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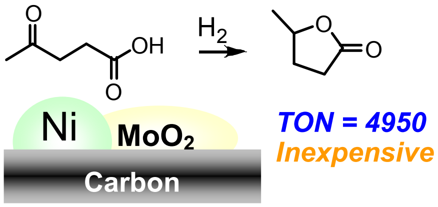

Ni-MoOx/C showed more than 300 times higher TON than the previously reported noble metal-free catalysts for the title reaction.

Hydrogenation of levulinic acid to γ-valerolactone by Ni and MoO_x co-loaded carbon catalyst

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Abstract

To develop a noble metal-free heterogeneous catalyst for liquid phase hydrogenation of levulinic acid to γ-valerolactone under H_2, we tested a series of base-metal (Ni, Co, Cu, Fe) and metal oxides (Mo, V, and W oxides) co-loaded carbon (C) and Ni-loaded metal oxides for the reaction. Ni-MoO_X/C pre-reduced at 500 °C showed the highest activity and showed more than 300 times higher turnover number (TON) than the previously reported noble metal-free catalysts. Structure-activity relationship study showed that co-presence of metallic Ni^0 species and partially reduced MoO_2 can be responsible for the high activity.

Introduction

To achieve sustainable production of chemicals, biomass-derived platform compounds should not compete with food for their feedstock. Levulinic acid (LA) has been identified as a key intermediate in converting non-food biomass into chemicals and fuels,[1-3] because it can be easily and economically produced from lignocellulosic materials by using a conventional hydrolysis process. LA can be transformed to various attractive chemicals. In particular, γ-valerolactone (GVL) has been proposed as one of the key components in biorefinery systems,[1-3] because it can be used as an intermediate of chemicals (1,4-pentanediol,[4] 2-methyltetrahydrofuran,[4] adipic acid[5]), fuels[6] and solvent.[7] Recently, numerous papers were published on the hydrogenation of LA to GVL by using heterogeneous[7-26] or homogeneous[27-31] catalytic systems. Since early screening studies[10,12] demonstrated the higher activity of noble metal catalysts than Ni catalysts, most of the catalysts reported were based on noble metals (mainly Ru, Ir and Au).[10-19,27-31] For a practical application, homogeneous catalysts suffer from high costs of noble metals and ligands and difficulty in the catalyst/product separation. Heterogeneous noble metal-based catalysts also suffer from high cost. Thus, development of noble metal-free heterogeneous catalyst for this reaction is an important research target. Recently, noble metal-free heterogeneous catalysts,[19-26] such as supported Cu and Ni catalysts, were reported. For example, Cu-ZrO_2 can be utilized to perform the reaction with complete LA conversion and 90% selectivity to GVL, and the catalyst can be reused for 3 times.[22] However, turnover number (TON) and turnover frequency (TOF) of the noble metal-free catalysts for LA reduction by H_2 is generally 1-2 orders of magnitude lower than those of Ru-based heterogeneous catalysts.[13-15] There are no noble metal-free catalysts with activity comparable to the Ru-based catalysts for hydrogenation of LA to GVL. We report herein the first noble metal-free catalysts, Ni-MoOx/C, with TON comparable to the previously reported Ru-based heterogeneous catalysts[13-15] for the title reaction. Structure-activity relationship study is also carried out to discuss the structure of the active Ni and Mo species.

Experimental Section

Commercially available organic and inorganic compounds (from Tokyo Chemical Industry and WAKO Pure Chemical Industries) were used without further purification. The GC (Shimadzu GC-2014) and GCMS (Shimadzu GCMS-QP2010) analyses were carried out with Ultra ALLOY capillary column UA$^+$-5 (Frontier Laboratories Ltd.) using nitrogen as the carrier gas. Catalyst supports used in this study were as follows: carbon (Lion, Ketjenblack EC-600JD, 1310 $m^2\ g^{-1}$), SiO_2 (Fuji Silysia Chemical Ltd., Q-10, 300 $m^2\ g^{-1}$), MgO (Catalysis Society of Japan, CSJ, JRC-MGO-3), TiO_2 (CSJ, JRC-TIO-4), CeO_2 (CSJ, JRC-CEO-3), γ-Al_2O_3 (calcination of γ-AlOOH, Catapal B Alumina, Sasol) at 900 °C for 3 h.

