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Author(s)	Kobayashi, Hirokazu; Hosaka, Yuto; Hara, Kenji et al.
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Control of selectivity, activity and durability of simple supported nickel catalysts for hydrolytic hydrogenation of cellulose

Hirokazu Kobayashi,[a] Yuto Hosaka,[a,b] Kenji Hara,[a] Bo Feng,[a] Yoshihiko Hirosaki[a,b] and Atsushi Fukuoka*[a]

[a]Catalysis Research Centre, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan.

[b]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan.

Average particle diameter.

This average value (d_{av}) is defined to have the same surface area per volume between original particles and the average-diameter particles.

Definition.

Let P be a set of n spherical particles $\{P_1, P_2, \ldots P_n\}$, where their diameters are $d_1, d_2, \ldots d_n$, respectively.

Let Q be a set of m spherical particles $\{Q_1, Q_2, \ldots Q_m\}$, where their diameters are d_{av}.

Total volume (V_Q) and surface area (S_Q) of Q are the same as those of P (V_P, S_P).

Proposition.

$$d_{av} = \sum_{k=1}^{n} d_k^3 \Big/ \sum_{k=1}^{n} d_k^2$$

Proof.

V_P is shown as $\frac{\pi}{6}\sum_{k=1}^{n} d_k^3$ (S1)

S_P is described as $\pi\sum_{k=1}^{n} d_k^2$ (S2)

V_Q is shown as $\frac{\pi}{6} m d_{av}^3$ (S3)

S_Q is described as $\pi m d_{av}^2$ (S4)

Since $V_P = V_Q$, (S1) = (S3). Therefore, $m = \frac{\sum_{k=1}^{n} d_k^3}{d_{av}^3}$ (S5)

Substitute (S5) for (S4), $S_Q = \frac{\pi\sum_{k=1}^{n} d_k^3}{d_{av}}$ (S6)

Since $S_P = S_Q$, (S2) is equal to the right-hand side of (S6). Accordingly, $d_{av} = \sum_{k=1}^{n} d_k^3 \Big/ \sum_{k=1}^{n} d_k^2$

Q.E.D.

Identification of hexanetetrol

^{1}H NMR (400 MHz, D_2O) δ_H 3.69 [2 H, m (dddd), C*H*OD], 3.59 (2 H, dd, *J* = 4.0, 11.6 Hz, C*H*HOD), 3.47 (2 H, dd, *J* = 6.8, 11.6 Hz, CH*H*OD), 1.38–1.68 [4 H, m, methylene]. LC/MS [M + Na]$^+$ calculated 173.08, found 173.09.

This product might be almost 1:1 mixture of *threo*- and *erythro*-1,2,5,6-hexanetetrols.

