7a) shows an isolated OH group peak similar to AL-775 in Fig. 6a. After hydrogen pretreatment (Fig. 7b), the peaks increased as shown in Fig. 6b, but the intensities were much stronger than for AL-775. After hydrogenolysis (Fig. 7c), characteristic peaks of carboxylate at 2930, 2840, 1760, 1570 and 1460 cm^{-1} appeared. It was considered, from Fig. 7c, that carboxylate was produced from a fatty acid ester on the catalyst's surface during reaction. The difference in spectrum between Fig. 7b and c is shown in Fig. 7d. Fig. 7d suggests that the peak of the isolated OH group decreased and carboxylate was developed in turn.

3.6. Discussion

The hydrogenolysis catalyst was derived from oxidative pretreatment of Mg_2Cu alloy (denoted as AL-775). Its steady state activity in a continuous flow reactor was obtained in the gas phase at atmospheric pressure. On the other hand, a catalyst prepared according to the coprecipitation method with the same composition (denoted as PR-775) did not have steady state activity.

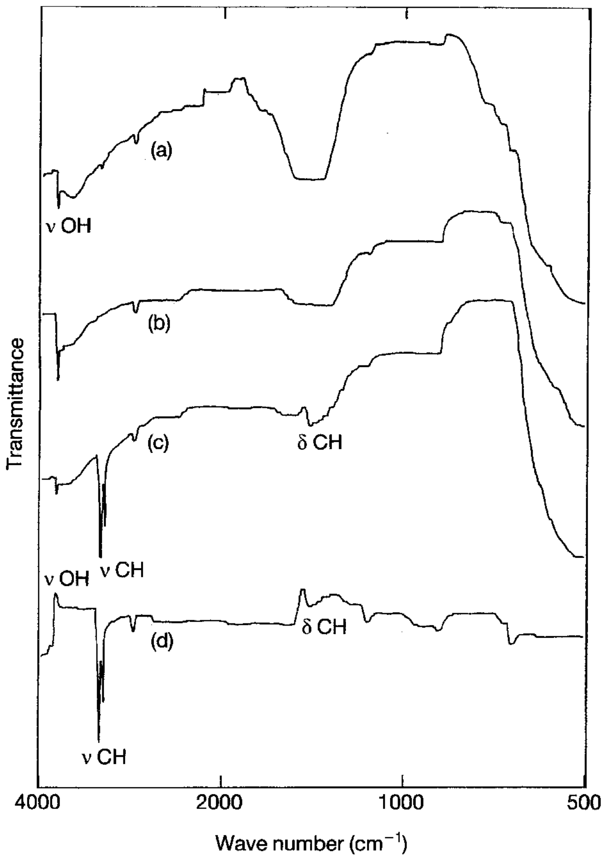


Figure 6 Infrared spectra of AL-775: (a) fresh, (b) after hydrogen pretreatment at 553 K for 2 h, (c) after hydrogenolysis, (d) spectrum in (c)– spectrum in (b).

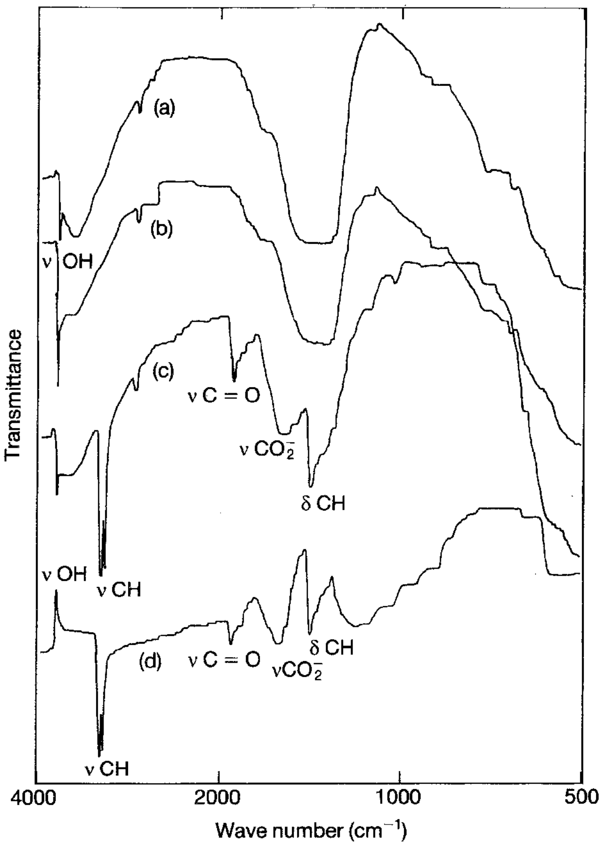


Figure 7 Infrared spectra of PR-775: (a) fresh, (b) after hydrogen pretreatment at 553 K for 2 h, (c) after hydrogenolysis, (d) spectrum in (c)– spectrum in (b).

The surface of AL-775 had many whiskers in the copper oxide state. XRD results revealed that the whiskers were reduced to well dispersed copper metal on MgO. The surface of PR-775 contained many isolated OH groups. Carboxylates were developed at the surface of PR-775 during the reaction and isolated OH groups became smaller. These indicate that the following transesterification between fatty acid ester and the isolated OH group on copper, should take place to form copper ester.

$$RCOOCH_3 + Cu\text{–}OH \longrightarrow RCOO\text{–}Cu + CH_3OH \quad (1)$$

The product, RCOO–Cu might have flown to the exit. Therefore, the effluent contained copper salt, and the catalytic activity of PR-775 decreased with time. The difference in the OH group on copper was concerned with the co-ordination number of the copper oxide, which is the precursor of the copper species. It is considered that the copper oxide in PR-775 has a disadvantageous co-ordination character because of preparation by way of copper hydroxide.

4. Conclusions

The synthesis of alcohols can be realized by high selectivity at steady state using AL-775. It was suggested that reduced copper species dispersed on an MgO support was the active site for hydrogenolysis. The catalyst prepared by the coprecipitation method (PR-775) deactivated with time and could not reach a steady state.

The reason for the difference between AL-775 and PR-775 was concerned with the co-ordination number of each copper species at the surface. Isolated OH groups were presented at the catalyst surface of PR-775. It was suggested that the deactivation of PR-775 occurred during transesterification between fatty acid ester and copper hydroxide.

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