Precursor of the standard Ni-MoO_x/C catalyst with Ni loading of 10 wt% and Mo loading of 7 wt% was prepared by co-impregnation method; the support (carbon) and $(NH_4)_6Mo_7O_{24}$•$4H_2O$ were added to aqueous solution of $Ni(NO_3)_2$ nitrates, followed by evaporation to dryness at 50°C, and by drying at 90 °C for 12 h. Other Ni and MoO_X co-loaded catalysts (designated as Ni-MoO_x/support), Ni and MO_y co-loaded carbon (Ni-MO_y/C, M = 7 wt% V, W) with Ni loading of 10 wt% and metal and MoO_X co-loaded catalysts (M'-MoO_x/C, M' = 10 wt% Ni, Cu, Co, Fe) with Mo loading of 7 wt% were prepared by the same method using metal nitrates (Ni, Cu, Co or Fe) and ammonium salts of M, $(NH_4)_6Mo_7O_{24}$•$4H_2O$, NH_4VO_3 or $(NH_4)_{10}W_{12}O_{41}$•$5H_2O$. 10 wt% Ni loaded catalysts (Ni/support) were prepared by impregnation method using aqueous solution of $Ni(NO_3)_2$. Before each catalytic experiment, these catalyst precursor were pre-reduced in a pyrex tube under a flow of H_2 (20 $cm^3\ min^{-1}$) at 500 °C for 0.5 h and was used for the reaction without exposure to air.

X-ray diffraction (XRD) patterns of the powdered catalysts were recorded with a Rigaku MiniFlex II/AP diffractometer with Cu Kα radiation. The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a JEOL JPS-9010MC with Mg*Kα* anode operated at 20 W and 10 kV.The binding energy was calibrated with respect to C 1s peak of the contaminated carbon (285.0 eV).

For the catalytic tests in Tables 1 and 2, Ni-MoOx/C (10 wt% Ni, 7 wt% Mo) pre-reduced at 500 °C was used as a standard catalyst. After the pre-reduction, the catalyst (5.8 mg) in the closed glass tube sealed with a septum inlet was cooled to room temperature under H_2 atmosphere. A mixture of levulinic acid (1 mmol, 0.116 g) and *n*-dodecane (0.05 g) was injected to the pre-reduced catalyst inside the glass tube through the septum inlet. Then, the septum was removed under air, and a magnetic stirrer was put in the tube, followed by inserting the tube inside stainless autoclave with a dead space of 28 cm^3. Soon after being sealed, the reactor was flushed with H_2 from a high pressure gas cylinder and charged with H_2 (2 bar) at room temperature. Then, the reactor was heated at 140 ˚C under stirring (150 rpm). For gram-scale catalytic tests in Fig. 1 and Table 3, 50 bar H_2 was changed to the reactor containing a mixture of LA (20 mmol, 2.322 g), *n*-dodecane (0.05 g) and 2.3 mg of Ni-MoOx/C (10 wt% Ni, 7 wt% Mo) pre-reduced at 500 °C, and the reactor was heated at 250 ˚C for 24 h. Conversion and yields of products were determined by GC using *n*-dodecane as an internal standard. The products were identified by GC-MS equipped with the same column as GC and by comparison with commercially pure products.

