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Electrocatalytic Hydrogenation on Nickel Microparticle Electrodes

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Nickel microparticle electrodes were prepared by electrodeposition in a Nafion film coated on graphite or nickel plate. The nickel particles were distributed three-dimentionally on and into the Nafion film and their diameters were in a range of 50 to 200 nm. These electrodes have shown higher activity for hydrogenation of 2-cyclohexen-1-one than the electrodeposited nickel cathode without Nafion or Raney-nickel particle cathode.

Raney-nickel (R-Ni), palladium-carbon, and platinum-carbon of hydrogenation catalysts have electric conductivity and can be used as cathode materials in electrocatalytic reduction.1) We examined successfully electrocatalytic hydrogenation of the compounds with C-C double bond, carbonyl, nitrile, nitro, or halogen group on these hydrogen active cathodes under atmospheric pressure and room temperature.1-5) However, these cathodes were not practically convenient because of their powdery property. We have carried out the electrodeposition of nickel particles in a Nafion (polyperfluorosulfuric acid) film coated on a graphite or nickel plate and investigated the electrocatalytic hydrogenation of 2-cyclohexen-1-one (1) on these electrodes. The electrodeposition of metal particles onto the polymer modified electrodes has been variously examined for catalytic purposes.6-8) Itaya et al. have studied electrochemical growth of platinum particles in Nafion films on glassy carbon electrodes.6) However the catalytic hydrogenation on metal microparticle electrodes has not been reported.

Preparation of the electrodes is as follows: nickel plate (plane surface area=20 cm^2) or graphite (24 cm^2) was dipped into a 5% Nafion (No. 117, EW 1100, Aldrich Chemical Company, Inc.) / ethanol solution and dried overnight at room temperature. Cyclic voltammetry was applied to deposit ultrafine nickel particles into the Nafion membrane. The anode was a platinum gauze and a 100 ml of a 0.1 mol/dm^3 Ni_2SO_4 aqueous solution was used as an electrolyte. Electrode potential was swept from -0.1 to -1.5 V vs. SCE for the first scan and from -0.8 to -1.2 V vs. SCE for the successive ones. Under these conditions, nucleation occurs on the first scan and fine nickel particles grow on the successive scans. Scan rate was 100 mV/s and the sweep was repeated 400 times. At this time a loading level of nickel was calculated on 55.9 μg/cm^2, assuming that no charge is consumed by evolving hydrogen gas etc.

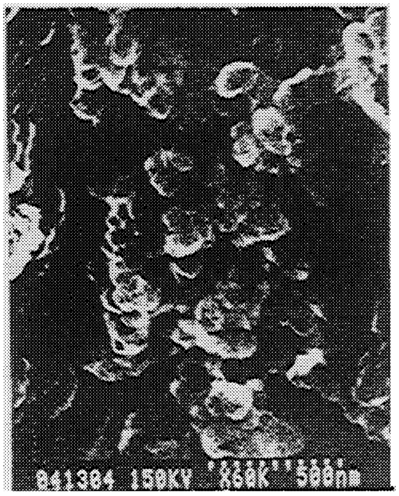

Fig. 1. SEM image of the nickel micloparticle electrode.

Table 1. Results of electrocatalytic hydrogenation of 2-cyclohexen-1-one[a]

Run[b]	Electrode[c]	Current/mA	CE/%[d]	Sel/%[e]
1(1)[f]	G-Naf-Ni	30	110	38
2(2)	G-Naf-Ni	25	75	19
3(1)[g]	G-Naf-Ni	100	75	28
4(2)	G-Naf-Ni	50	60	16
5(3)	G-Naf-Ni	30	60	16
6(1)[f]	G-Ni	20	50	10
7(1)	G	<5	0	—
8(1)	Np-Naf-Ni	25	85	22
9(1)	Np-Ni	15	65	7
10(1)	Np	15	0	—
11(1)	R-Ni (0.1 g)[h]	10	85	31

a) Results at passage of 2x96500 C/mol of charge.
b) ( ) indicates times reused.
c) G; graphite plate, Np; nickel plate, Ni; nickel particles, Naf; Nafion.
d) Current efficiency.
e) Selectivity for 3 formation = (3 / (2 + 3)) x 100
f) 1.8% Nafion ethanol solution was used.
g) Scan to deposit nickel particles was repeated 600 times.
h) This nickel amount corresponds to ca. 100 times of that in Run 1.

From the results of scanning electron microscope (SEM, Hitachi H-8010), nickel particles are seems to be almost spherical and randomly dispersed in cracks and on surface of the Nafion film (Fig. 1). The diameters of the nickel particles are in the range of ca. 50 to 200 nm on both electrodes.

The electrocatalytic hydrogenation of 1 (2 mmol) on these electrodes is summarized in Table 1. Electrolysis was carried out at -1.2 V vs. SCE. The catholyte was 0.5 mol/dm^3 $NaClO_4$ aqueous solution. The products of electrolyses were cyclohexanone (2) and cyclohexanol (3), and the selectivity for 3 formation, which indicates hydrogenation activity, was considerably high. The hydrogenation activity of the nickel microparticle electrode (Run 1) was superior to that of freshly prepared R-Ni cathode (Run 11).[1,2] Deposited nickel particles on a graphite (Run 6) or nickel plate (Run 9) without Nafion also showed marked ability for hydrogenation, but the current and current efficiency seemed to be fairly low compared with those observed on the electrodes with Nafion.

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