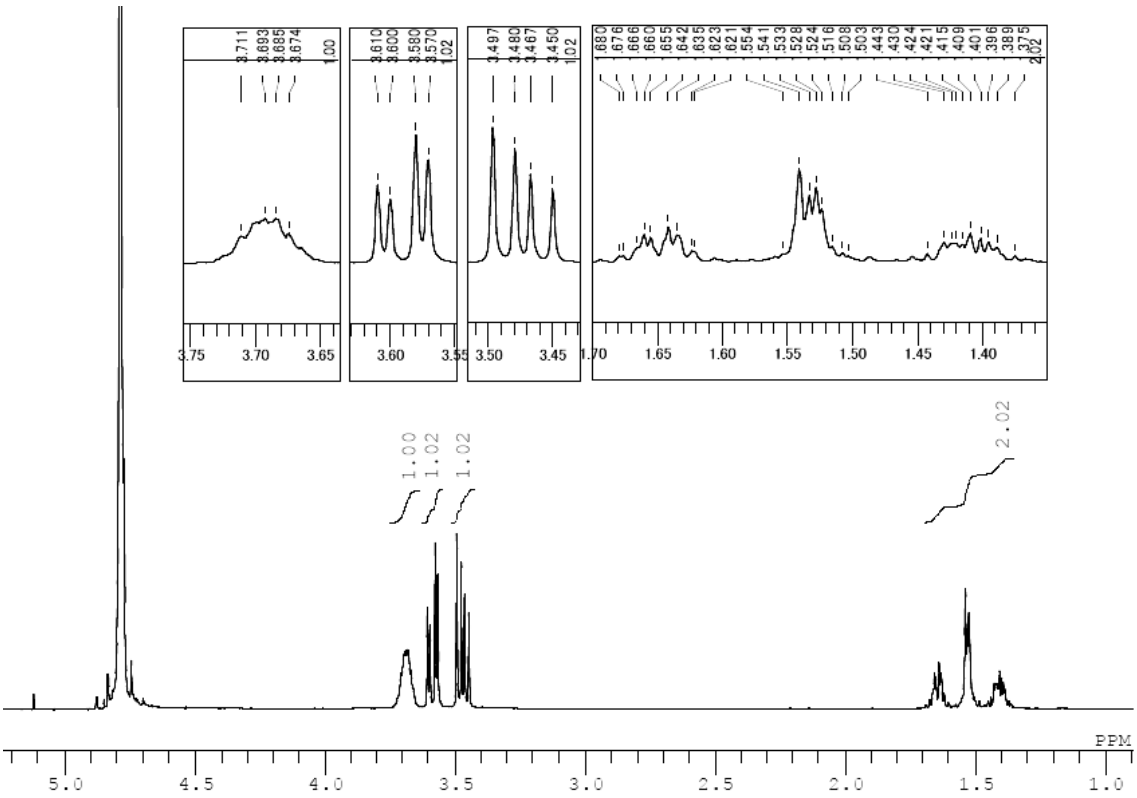

Fig. S1 ^{1}H NMR spectrum of the product identified as hexanetetrol.

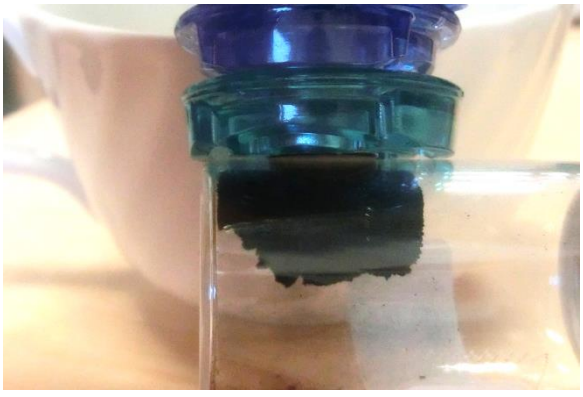

Fig. S2 Ni(50)/KB catalyst attracted by a magnet.

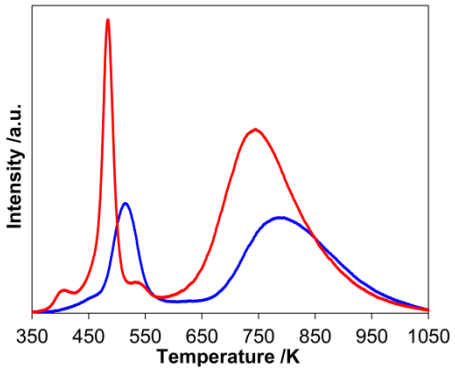

Fig. S3 H_2-TPR measurements for Ni(10)/KB (blue) and Ni(70)/KB (red).

Peaks at 350–600 K are assigned to reduction of Ni, and those at 600–1000 K are to hydrogenation of carbon support.[S1] If the latter peak for Ni(10)/KB were due to reduction of Ni, the stoichiometry would far exceed 100%.

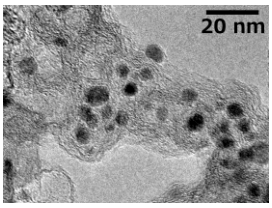

Fig. S4 TEM image of Ni(10)/KB catalyst.

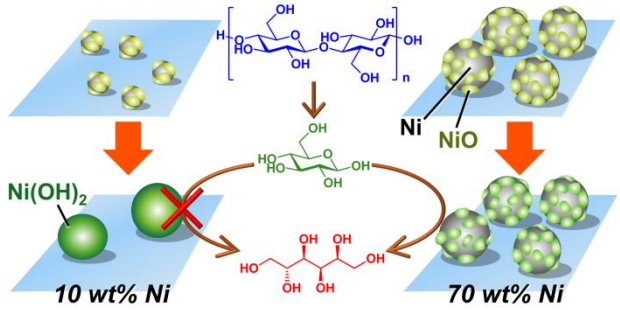

Fig. S5 Schematic of the difference between Ni(10)/KB and Ni(70)/KB catalysts in the hydrolytic hydrogenation of cellulose.

Table S1 Effect of catalyst amount on the hydrolytic hydrogenation of cellulose.

Catalyst amount /mg (S/C [wt/wt])		Conv. /%	Yield /%C										
			Hexitols			Sorbitan	Cellobitol	HT[b]	ET[c]	PG[d]	EG[e]	Glucose	Others[f]
			Sorbitol	Mannitol	Total								
10	(32)	84	21	3.5	25	1.4	0.5	9.3	1.3	5.7	2.3	0.6	38
50	(6.5)	85	36	5.6	41	3.2	0.4	9.0	1.7	3.8	1.8	0.1	24
300	(1.1)	92	22	7.8	30	7.0	0.4	9.2	2.7	2.3	1.6	0.0	39

[a] Reaction conditions: cellulose 324 mg, catalyst Ni(50)/TiO_2, water 40 mL, reaction time 6 h, T = 483 K, $p(H_2)$ = 5.0 MPa at r.t. [b] Hexanetetrol. [c] Erythritol. [d] Propylene glycol. [e] Ethylene glycol. [f] Difference of the conversion and total yield of the identified products.

S1 T. Komanoya, H. Kobayashi, K. Hara, W.-J. Chun and A. Fukuoka, *Appl. Catal. A*, 2011, **407**, 188-194.