Results and Discussion

Catalytic study

We studied the influence of various catalyst parameters on the catalytic activity for hydrogenation of LA to γ-valerolactone (GVL) under solvent-free conditions in 8 bar H_2 at 140 °C for 5 h in the presence of 1 mol% of the supported metal catalysts (Table 1). First, we tested a series of 10 wt% Ni-loaded catalysts pre-reduced at 500 °C (entries 2-14). Generally, the Ni and MoO_x co-loaded catalysts (entries 2-5) showed higher yield (50-97%) than the conventional Ni-loaded metal oxides (entries 9-14, 0-38% yield). The Ni/C co-loaded with Mo, V, and W oxides (entries 2,6,7) showed higher GVL yield than Ni/C (entry 8), and MoO_x (entry 2) was found to be the best co-catalyst. MoOx/C (entry 1) was completely inactive, indicating that the MoOx does not catalyze the reaction. The effect of support material on the activity of Ni and MoOx co-loaded catalysts (entries 2-5) showed that carbon is the best support. In a series of metals (Ni, Cu, Co, Fe)-loaded on MoO_x/C (entries 2,15-17), Ni-MoOx/C showed the highest yield. To optimize the Mo content in Ni-MoOx/C catalysts, the catalysts with different Mo content (3, 7, 10, 30 wt%) were also tested for the reaction, and it was found that the Ni-MoOx/C catalyst with Mo content of 7 wt% gives the highest yield of GVL (result not shown). Table 2 shows the effect of solvent on the activity of Ni-MoOx/C for hydrogenation of LA. Clearly, the solvent-free conditions gave the highest yield of GVL. After the reaction, the catalyst was easily separated from the reaction mixture by a filtration. The filtered catalyst was washed with acetone, followed by drying in air at 90 ˚C for 1 h, and by reducing in H_2 at 500 ˚C for 0.5 h. The recovered catalyst showed lower yield of GVL (50%) than the first cycle (97%).

Fig. 1 shows the effect of pre-reduction temperature of the standard Ni-MoOx/C catalyst (Mo = 7 wt%) on its activity for the gram-scale hydrogenation of 20 mmol LA in 50 bar H_2 at 200 °C for 24 h under low catalyst loading condition (0.02 mol% Ni with respect to LA). The activity showed a volcano-type dependence on the reduction temperature, and the catalyst reduced at 500 °C gave the highest activity. From these results, we fixed the solvent-free system with the Ni-MoOx/C catalyst (Ni = 10 wt%, Mo = 7 wt%) reduced at 500 °C as the most effective catalytic system for the LA reduction.

Next, we discuss the performance of the present system in comparison with the previous catalysts. The most important aspect of this catalytic system is high TON. As shown in Fig. 1 and Table 3, 20 mmol LA were nearly quantitatively converted to GVL by 2.3 mg (0.02 mol%) of Ni-MoOx/C at 250 °C in 24 h, corresponding to TON of 4950 and TOF of 206 h^{-1} (with respect to total number of Ni atoms in the catalyst), respectively.[33] As compared in Table 3, this TON value is more than 300 times larger than those of previously reported non-noble metal catalysts. Recently, Ni/HZSM5 with Ni content of 30 wt% has been reported as effective catalyst for vapor phase hydrogenation of LA by H_2 to GVL.[23] We prepared Ni/HZSM5 by the similar method[23] and tested for the liquid phase LA reduction. As listed in Table 3, Ni/HZSM5 showed 2% yield of GVL. Under the same reaction conditions, Ni-MoOx/C showed about 50 times higher TON than Ni/HZSM5. Note that TOF of Ni-MoOx/C (206 h^{-1}) is two orders of magnitude higher than that of Ni/ZSM5 in the literature for vapor phase LA reduction to GVL at 250 °C (TOF = 1.8 h^{-1}).[23] By comparison of the literature data, Ru catalysts, especially Ru/TiO_2,[15] have been identified as the most effective heterogeneous catalysts in terms of TON. Table 3 demonstrates that Ni-MoOx/C shows high TON comparable to Ru/TiO_2.[15] This is the first noble metal-free catalysts with TON comparable to the state-of-the-art catalysts for LA reduction to GVL. However, the TON of Ni-MoOx/C is lower than that of a homogeneous catalysis of a Ir pincer complex under basic conditions, which showed 71% yield of GVL with 0.001 mol% of the catalyst, corresponding to TON of 71000.[30]

Structure-activity relationship

On the basis of the spectroscopic characterization results, we discuss the structure of active Ni and MoO_x species in Ni-MoOx/C (pre-reduced at 500 °C). A reference catalyst, $NiO-MoO_3/C$, prepared by calcination of the catalyst precursor in air at 300 °C was completely inert (result not shown). When the standard Ni-MoOx/C catalyst pre-reduced at 500 °C was exposed to air at room temperature for 0.5 h, the oxidized catalyst showed lower yield (55%) than the standard catalyst (99%). This suggests that the metallic Ni^0 species on the surface of Ni metal particles are the active species and re-oxidation of them results in the decrease in the activity probably due to a decrease in the amount of surface Ni^0 species. Fig. 2 shows the XRD patterns of the catalyst after various reduction temperatures. The catalyst pre-reduced at 300 °C showed diffraction lines due to Ni metal and NiO, and the catalyst showed relatively low activity (Fig. 1). The catalysts reduced at higher temperatures (500 °C and 600 °C) showed no lines due to NiO but lines due to metallic Ni. The lines due to the metallic Ni shift to lower angle with increase in the pre-reduction temperature, which suggests that Mo atom, having larger size than Ni atom, is incorporated into Ni metal forming Ni-Mo alloy phase.

To discuss the oxidation states Ni and Mo species in the catalysts reduced at 500 °C and 600 °C, we carried out XPS study (Fig. 3). As expected the oxidized reference sample, $NiO-MoO_3/C$, showed a Ni $2p_{3/2}$ peak (855 eV) due to NiO and Mo $3d_{5/2}$ peak (231.8 eV) due to MoO_3.[34] In contrast, the $Ni-MoO_X/C$ catalyst reduced at 500 °C showed a Ni $2p_{3/2}$ peak (852.4 eV) due to Ni metal and Mo $3d_{5/2}$ peak (228.4 eV) due to MoO_2 with a weak shoulder peak at 227.9 eV due to Mo metal.[34] The catalyst reduced at 600 °C showed a Ni $2p_{3/2}$ peak (852.4 eV) due to Ni metal and the Mo $3d_{5/2}$ peak (227.9 eV) due to Mo metal. Combined with the fact that the catalyst reduced at 500 °C showed higher activity than that reduced at 600 °C, we propose that co-presence of metallic Ni and partially reduced MoO_2 species is responsible for the highest activity of the catalyst reduced at 500 °C.

Conclusions

We demonstrated an effective non-noble-metal catalyst, $Ni-MoO_X/C$, for the liquid phase hydrogenation of levulinic acid to γ-valerolactone under H_2, which showed more than 300 times higher TON than previously reported non-noble-metal catalysts. This is the first noble metal-free catalysts with TON comparable to the state-of-the-art Ru catalyst for this reaction.

Structure-activity relationship study showed that co-presence of metallic Ni^0 species and MoO_2 species can be responsible for the catalytic activity.

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Notes and references

1 M. J. Climent, A. Corma and S. Iborra, *Green Chem*., 2014, **16**, 516–547.

2 M. Besson, P. Gallezot and C. Pinel, *Chem. Rev*., 2013, **114**, 1827–1870.

3 T. Horváth, H. Mehdi, V. Fábos, L. Boda and L. T. Mika, *Green Chem*., 2008, **10**, 238–242.

4 X. Du, Q. Bi, Y. Liu, Y. Cao, H. He and K. Fan, *Green Chem*., 2012, **14**, 935–939.

5 S. Van de Vyver and Y. Román-Leshkov, *Catal. Sci. Technol*., 2013, **3**, 1465–1479

6 Q. Bond, D. M. Alonso, R. M. West and J. A. Dumesic, *Science*, 2010, **327**, 1110–1114.

7 D. M. Alonso, S. G. Wettstein and J. A. Dumesic, *Green Chem*., 2013, **15**, 584–595.

8 W. R. H. Wright and R. Palkovits, *ChemSusChem*, 2012, **5**, 1657–1667.

9 J. Zhang, S. Wu, B. Li and H. Zhang, *ChemCatChem*, 2012, **4**, 1230–1237.

10 E. Manzer, *Appl. Catal., A*, 2004, **272**, 249–256.

11 R. A. Bourne, J. G. Stevens, J. Ke and M. Poliakoff, *Chem. Commun*., 2007, **43**, 4632–4634.

12 Z. P. Yan, L. Lin and S. J. Liu, *Energy Fuels*, 2009, **23**, 3853–3858.

13 A. M. R. Galletti, C. Antonetti, V. D. Luise and M. Martinelli, *Green Chem*., 2012, **14**, 688–694

14 G. Al-Shaal, W. R. H. Wrigt and R. Palkovits, *Green Chem*., 2012, **14**, 1260–1263.

15 W. H. Luo, U. Deka, A. M. Beale, E. R. H. van Eck, P. C. A. Bruijnincx and B. M. Weckhuysen, *J. Catal*., 2013, **301**, 175–186.

16 X. L. Du, L. He, S. Zhao, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem., Int. Ed*., 2011, **50**, 7815–7819

17 P. A. Son, S. Nishimura and K. Ebitani, *RSC Adv*., 2014, **4**, 10525–10530.

18 A. M. Hengne, A. V. Malawadkar, N. S. Biradar and C. V. Rode, *RSC Adv*., 2014, **4**, 9730–9736

19 J. M. Tukacs, R. V. Jones, F. Darvas, G. Dibó, G. Lezsák and L. T. Mika, *RSC Adv*., 2013, **3**, 16283–16287.

20 M. Chia and J. A. Dumesic, *Chem. Commun*., 2011, **47**, 12233–12235.

21 (a) P. P. Upare, J.-M. Lee, Y. K. Hwang, D. W. Hwang, J.-H. Lee, S. B. Halligudi, J.-S. Hwang and J.-S. Chang, *ChemSusChem*, 2011, **4**, 1749–1752; (b) K. Yan, J. Liao, X. Wu and X. Xie, *RSC Adv*., 2013, **3**, 3853–3856.

22. A. M. Hengne and C. V. Rode, *Green Chem*., 2012, **14**, 1064–1072.

23 V. Mohan, C. Raghavendra, C. V. Pramod, B. D. Raju and K. S. R. Rao, *RSC Adv*., 2014, **4**, 9660–9668

24 V. Mohan, V. Venkateshwarlu, C. V. Pramod, B. D. Raju and K. S. R. Rao, *Catal. Sci. Technol*., 2014, **4**, 1253–1259.

25 J.Yuan, S. Li, L. Yu, Y. Liu, Y. Cao, H. He and K. Fan, *Energy Environ. Sci*., 2013, **6**,

3308–3313

26 J. Wang, S. Jaenicke and G. Chuah, *RSC Adv*., 2014, **4**, 13481–13489.

27 H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L. T. Mika and I. T. Horváth, *Top. Catal*., 2008, **48**, 49–54.

28 F. M. A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer and W. Leitner, *Angew. Chem., Int. Ed*., 2010, **49**, 5510–5514.

29 J. M. Tukacs, D. Király, A. Strádi, G. y. Novodárszki, Z. s. Eke, G. Dibó, T. Kégl and L. T. Mika, *Green Chem*., 2012, **14**, 2057–2065.

30 W. Li, J.-H. Xie, H. Lin and Q.-L. Zhou, *Green Chem*., 2012, **14**, 2388–2390.

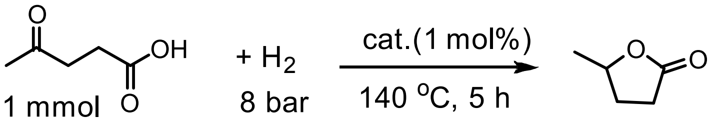
31 J. Deng, Y. Wang, T. Pan, Q. Xu, Q.-X. Guo, and Y. Fu, *ChemSusChem*, 2013, **6**, 1163–1167.

32 V. Fábos, L. T. Mika and I. T. Horváth, *Organometallics*, 2014, **33**, 181−187.

33 After the reaction by the standard catalyst, ICP-AES analysis of the solution showed low level of metal leaching (0.14 ppm Ni and 0.59 ppm Mo).

34 C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy* , Perkin-Elmer, Eden Prairie, MN, 1979).

Table 1 Hydrogenation of LA to GVL by various catalysts.



Entry	Catalysts	Conv. (%)	Yield (%)
1	MoOx/C	0	0
2	Ni-MoOx/C	100	97
3	Ni-MoOx/SiO_2	64	64
4	Ni-MoOx/Al_2O_3	59	59
5	Ni-MoOx/TiO_2	50	50
6	Ni-VOx/C	38	38
7	Ni-WOx/C	14	14
8	Ni/C	15	10
9	Ni/MoOx	7	1
10	Ni/CeO_2	18	5
11	Ni/SiO_2	8	8
12	Ni/Al_2O_3	18	11
13	Ni/MgO	12	0
14	Ni/TiO_2	38	38
15	Cu-MoOx/C	5	5
16	Co-MoOx/C	1	1
17	Fe-MoOx/C	0	0

Table 2 Hydrogenation of LA to GVL by Ni-MoOx/C in various solvents.[a]

Solvents	Conv. (%)	Yield (%)
no solvent	100	97
toluene	24	21
1,4-dioxane	13	4
H_2O	2	2

[a] LA (1 mmol) in 0 or 2 g solvent, 8 bar H_2, 6 mg catalyst (1 mol% Ni), 140 °C, 5 h.

Table 3 Heterogeneous catalysts for hydrogenation of LA to GVL by H_2.

catalyst	mol%	solvent	$P(H_2)$ / bar	T / °C	t / h	yield (%)	TON	ref.
Cu-CrO_x	6.4	water	70	200	4	91	14	21b
Cu-ZrO_2	10	methanol	34	200	5	90	9	22
Ru/TiO_2	0.029	dioxane	40	200	4	98	3400	15
Ni-MoOx/C	0.02	solvent-free	50	250	24	99	4950	this study
Ni/C	0.02	solvent-free	50	250	24	3	150	this study
Ni/HZSM5[a]	0.02	solvent-free	50	250	24	2	100	this study

[a] Ni content in Ni/HZSM5 was 30 wt%.

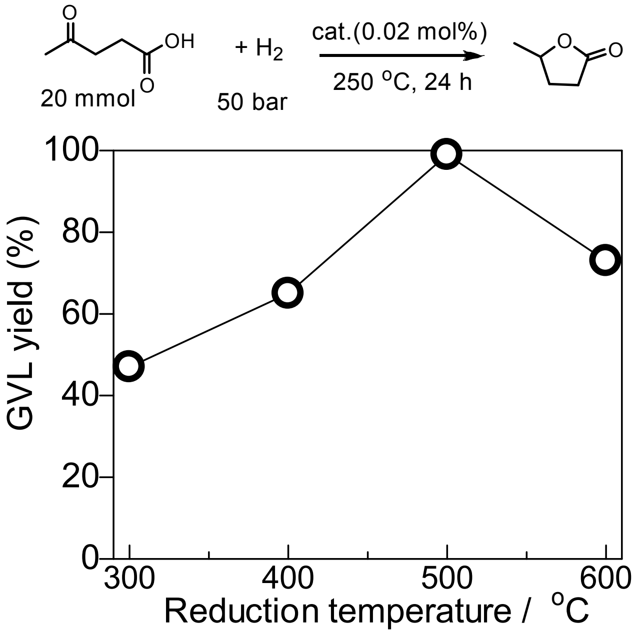


Fig. 1 Catalytic activity of Ni-MoO_X/C for hydrogenation of LA under solvent-free and low catalyst loading (0.02 mol% Ni) conditions versus catalyst reduction temperature.

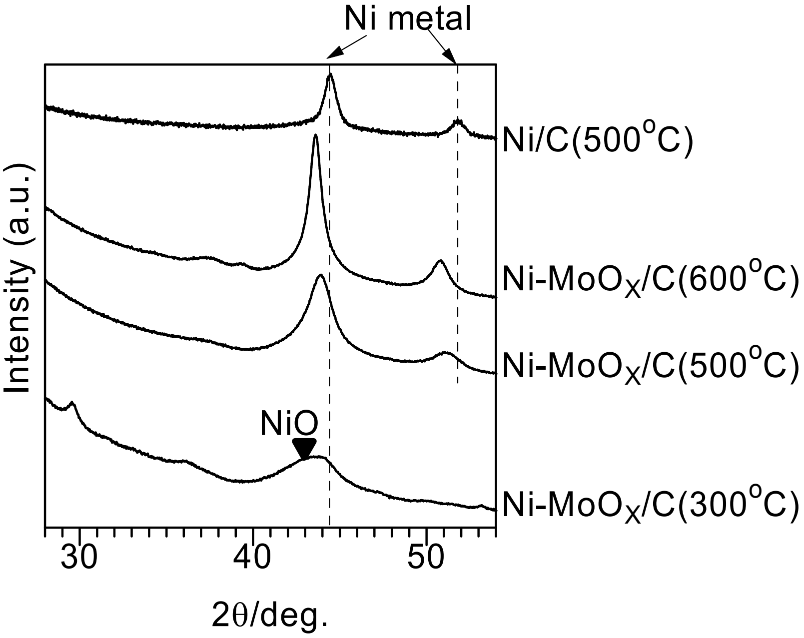


Fig. 2 XRD patterns of the Ni-MoO_X/C after pre-reduction by H_2 at various temperatures.

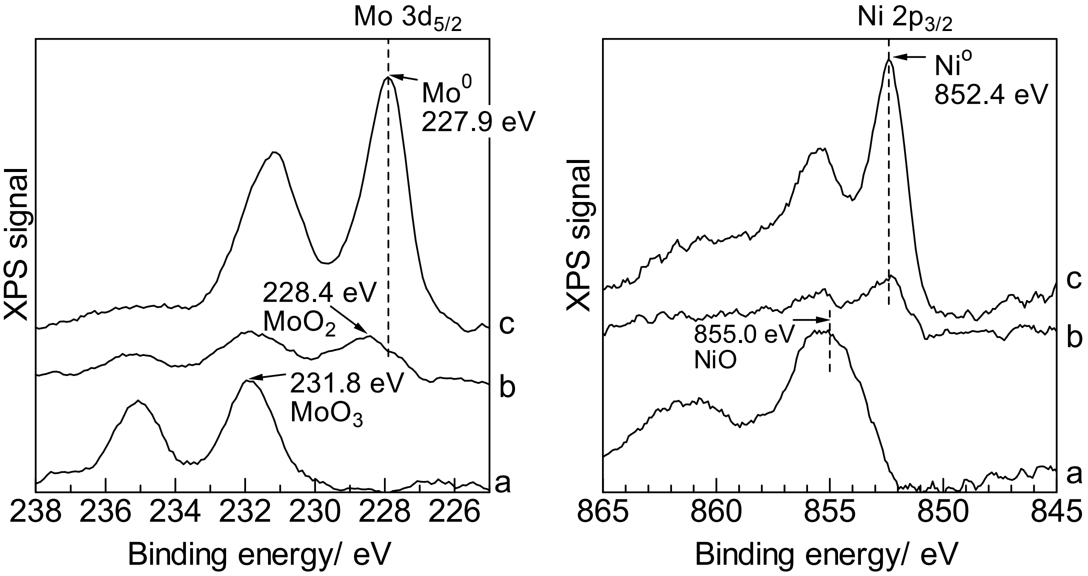


Fig. 3 XPS spectra in Mo $3d_{5/2}$ and Ni $2p_{3/2}$ regions: (a) NiO-MoO_3/C pre-oxidized at 300 °C in air for 3 h; Ni-MoO_X/C pre-reduced at (b) 500 °C and (c) 600 °C.